

Three- and Four-membered Rings

BY S. A. MATLIN

1 Introduction, Theory, and Structure

Since the last Report,¹ the number of publications relevant to this chapter has increased by 35%. There have been numerous reviews and articles concerning aspects of the chemistry of three- and four-membered rings.²

Amongst theoretical calculations³ for these systems is included a quantum chemical study of the π -electron delocalization in triphenylphosphonium ylides, leading to an evaluation of the criteria for reactivity and aromaticity in the Wittig reaction. It was predicted that the as yet unknown ylide (1; X = PPh₃) will not take part in the Wittig reaction.⁴

Geometry-optimized INDO calculations on substituted cyclopropenyl cations indicate that F and NH₂ groups conjugate strongly with the ring whereas resonance interaction of a phenyl substituent is weak. Stronger conjugation of all three substituents is seen with the cyclobutadienyl dication. In spite of the strong polarization of the carbonyl group in cyclopropenone (1; X = O) there was very little indication of charge build-up in the ring or of aromatic character, but protonated cyclopropenone does resemble a 2π aromatic system.⁵ Comparisons of cyclopropenone with thiiren 1,1-dioxide have also been made.⁶

¹ S. A. Matlin, in 'Alicyclic Chemistry', ed. W. Parker, Specialist Periodical Reports, The Chemical Society, London, 1975, Vol. 3, Chapter 1.

² D. L. Bunker, *Accounts Chem. Res.*, 1974, 7, 195; D. Ginsburg, *ibid.*, p. 286; M. Jones, jun., *ibid.*, p. 415; E. H. White, J. D. Miano, C. J. Watkins, and E. J. Breaux, *Angew. Chem. Internat. Edn.*, 1974, 13, 229; W. Adam, *ibid.*, p. 619; D. Hoppe, *ibid.*, p. 789; W. A. Noyes, jun. and K. E. Al-ani, *Chem. Rev.*, 1974, 74, 29; J. L. Kricka and A. Ledwith, *ibid.*, p. 101; D. E. Pearson and C. A. Buehler, *ibid.*, p. 45; N. L. Holy, *ibid.*, p. 243; W. H. Flygare, *ibid.*, p. 653; J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 1974, 3, 87; S. R. Hartshorn, *ibid.*, p. 167; J. D. Coyle, *ibid.*, p. 329; R. C. Dougherty, *Fortschr. Chem. Forsch.*, 1974, 45, 93; F. D. Mango, *ibid.*, p. 39; L. J. Schaad and B. A. Hess, jun., *J. Chem. Educ.*, 1974, 640; D. Seyferth, *J. Organometallic Chem.*, 1974, 75, 13; H. Suhr, *Pure Appl. Chem.*, 1974, 39, 395; B. M. Mikhailov, *ibid.*, p. 505; A. M. Glatz, *Rev. Roumaine Chim.*, 1974, 19, 455; D. Ginsburg, *Tetrahedron*, 1974, 30, 1487; K. B. Wiberg and G. B. Ellison, *ibid.*, p. 1573; J. K. Sutherland, *ibid.*, p. 1651; P. Crabbé, *ibid.*, p. 1979; R. M. Moriarty, *Topics in Stereochem.*, 1974, 8, 271; V. I. Labunskaya, A. B. Shebaldova, and M. L. Khidekel, *Uspekhi Khim.*, 1974, 43, 3 (*Chem. Abs.*, 1974, 80, 94768); J. D. Coyle, *Ed. Chem.*, 1974, 11, 62; M. Walkowicz, *Wiad. Chem.*, 1974, 28, 87 (*Chem. Abs.*, 1974, 80, 145498).

³ H.-D. Holtje, *Arch. Pharm.*, 1974, 307, 969; S.-S. Sung, *Compt. rend.*, 1974, 278, C, 37; R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, 1974, 74, 127; D. Lenoir, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, 96, 2138; G. A. Russell, P. R. Whittle, C. S. C. Chung, Y. Kosugi, K. Schmitt, and E. Goertert, *ibid.*, p. 7053; J. H. McCreery and G. G. Hall, *ibid.*, p. 7875; H. J. Lindner, *Tetrahedron*, 1974, 30, 1127; *Tetrahedron Letters*, 1974, 2479.

⁴ J. M. F. van Dijk and H. M. Buck, *Rec. Trav. chim.*, 1974, 93, 155.

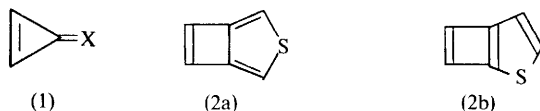
⁵ C. U. Pittman, jun., A. Kress, T. B. Patterson, P. Walton, and L. D. Kispert, *J. Org. Chem.*, 1974, 39, 373;

C. U. Pittman, jun., A. Kress, and L. D. Kispert, *ibid.*, p. 378.

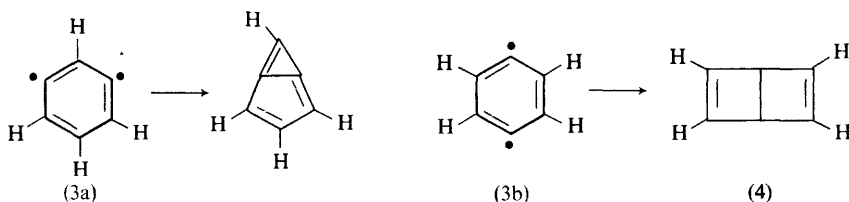
⁶ F. de Jong, A. J. Noorduyn, T. Bouwman, and M. J. Janssen, *Tetrahedron Letters*, 1974, 1209.

Using graph-theoretical technique, Hearndon and Ellzey have identified, within the Hückel MO formalism, a new class of π -structures containing even numbers of π -orbitals of which 2-cyclopropenylallyl is the smallest member. This has a closed shell of electrons according to HMO theory, but is required to have a biradical valence bond structure, and dicationic species should be obtainable.⁷

From a graphical study of positional isomers containing bivalent sulphur,⁸ it was predicted that (2a) should be more stable than (2b). The former has been synthesized, whereas the latter is not a known compound.



Following the development of the MINDO/3 method, which is considerably more successful than MINDO/2 in taking account of strain factors, the possibility of collapse of bisdehydrobenzenes (3) to bicyclic structures has been examined. The most striking conclusion was that (3a) should have a stability comparable to that of *o*-benzyne, and this suggests that *m*-benzynes may be viable reaction intermediates.⁹



MINDO/3 calculations of the cycloreversion of vinylcyclobutane to ethylene and butadiene show a biradical transition state to be involved, and the cycloaddition of cyclobutadiene and acetylene, affording Dewar benzene (4), was also examined.¹⁰ The equilibrium geometry of the latter, predicted by semi-empirical INDO calculations, was in good agreement with experimental results and the calculated dipole moment of <0.04 D suggests that the likelihood of obtaining a microwave spectrum is marginal at best.¹¹

The calculated potential curves for the $(\text{CH})_3\text{CH}_2^+$ system show that the cyclopropenylcarbinyl, cyclobutenyl, and bicyclobutyl cations are surrounded by relatively low-energy barriers and that they would readily collapse to the most stable conformer, the puckered homocyclopropenyl cation (5).¹²

The iterative maximum overlap approximation (IMOA) method is useful for the semiquantitative prediction of the geometry of hydrocarbons, and has been applied

⁷ W. C. Hearndon and M. L. Ellzey, jun., *Tetrahedron Letters*, 1974, 1399.

⁸ J. V. Knop, N. Trinajstić, and T. Živković, *Coll. Czech. Chem. Comm.*, 1974, **39**, 2431.

⁹ M. J. S. Dewar and W.-K. Li, *J. Amer. Chem. Soc.*, 1974, **96**, 5569.

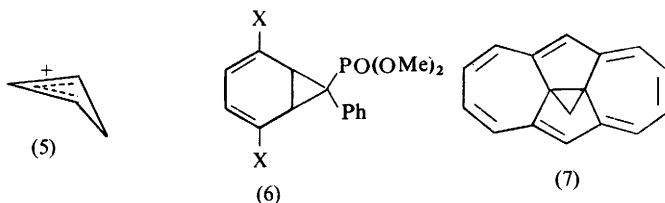
¹⁰ M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, **96**, 6225.

¹¹ M. D. Newton, J. M. Schulman, and M. M. Manus, *J. Amer. Chem. Soc.*, 1974, **96**, 17.

¹² K. Mori and S. Masamune, *Chem. Letters*, 1974, 1251.

to several cyclopropyl and cyclobutyl derivatives.¹³ An intramolecular force field for amides has been derived and used to calculate the crystal structure of cyclopropanecarboxamide.¹⁴

Several *X*-ray structure determinations of three-membered-ring compounds have been reported, including a cyclopropenium salt,¹⁵ 7-*PO*-substituted norcaradienes (6; X = H, Cl, or Br),¹⁶ chrysanthemic acid derivatives,¹⁷ and 1,6:8,13-cyclopropanylidene[14]annulene (7).¹⁸ The photoelectron spectrum of (7) has also been reported.¹⁹



Squaric acid and its derivatives continue to be the subject of detailed *X*-ray examinations.²⁰ Evidence for strong intramolecular H-bonding has been obtained.²¹ This is of two types in the acid, with O...O distances of 2.532 and 2.544 Å, and whilst the acid is planar it is not square but asymmetric.²²

Whereas the cyclobutane rings in (8; X = O or S) are planar,²³ that in (9) is puckered, and two short Br...Br distances of 3.55 Å are observed in the crystals.²⁴ Planarity is also seen in *cis*-cyclobutene-3,4-dicarboxylic acid²⁵ and in substituted cyclopentadienyl cobalt complexes of tetraphenylcyclobutadiene, in which each metal atom is sandwiched between parallel, planar four- and five-membered rings.²⁶ Crystal structures have been obtained for a variety of polycyclic compounds containing cyclobutane rings.²⁷

Photoelectron spectroscopy is a method of growing importance for structural investigation, particularly for revealing the fine details of bond interactions. Thus,

¹³ K. Kovacevic and Z. B. Maksic, *J. Org. Chem.*, 1974, **39**, 539.

¹⁴ A. T. Hagler and S. Lifson, *J. Amer. Chem. Soc.*, 1974, **96**, 5327; A. T. Hagler, E. Huler, and S. Lifson, *ibid.*, p. 5319.

¹⁵ R. L. Sime and R. J. Sime, *J. Amer. Chem. Soc.*, 1974, **96**, 892.

¹⁶ G. Maas, K. Fischer, and M. Regitz, *Acta Cryst.*, 1974, **B30**, 1140, 2853.

¹⁷ J. D. Owen, *J.C.S. Chem. Comm.*, 1974, 859; M. J. Begley, L. Crombie, J. D. Simmonds, and D. A. Whiting, *J.C.S. Perkin I*, 1974, 1230.

¹⁸ A. Mugnoli and M. Simonetta, *Acta Cryst.*, 1974, **B30**, 2896.

¹⁹ C. Batich, E. Heilbronner, and E. Vogel, *Helv. Chim. Acta*, 1974, **57**, 2288.

²⁰ H. J. Lindner and B. von Gross, *Chem. Ber.*, 1974, **107**, 598; F. J. Hollander and D. Coucouvanis, *J. Amer. Chem. Soc.*, 1974, **96**, 5646.

²¹ Y. Wang and G. D. Stucky, *J.C.S. Perkin II*, 1974, 925.

²² Y. Wang, G. D. Stucky, and J. M. Williams, *J.C.S. Perkin II*, 1974, 35.

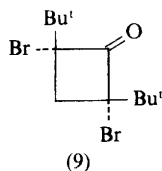
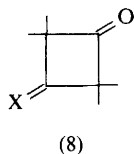
²³ C. D. Shirrell and D. E. Williams, *Acta Cryst.*, 1974, **B30**, 245, 1974.

²⁴ P. C. Riche, *Acta Cryst.*, 1974, **B30**, 587.

²⁵ E. Benedetti, M. R. Cjajolo, J. P. Declerq, and G. Germain, *Acta Cryst.*, 1974, **B30**, 2873.

²⁶ A. C. Villa, L. Coghi, A. G. Manfredotti, and C. Guastini, *Acta Cryst.*, 1974, **B30**, 2101.

²⁷ K. Yvon, *Acta Cryst.*, 1974, **B30**, 1638; J. Bernstein, *ibid.*, p. 1728; F. A. Cotton and B. A. Frenz, *ibid.*, p. 1772; J. V. Silverton, G. W. A. Milne, P. E. Eaton, K. Nyi and G. H. Temme, *tert. J. Amer. Chem. Soc.*, 1974, **96**, 7429; Mazher-Ul-Haque and D. Rogers, *J.C.S. Perkin II*, 1974, 228; J. Iball and J. N. Low, *ibid.*, p. 1423.



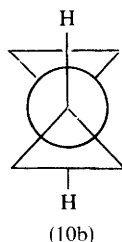
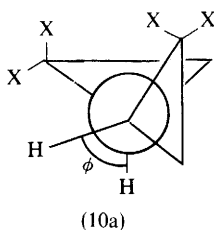
the technique has been used to demonstrate σ - σ conjugation between the C—Sn bond and cyclopropane orbitals in cyclopropylcarbonyltrimethyltin,²⁸ hyperconjugation in unsaturated small rings,²⁹ and inductive and conjugative interactions in cyclopropenones.³⁰ In contrast to the theoretical calculations outlined above, the photoelectron spectroscopy data suggest that there is indeed some resemblance between cyclopropenone and the aromatic cyclopropenyl cation.

Photoelectron spectral data indicate much weaker interactions between a four-membered ring and a π -system than between a three-membered ring and a π -system.³¹

The photoion spectrum of cyclopropane has been measured, giving appearance potentials in good agreement with those obtained from photoelectron spectroscopy.³²

Conformational aspects of small-ring carbocycles³³ have been reviewed³⁴ and a linear combination of hybrid orbitals treatment has been applied to cyclobutane.³⁵

I.r. and n.m.r. show the *gauche* conformation (10a; X = H, $\phi = 45 \pm 10^\circ$) of bicyclopropyl to be more stable than the *s-trans* (10b) by *ca.* 150 cal mol⁻¹,³⁶ but the rotation angle (ϕ) is considerably increased in *meso*-2,2,2',2'-tetrahalogenobicyclopropyls (10a; X = Cl or Br, $\phi = 166^\circ$).³⁷



²⁸ R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organometallic Chem.*, 1974, **66**, 249.

²⁹ R. A. Wielesek and T. Koenig, *Tetrahedron Letters*, 1974, 2429.

³⁰ W. Schäfer, A. Schweig, G. Maier, T. Syrac, and J. K. Crandall, *Tetrahedron Letters*, 1974, 1213.

³¹ R. Bruckmann and M. Klessinger, *Chem. Ber.*, 1974, **107**, 1108; H.-D. Martin, S. Kagabu, and R. Schwesinger; *ibid.*, p. 3130; P. Bischof, R. Gleiter, A. de Meijere, and L.-U. Meyer, *Helv. Chim. Acta*, 1974, **57**, 1519.

³² R. Kraessig, D. Reinke, and H. Baumgaertel, *Ber. Bunsengesellschaft phys. Chem.*, 1974, **78**, 425.

³³ L. Radom, J. Paviot, J. A. Pople, and P. von R. Schleyer, *J.C.S. Chem. Comm.*, 1974, 58; R. L. Cook and T. B. Malloy, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 1703; B. A. Arbuzov, G. G. Butenko, A. N. Vereshchagin, and N. A. Shishkina, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1974, 313 (*Chem. Abs.*, 1974, **81**, 37 151).

³⁴ F. A. Cotton and B. A. Frenz, *Tetrahedron*, 1974, **30**, 1587; J. A. Pople, *ibid.*, p. 1605.

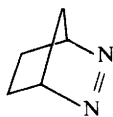
³⁵ A. Y. Meyer and R. Pasternak, *Theor. Chim. Acta*, 1974, **33**, 215.

³⁶ A. de Meijere, W. Lüttke, and F. Heinrich, *Annalen*, 1974, 306.

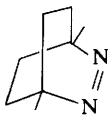
³⁷ M. J. Aroney, K. E. Calderbank, and H. J. Stootman, *Austral. J. Chem.*, 1974, **27**, 1563.

Optical activity in high-symmetry chiral molecules has been discussed,³⁸ and the importance of the role of conformational dissymmetry emphasized by comparison of allenes and spiro[3, 3]heptanes.³⁹ Baboulène and Sturtz have discussed the relationship between stereochemistry and pharmacological activity in 1-aminomethyl-2-benzoylcyclopropanes.⁴⁰

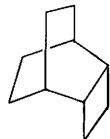
Included in reports of thermochemical studies⁴¹ are estimates of the heats of formation and strain energies of the azoalkenes (11) and (12)⁴² and hydrocarbon (13).⁴³ The conversion of the azoalkenes into bicyclo[*n*, 2, 0]alkanes is now suggested to be much less exothermic than previously estimated.



(11)



(12)



(13)

2 Synthesis of Three-membered Rings

Condensation Reactions.—Trost⁴⁴ has reviewed the preparation and synthetic uses of cyclopropyldiphenylsulphonium ylides. The regioselectivity and chemospecificity of the cyclopentane and cyclopentenone annelation reactions have been examined.⁴⁵

Whereas diphenylsulphonium methylyde does not cyclopropanate simple, unactivated olefins such as tetramethylethylene, transfer of a methylene group from the ylide can be effected stereospecifically in the presence of a copper catalyst⁴⁶ and this reaction may provide a model for biological cyclopropanations by the ylide derived from *S*-adenosyl-methionine. Attempts to catalyse a similar transfer to unactivated olefins using PdCl₂ were not successful.⁴⁷

The ylide (14), stabilized by both sulphonium and phosphinyl substituents, has been prepared⁴⁸ and reacts with Michael acceptors to give phosphonocyclopropanes. The same cyclopropane (15) results from addition to both maleate and fumarate, implicating the betaine (16) as a common intermediate.

As reported earlier by Trost, racemization of chiral sulphonium ylides inhibits their utility for asymmetric cyclopropanations. The rates of racemization of a series of sulphonium acylylide derivatives have now been measured and their ease of racemiza-

³⁸ M. Farina and C. Morandi, *Tetrahedron*, 1974, **30**, 1819.

³⁹ H. Wynberg and L. A. Hulshof, *Tetrahedron*, 1974, **30**, 1775.

⁴⁰ M. Baboulène and G. Sturtz, *Bull. Soc. chim. France*, 1974, 2929.

⁴¹ S. M. Pimenova, L. Fogel, M. P. Kozina, and G. L. Gal'chenko, *Zhur. obshchei Khim.*, 1974, **44**, 1383 (*Chem. Abs.*, 1974, **81**, 62983); R. M. Varushchenko, A. I. Druzhinina, O. Y. Kovner, E. M. Mil'vitskaya, A. A. Bobyleva, N. A. Belinkova, and G. L. Galchenko, *Zhur. fiz. Khim.*, 1974, **48**, 1886 (*Chem. Abs.*, 1974, **81**, 119 646).

⁴² P. S. Engel, J. L. Wood, J. A. Sweet, and J. L. Margrave, *J. Amer. Chem. Soc.*, 1974, **96**, 2381.

⁴³ E. Osawa, P. von R. Schleyer, L. W. K. Chang, and V. V. Kane, *Tetrahedron Letters*, 1974, 4189.

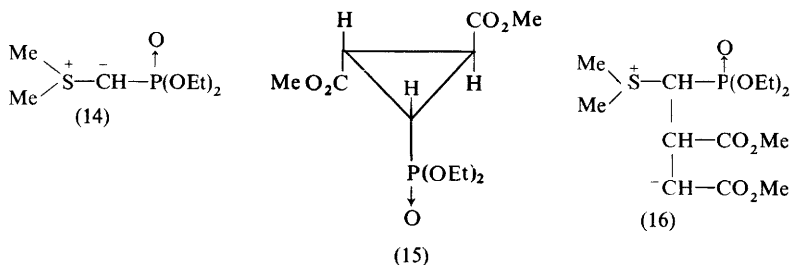
⁴⁴ B. M. Trost, *Accounts Chem. Res.*, 1974, **7**, 85.

⁴⁵ B. M. Trost and S. Kurozumi, *Tetrahedron Letters*, 1974, 1929.

⁴⁶ T. Cohen, G. Herman, T. M. Chapman, and D. Kuhn, *J. Amer. Chem. Soc.*, 1974, **96**, 5627.

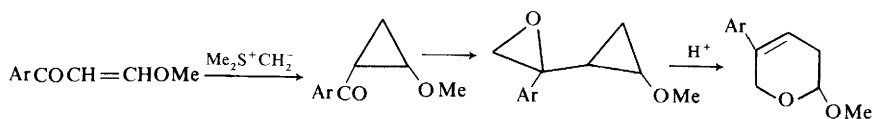
⁴⁷ P. Bravo, G. Fronza, C. Ticozzi, and G. Gaudiano, *J. Organometallic Chem.*, 1974, **74**, 143.

⁴⁸ K. Kondo, Y. Liu, and D. Tunemoto, *J.C.S. Perkin I*, 1974, 1279.



tion and reduced nucleophilicity compared with simple sulphonium ylides noted. It seems that chiral sulphonium ylides will serve as useful asymmetric transfer reagents only when significant free-energy differences exist between diastereomeric transition states.⁴⁹

Condensation of the enol ethers of β -dicarbonyl compounds with dimethylsulphonium methylide generally takes place by attack on the carbonyl group, leading to furans. However, enol ethers derived from β -keto-aldehydes are attacked first at the double bond to give cyclopropanes.⁵⁰ These further react at the carbonyl group, the resulting cyclopropyl epoxides rearranging to dihydropyrans (Scheme 1).



Scheme 1

Tropone is cyclopropanated in good yield at the 2,3-double bond with phenacyl dimethylsulphonium ylide.⁵¹

A number of cyclopropyl ketones have been prepared by reaction of $\alpha\beta$ -unsaturated ketones with dimethylsulphoxonium methylide. With the aid of kinetic results, the principal factors governing the reactivity and stereochemistry of the cyclopropanes were analysed. From both *cis* and *trans* acyclic enones, only *E*-cyclopropyl ketones were isolated, the *trans*-isomer reacting much faster than the *cis* and the products being formed *via* conformationally equilibrating zwitterionic intermediates. It was noted that much less stereoselectivity was observed when the acyl group of the enone was replaced by a CN function. With conjugated cyclohexenones, the conformational changes in the intermediates are suppressed so that epimerizations are not observed. The stereochemistries of the cyclopropyl ketones formed then reflect the direction of attack of the ylide on the ring, with axial attack at C-3 of the enone being favoured in the absence of steric effects.⁵²

The condensation of dimethylsulphoxonium methylide with ethylenic ketones⁵³

⁴⁹ S. J. Campbell and D. Darwish, *Canad. J. Chem.*, 1974, **52**, 2953.

⁵⁰ C. M. Harris, J. J. Cleary, and T. M. Harris, *J. Org. Chem.*, 1974, **39**, 72.

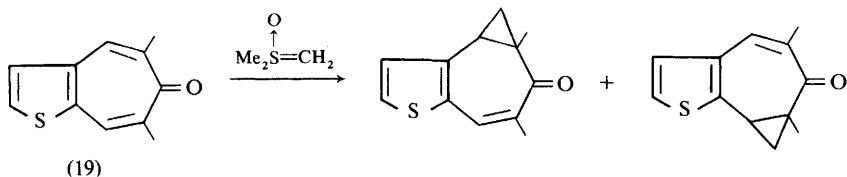
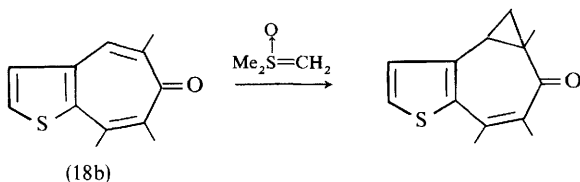
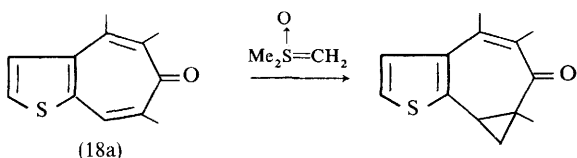
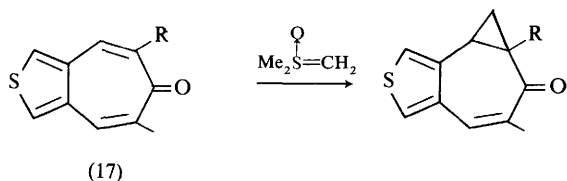
⁵¹ N. Soma, H. Takagi, and M. Sugimura, Japan P. 7343737 (*Chem. Abs.*, 1974, **81**, 13181).

⁵² F. Roquet and A. Sevin, *Bull. Soc. chim. France*, 1974, 881, 888.

⁵³ J. A. Donnelly, S. O'Brien, and J. O'Grady, *J.C.S. Perkin I*, 1974, 1674; E. J. Cragoe jun. and O. W. Woltersdorf, Ger. Offen., 2351411 (*Chem. Abs.*, 1974, **81**, 13323).

may be successful when other methods, such as the Simmons–Smith procedure, fail, as for example in the reaction with pyridyl styryl ketones which gives *trans*-cyclopropanes in moderate to good yields.⁵⁴

Attack occurs exclusively at the least substituted double bond of the seven-membered ring in the cyclohepta[*c*]thiophenes (17; R = H or Me), and similar specificity is seen with the cyclohepta[*b*]thiophenes (18a) and (18b). Compound (19) affords a mixture of two products.⁵⁵



Phenalenone (20; R = H) did not give the expected cyclopropylketone (21; R = H) on reaction⁵⁶ with dimethylsulfoxonium methylide, attack at the 9-position instead generating the betaine (22), which collapsed to 9-methylphenalenone (20; R = Me). However, treatment of the latter gave the cyclopropane (21; R = Me).

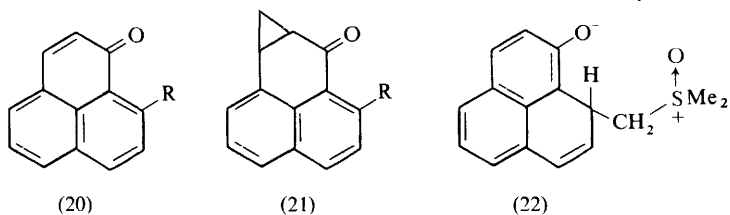
Steric effects on the formation of 6,7-methano-steroids from steroidal 4,6-dien-3-ones have been examined.⁵⁷ The results (Scheme 2) show that the reaction is governed by steric approach control, as axial attack from the least hindered side would give

⁵⁴ M. Coussac, A. Boucherle, and J.-L. Pierre, *Bull. Soc. chim. France*, 1974, 1442.

⁵⁵ R. Guillard and B. Hanquet, *Compt. rend.*, 1974, **278**, C, 295.

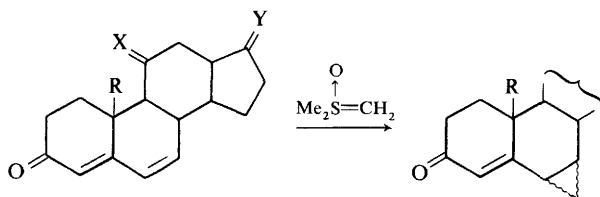
⁵⁶ R. M. Pagni and C. R. Watson, jun., *J.C.S. Chem. Comm.*, 1974, 224.

⁵⁷ G. E. Arth, G. F. Reynolds, and G. H. Rasmusson, *Tetrahedron Letters*, 1974, 291.



α -cyclopropanation. Van der Waals attractive forces of the 10 β methyl group are probably not involved, as the rates are A, B > C, D, F > E, indicating a rate-retarding effect of the 10 β and 11 β substituents. The most likely explanation is that the initial step of ylide addition to the dienone is reversible and axial (α) attack is preferred. However, the second step is subject to secondary steric interactions caused by torsional changes in forming the final ring system, and it appears that ring-closure to form α -methylene adducts with a 10 β methyl substituent is inhibited by diaxial interactions involving the functions at 8 β , 10 β , and 11 β . In the case of the 19-nor-dienes A and B these interactions are minimized, and product formation is governed by the concentration of the most rapidly formed α -intermediate.

Both *cis*- and *trans*-1,2-diphenylcyclopropanes, on treatment with DMSO⁻, afford exclusively the *trans*-cyclopropane after work-up, which is taken as evidence that cyclopropanes are *not* intermediates in the alkylation of activated double bonds with DMSO⁻.⁵⁸



	R	X	Y	α : β
A	H	H	β -OAc	90:10
B	H	H	$\text{CH}_2\text{O}(\text{CH}_2)_3$	90:10
C	Me	H	β -OAc	40:60
D	Me	H	$\text{CH}_2\text{O}(\text{CH}_2)_3$	40:60
E	Me	β -OH	$\text{CH}_2\text{O}(\text{CH}_2)_3$	< 5:95
F	Me	O	$\text{CH}_2\text{O}(\text{CH}_2)_3$	50:50

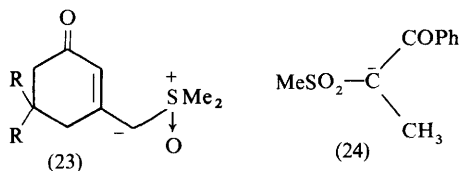
Scheme 2

Further details have appeared of the condensation of the dimethylsulfoxonium ylide (23; R = H or Me) with $\alpha\beta$ -unsaturated carbonyl compounds,⁵⁹ which were discussed in an earlier Report.¹ In the attempted alkylation of the ylide (24) with phenacyl bromide the ylide functions solely as a base, *trans*-1,2,3-tribenzoylcyclopropane being the sole product formed in high yield.⁶⁰

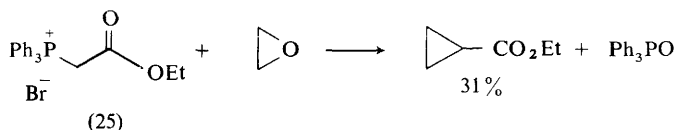
⁵⁸ B. G. James and G. Pattenden, *J.C.S. Perkin I*, 1974, 1204.

⁵⁹ Y. Tamura, T. Miyamoto, H. Kiyokawa, and Y. Kita, *J.C.S. Perkin I*, 1974, 1125.

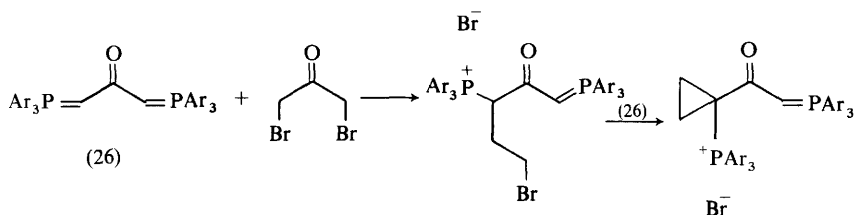
⁶⁰ B. Koutek, L. Pavlickova, and M. Soucek, *Coll. Czech. Chem. Comm.*, 1974, 39, 192.



Cyclopropanes are formed in the condensation of epoxides with ylides derived from phosphonates.⁶¹ Attempts to carry out similar reactions with phosphonium ylides were generally unsuccessful, an exception being the reaction of the phosphonium halide (25) with oxiran.⁶²



The bis-ylide (26) is alkylated by dibromoacetone and in the presence of excess ylide the initial product cyclizes, providing a route to cyclopropyl ketones.⁶³



The condensation of stabilized carbanions with epoxides,⁶⁴ activated olefins,⁶⁵ or alkanes bearing a good leaving group β to a second good leaving group,⁶⁶ or a carbanion-stabilizing function,⁶⁷ provides a general series of routes to cyclopropanes. In the reaction of the phosphonate (27) with methacrylate in the presence of sodium hydride, a mixture of *cis*- and *trans*-isomers of the phosphonate-substituted cyclopropane (28) was obtained in all solvents examined. A plot of the logarithm of the *trans/cis* ratio against the Kirkwood–Onsager term for solvent polarity gave a straight

⁶¹ M. Baboulène and G. Sturtz, *Bull. Soc. chim. France*, 1974, 1585; Fr. Demande, 2 168 947 (*Chem. Abs.*, 1974, **80**, 47 531).

⁶² J. Buddrus, *Chem. Ber.*, 1974, **107**, 2050.

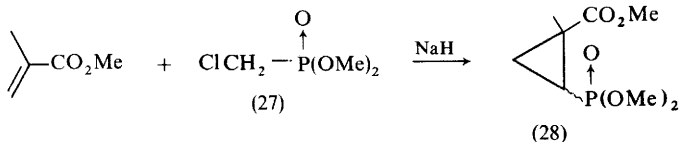
⁶³ A. Hercouet and M. Le Corre, *Tetrahedron Letters*, 1974, 2491.

⁶⁴ S. Nogami, K. Waki, and K. Toyamoto, Japan Kokai, 74 11867 (*Chem. Abs.*, 1974, **81**, 49 338); H. Cousse and G. Mouzin, Ger. Offen., 2351 729 (*Chem. Abs.*, 1974, **81**, 13 173).

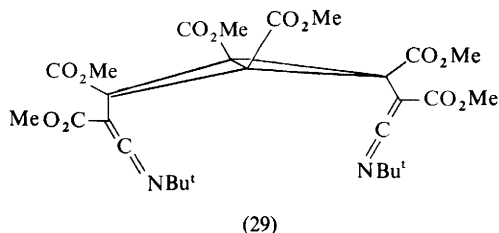
⁶⁵ C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, 1974, **39**, 918; J. Villieras, J.-R. Disnar, and J.-F. Normant, *J. Organometallic Chem.*, 1974, **81**, 295; T. Oishi, H. Takechi, and Y. Ban, *Tetrahedron Letters*, 1974, 3757; J. D. Bacha and C. M. Selwitz, U.S.P. 3 769 356 (*Chem. Abs.*, 1974, **80**, 3 160); L. H. Shepherd jun., U.S.P. 3 770 840 (*Chem. Abs.*, 1974, **80**, 14640); R. H. Rynbrandt, U.S.P. 3 770 747 (*Chem. Abs.*, 1974, **80**, 59 557); W. I. Fanta and J. I. Shulman, U.S.P. 3 823 177 (*Chem. Abs.*, 1974, **81**, 77 562).

⁶⁶ J. D. Bacha and C. M. Selwitz, U.S.P. 3 769 357 (*Chem. Abs.*, 1974, **80**, 3163).

line, with the slope being the inverse of that found in nearly all similar cases previously reported, *i.e.* the *cis*-isomer predominates in polar solvents and the *trans* in non-polar media. This inversion of the solvent-isomer ratio relationship was seen as a consequence of the presence of the polar, activating phosphonate group⁶⁸ and the result is consistent with the general concept of stereochemical control by transition-state dipole-solvent interactions proposed by Inouye. It should be noted, however, that the assignment of configuration to the cyclopropanes was based essentially on n.m.r. evidence, and a rigorous examination of product geometries is clearly important in a case of this type.



The kinetically controlled product of condensation of *t*-butyl isocyanide with acetylene dicarboxylic ester has been shown to have the bicyclobutane structure (29).⁶⁹



Intramolecular Cyclizations.—Theoretical calculations have been reported for the conversion of 1,3-disubstituted propanes into cyclopropanes.⁷⁰ Metal-promoted eliminations in 1,3-dihalogenoalkanes afford cyclopropanes, generally in good yields.⁷¹

The *trans*-1,2-dipropylcyclopropane formed in the Li(Hg)-induced debromination of *R,R*-4,7-dibromononane is generated with inversion of configuration at both centres. This stereochemical result rules out the possibility that the popular 'π-cyclopropane' takes part as an intermediate, and suggests a process in which metal-halogen exchange is followed by an internal displacement of the second halide group.⁷² The stereoconvergence observed in such cyclization reactions⁷³ (*i.e.* formation of the

⁶⁷ Z. Csuros, R. Soos, E. Fogassy, J. Palinkas, and G. Hernandi, Hung. Teljes., 8014 (*Chem. Abs.*, 1974, **81**, 37316).

⁶⁸ E. W. Hellmuth, J. A. Kaczynski, J. Low, and L. I. McCoy, *J. Org. Chem.*, 1974, **39**, 3125.

⁶⁹ H. J. Dillinger, G. Fengler, D. Schumann, and E. Winterfeld, *Tetrahedron*, 1974, **30**, 2553; see also p. 2561.

⁷⁰ O. S. Tee, J. A. Altmann, and K. Yates, *J. Amer. Chem. Soc.*, 1974, **96**, 3141.

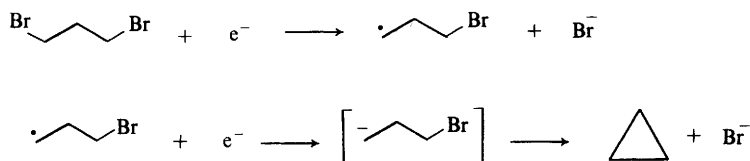
⁷¹ Y. Ito, K. Nakayama, K. Yonezawa, and T. Saegusa, *J. Org. Chem.*, 1974, **39**, 3273; A. A. Kamysheva, E. T. Chukovskaya, and R. K. Friedlina, *Izvest. Akad. Nauk, S.S.S.R., Ser. khim.*, 1974, 896 (*Chem. Abs.*, 1974, **81**, 37279); S. Takahashi, Y. Suzuki, and N. Hagihara, *Chem. Letters*, 1974, 1363.

⁷² M. Schlosser and G. Fouquet, *Chem. Ber.*, 1974, **107**, 1162.

⁷³ M. Schlosser and G. Fouquet, *Chem. Ber.*, 1974, **107**, 1171.

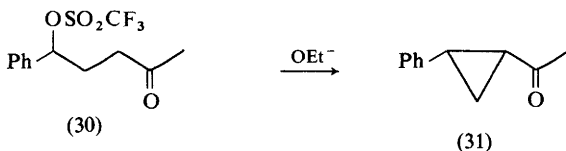
same mixture of *cis/trans* isomeric reaction products from diastereomeric dihalides) strongly suggests a non-concerted mode of reaction.

Evidence for a two-step mechanism has been adduced in the electrochemical reduction of 1,3- and 1,4-dibromides. For 1,3-dibromopropane studied by cyclic voltammetry in DMF solution with a silver-coated platinum electrode at moderately low sweep rate (0.3 V s^{-1}), surprisingly, two irreversible waves were observed. The results obtained⁷⁴ were suggestive of a mechanism involving two irreversible one-electron transfers, such as:



Cyclopropanes are formed by the intramolecular insertion of a carbene into a C—H bond.⁷⁵ A MINDO/2 study of the rearrangement of singlet ethylmethylene to propene and cyclopropane revealed that olefin formation (hydrogen migration) presents no energy barrier, but a critical energy of $1.4 \text{ kcal mol}^{-1}$ was found in the pathway to cyclopropane formation.⁷⁶

Intramolecular cyclization occurs when a carbanion is generated γ to a leaving group. Carbanion-stabilizing functions are carbonyl,⁷⁷ cyano,⁷⁸ nitro,⁷⁹ and pyridyl⁸⁰ groups whilst leaving groups may be halide,⁸¹ mesylate,⁸² and triflate. An example involving the latter⁸³ is the ethoxide-ion-induced cyclization of (30) to (31) which takes place in 65% yield at room temperature. It is noteworthy that closure to the three-membered ring is preferred to cyclopentanone formation.



⁷⁴ K. Wiberg and G. A. Epling, *Tetrahedron Letters*, 1974, 1119.

⁷⁵ T. R. Fields and P. J. Kropp, *J. Amer. Chem. Soc.*, 1974, **96**, 7559; W. E. Slack, C. G. Moseley, K. A. Gould, and H. Schechter, *J. Amer. Chem. Soc.*, 1974, **96**, 7596; A. Viola, S. Madhavan, and R. J. Proberb, *J. Org. Chem.*, 1974, **39**, 3154.

⁷⁶ M. Martin, V. Menezes, and J. M. Figuera, *Chem. Phys. Letters*, 1974, **27**, 292.

⁷⁷ D. L. Coffen, D. A. Katonak, and F. Wong, *J. Amer. Chem. Soc.* 1974, **96**, 3966; J. J. Koenig and C. G. Wermuth, *Tetrahedron*, 1974, **30**, 501; T. Kamiya, T. Teraji, M. Hashimoto, O. Nakaguti, and T. Oku, *Ger. Offen.*, 2358178 (*Chem. Abs.*, 1974, **81**, 49674).

⁷⁸ T. Sugiyama, A. Kobayashi, and K. Yamashita, *Agric. and Biol. Chem. (Japan)*, 1974, **38**, 979.

⁷⁹ J. D. Bacha and C. M. Selwitz, U.S.P. 3769355 (*Chem. Abs.*, 1974, **80**, 3162).

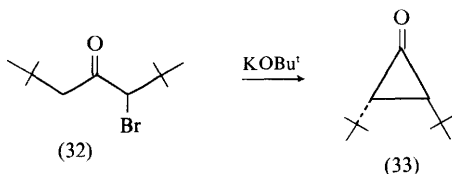
⁸⁰ J. J. Eisch, H. Gopal, and D. A. Russo, *J. Org. Chem.*, 1974, **39**, 3110.

⁸¹ M. Oda, T. Sato, and Y. Kitahara, *Synthesis*, 1974, 721.

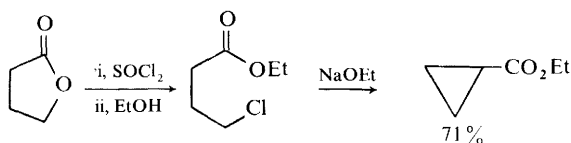
⁸² J. Kuszmann, P. Schar G. Horvath, and Z. Mehesfalvi-Vajna, *Tetrahedron*, 1974, **30**, 3905; K. Kondo, K. Matsui, and A. Negishi, *Chem. Letters*, 1974, 1371.

⁸³ J. B. Hendrickson, A. Giga, and J. Wareing, *J. Amer. Chem. Soc.*, 1974, **96**, 2275.

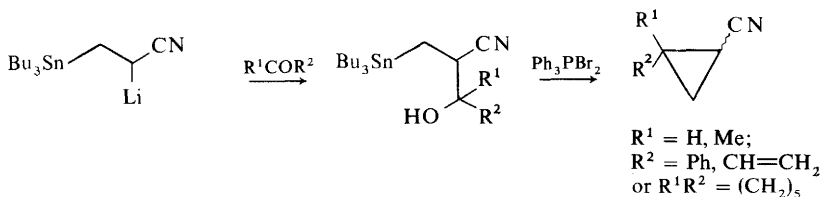
trans-Di-*t*-butylcyclopropanone (33) has been prepared⁸⁴ by the action of potassium *t*-butoxide on the bromoketone (32) and partly resolved by asymmetric destruction with *d*-amphetamine. The isomer (+)-(33) racemizes at 80°C and decarbonylates at 150°C or on irradiation. (Further reactions of this rare example of an isolable cyclopropanone are detailed on p. 102).



An improved two-step synthesis of cyclopropane-carboxylic ester from γ -butyrolactone makes use of a base-induced elimination:⁸⁵



Rate and product studies of the 1,3-deoxystannylation of 3-stannylalcohol derivatives implicate a concerted mechanism for cyclopropane formation.⁸⁶ This elimination reaction has been developed into a general synthesis of cyanocyclopropanes, based on the condensation of lithium tributyl-(2-cyanoethyl)tin with carbonyl compounds (Scheme 3).⁸⁷



Scheme 3

Oxidation of compound (34) with lead tetra-acetate affords the cyclopropane (35). This is the first observation of a homovinylic oxidation of a 2-pyrazoline.⁸⁸

Further details of the alkylation of eucarvone anions have appeared,⁸⁹ as have full

⁸⁴ J. F. Pazos, J. G. Pacifici, G. O. Pierson, D. B. Sclove, and F. D. Greene, *J. Org. Chem.*, 1974, **39**, 1990.

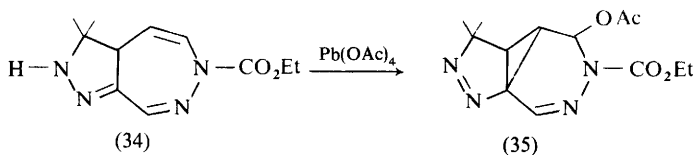
⁸⁵ S. C. Bunce and R. A. Kent, *Org. Prep. Proced. Internat.*, 1974, **6**, 193.

⁸⁶ D. D. Davis and R. H. Black, *J. Organometallic Chem.*, 1974, **82**, C30.

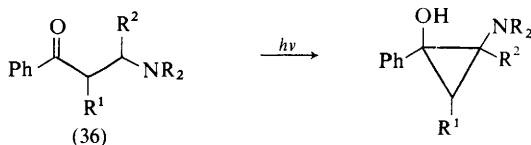
⁸⁷ S. Taretake, *Chem. Letters*, 1974, 1123.

⁸⁸ J. Streith, G. Kiehl, and H. Fritz, *Tetrahedron Letters*, 1974, 631.

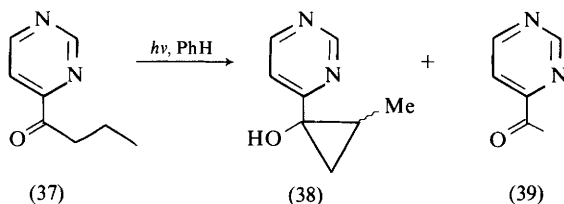
⁸⁹ A. J. Bellamy, W. Crilly, J. Farthing, and G. M. Kellie, *J.C.S. Perkin I*, 1974, 2417. See also G. A. Russell, R. L. Blankespoor, J. Mattox, P. R. Whittle, D. Symalla, and J. R. Dodd, *J. Amer. Chem. Soc.*, 1974, **96**, 7249.



studies of the previously reported photocyclization of 3-amino-ketones (36) to 2-amino-cyclopropanols.⁹⁰



Irradiation in benzene of 4-butyrolypyrimidine (37) affords a 60:40 mixture of the cyclopropanol (38) and cleavage product (39). Only the former product is formed when *t*-butyl alcohol is used as solvent and only the latter in hexane. These results are best accounted for by formation of an $n-\pi^*$ triplet which abstracts a γ -hydrogen (a process rarely seen with nitrogen aromatic ketones), giving a 1,3-biradical which can ring-close. Fragmentation could come from the 1,3-biradical or from alternative 1,4-biradical formation. The solvent effects have not yet been clearly explained.⁹¹



Full details have now been published⁹² of the solvolysis of β -allenic tosylates, which gives rise to cyclopropyl ketones and methylenecyclobutanols as discussed in an earlier Report.¹ The homoallenic participation may involve a cation of the bicyclobutonium type in addition to a cyclopropylvinyl cation. Similarly, a cyclopropylcarbinyl cation has been implicated in the solvolysis of the vinyl triflate (40) which gives rise to the cyclic products (41), (42), and (43; $\text{R} = \text{CH}_2\text{CF}_3$) in addition to acyclic derivatives⁹³ (Scheme 4). The same cyclic products are formed in the solvolysis of the tosylate (43; $\text{R} = \text{Ts}$).

The base-induced ring contraction of cyclobutanones substituted with a leaving group in the α -position is now a well-established procedure for the synthesis of cyclopropylcarbonyl compounds.⁹⁴ This reaction has now been extended to include 2-

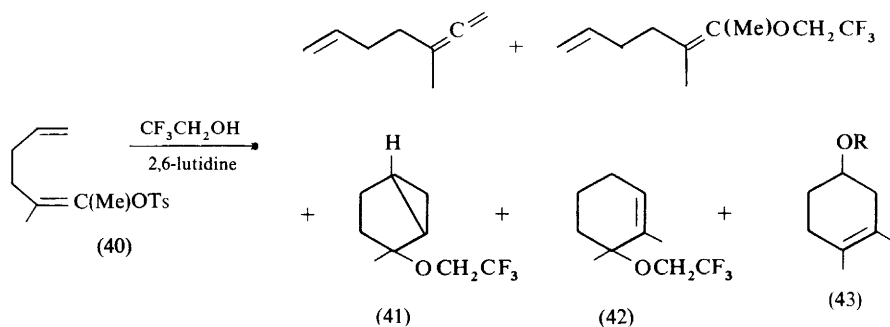
⁹⁰ H. J. Roth, M. H. El Raie, and T. Schrauth, *Arch. Pharm.*, 1974, **307**, 584.

⁹¹ E. C. Alexander and R. J. Jackson jun., *J. Amer. Chem. Soc.*, 1974, **96**, 5663.

⁹² M. Santelli and M. Bertrand, *Tetrahedron*, 1974, **30**, 227, 235, 243.

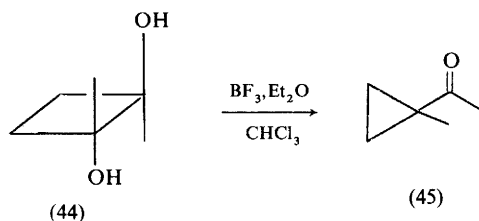
⁹³ T. C. Clarke and R. G. Bergman, *J. Amer. Chem. Soc.*, 1974, **96**, 7934.

⁹⁴ G. S. Krishnarao and L. R. Subramanian, *Indian P.* 105499 (*Chem. Abs.*, 1974, **81**, 169210).



Scheme 4

substituted cyclobutanols in what is essentially a pinacol rearrangement. For example, the diol (44) rearranges rapidly and quantitatively to cyclopropyl ketone (45) on addition of a trace of boron trifluoride etherate.⁹⁵



Cyclopropanes have been reported as products of decomposition of organometallic complexes⁹⁶ and in the irradiation of glutaric anhydride derivatives at elevated temperatures. The latter reaction also gives rise to smaller quantities of cyclobutanones in addition to cyclopropanes.⁹⁷

Moderate yields of 2- and 4-cyclopropylanisoles are obtained by irradiation of the corresponding allylanisoles.⁹⁸ The di- π -methane rearrangement provides a general photochemical route to cyclopropane derivatives and its mechanism and peculiarities are still under intensive investigation.⁹⁹ These are better discussed in detail in a review on photochemistry, as are the complex bond reorganizations observed¹⁰⁰ on irradiation of cyclohexanones and cyclohexadienones.

⁹⁵ J. P. Barnier, J. M. Denis, J. Salaun, and J. M. Conia, *Tetrahedron*, 1974, **30**, 1397; see also p. 1405.

⁹⁶ R. W. Hall, R. J. Puddephatt, K. R. Seddon, and C. F. H. Tipper, *J. Organometallic Chem.*, 1974, **81**, 423; B. F. G. Johnson, J. Lewis, and S. W. Tam, *Tetrahedron Letters*, 1974, 3793.

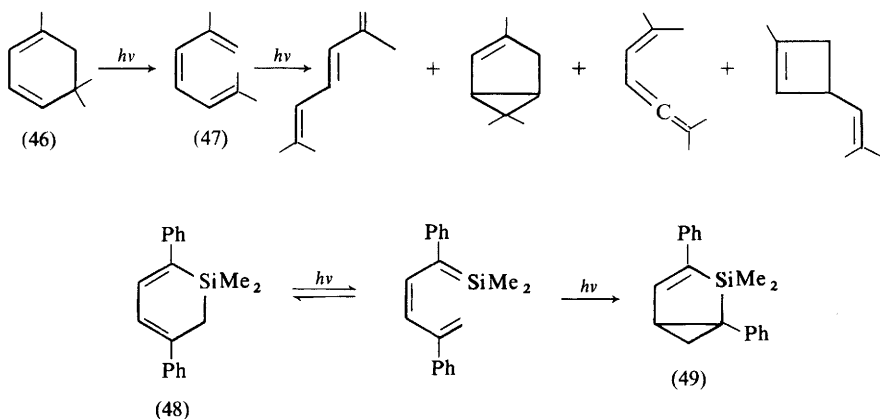
⁹⁷ H. Hiraoka, Fr. Demande, 2187 748 (*Chem. Abs.*, 1974, **81**, 3460).

⁹⁸ T. Clark and D. A. M. Watkins, *J.C.S. Perkin I*, 1974, 2124.

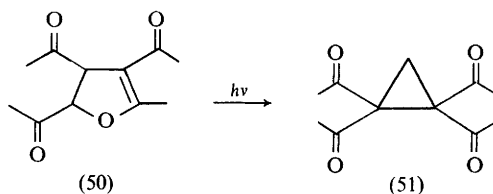
⁹⁹ R. C. Cookson, A. B. Ferreira, and K. Salisbury, *J.C.S. Chem. Comm.*, 1974, 665; H. E. Zimmerman, D. P. Wertheman, and K. S. Kamm, *J. Amer. Chem. Soc.*, 1974, **96**, 439; P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *ibid.*, p. 924; H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *ibid.*, p. 1459; H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *ibid.*, p. 1974; 4360; H. E. Zimmerman and R. D. Little, *ibid.*, p. 5143; H. E. Zimmerman and B. R. Cotter, *ibid.*, p. 7445; R. L. Coffin, R. S. Givens, and R. G. Carlson, *ibid.*, p. 7554; S. S. Hixson and J. C. Tausta, *Tetrahedron Letters*, 1974, 2007; Z. Goldschmidt and Y. Bakal, *ibid.*, p. 2809.

¹⁰⁰ D. Stuart, R. East, T. B. H. McMurry, and R. R. Talekar, *J.C.S. Chem. Comm.*, 1974, 450; J. Gloor and K. Schaffner, *Helv. Chim. Acta*, 1974, **57**, 1815; J. Repolles, F. Servera, and J.-J. Bonet, *ibid.*, p. 2454; D. I. Shuster, and K. V. Prabhu, *J. Amer. Chem. Soc.*, 1974, **96**, 3511; J. W. Pavlik and R. J. Pasteris, *ibid.*, p. 6107; D. L. Schuster and B. M. Resnik, *ibid.*, p. 6223; D. Caine and C. Y. Chu, *Tetrahedron Letters*, 1974, 703.

Photolysis of the cyclohexadiene (46) results in electrocyclic ring opening to the triene (47), which at wavelengths $> 280\text{nm}$ is further transformed into a mixture of products.¹⁰¹ The silacyclohexadiene (48), however, undergoes a specific photochemical rearrangement,¹⁰² giving only the cyclopropane (49).



Photochemical isomerization of dihydrofurans to cyclopropyl ketones has been adapted to provide a synthesis of 1,1,2,2-tetra-acylcyclopropanes. Thus, the tetra-acyl compound (51) is obtained¹⁰³ on irradiation of (50).



Whereas the chloro-ketone (52; $R^1 = \text{Cl}$; $R^2 = \text{H}$) affords the bicyclo[4,1,0]heptene (53) on irradiation in methanol, this product is not obtained from the isomer (52; $R^1 = \text{H}$; $R^2 = \text{Cl}$). Evidently the double bond in (52) assists in the departure of chloride and must attack from the back side of the $\text{C}-\text{Cl}$ bond.¹⁰⁴

A photochemical synthesis of 2,3-homoindoles (54; $R = \text{H}$ or OMe) has been described.¹⁰⁵

Cycloadditions of Carbenes and Carbenoids to Olefins.—*Base and Substituted Halogenomethane.* Dichlorocarbene adds to 1-aryl-1,3-dienes predominantly at the 3,4-double bond, the relative rate constants correlating with the σ^+ constants of sub-

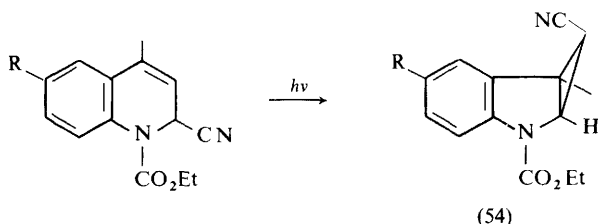
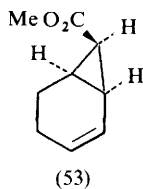
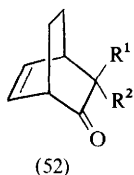
¹⁰¹ P. Courtot and R. Roumin, *J.C.S. Chem. Comm.*, 1974, 168; see also K. A. Burdett, F. L. Shenton, D. H. Yates, and J. S. Swenton, *Tetrahedron*, 1974, **30**, 2057.

¹⁰² Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Amer. Chem. Soc.*, 1974, **96**, 5621.

¹⁰³ K. Ohkata, T. Sakai, Y. Kubo, and T. Hanafusa, *J.C.S. Chem. Comm.*, 1974, 581.

¹⁰⁴ R. S. Givens, L. Strekowski, and R. Devonshire, *J. Amer. Chem. Soc.*, 1974, **96**, 1631.

¹⁰⁵ M. Ikeda, S. Matsugashita, F. Tabusa, H. Ishibashi, and Y. Tamura, *J.C.S. Chem. Comm.*, 1974, 433.



situents in the aromatic nucleus. The results agree with the hypothesis of an unsymmetrical and feebly polar transition state for the addition of the carbene to the double bond.¹⁰⁶ Interestingly, however, 2-phenylbuta-1,3-diene shows a 12:1 preference for reaction at the 1,2-double bond, as predicted by quantum chemical calculations by the Pariser-Parr-Pople method. These show that 2-substitution of butadiene by a phenyl group markedly lowers the π -bond order of the 1,2-bond.¹⁰⁷

Dihalogenocyclopropanations have been routinely carried out by reaction of an olefin with halogenoform and potassium t-butoxide in anhydrous medium.¹⁰⁸

Attempted cyclopropanation of 2,5-diphenylarsole (55; R = H) with dichlorocarbene led only to insertion into the As—H bond, giving (55; R = CHCl_2), but when this position was blocked (55; R = Ph) afforded 47% of (56; R = Cl) with chloroform-butoxide and 44% of (56; R = Ph) with benzal chloride-butoxide. The limitations of this cyclopropanation procedure are shown by the failure of 1-benzyl-2,5-diphenylarsole to react, but the dichlorocarbene adduct (57) could be obtained in 19% yield using $\text{PhHgCCl}_2\text{Br}$, and this adduct eliminated benzyl chloride on heating in acetonitrile, undergoing ring-expansion to (58). Thus, the pyrrole/3-chloropyridine conversion effected by dichlorocarbene now finds its analogy in the arsole series.¹⁰⁹

Ring-expansion of cyclic $\alpha\beta$ -unsaturated ketones by reaction of their pyrrolidine enamines with dichlorocarbene has been used in the synthesis of A-homo-steroids.¹¹⁰ An improved synthesis of *gem*-dichlorocyclopropanes uses lithium or potassium salts of triethylcarbinol as the base to effect HCl elimination from chloroform.¹¹¹

¹⁰⁶ R. R. Kostikov, V. S. Aksenov, and I. A. D'yakonov, *Zhur. org. Khim.*, 1974, **10**, 2099 (*Chem. Abs.*, 1975 **82**, 16423).

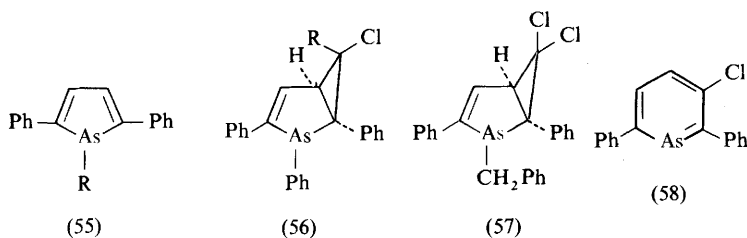
¹⁰⁷ R. R. Kostikov, A. P. Molchanov, and A. Y. Bepalov, *Zhur. org. Khim.*, 1974, **10**, 10 (*Chem. Abs.*, 1974, **80**, 107631).

¹⁰⁸ S. M. Shostakovskii, V. S. Aksenov, and V. A. Filimoshkina, U.S.S.R. P. 425892 (*Chem. Abs.*, 1974, **81**, 63231).

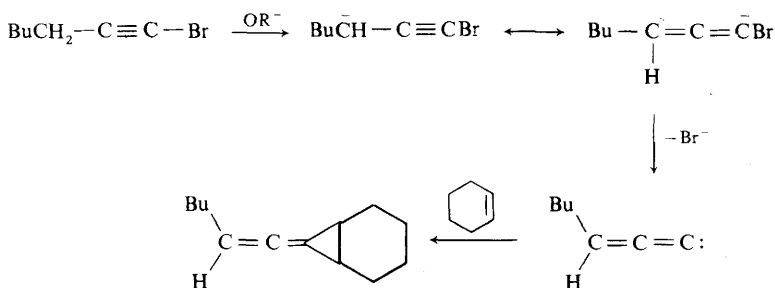
¹⁰⁹ G. Märkl, J. Advena, and H. Hauptmann, *Tetrahedron Letters*, 1974, 203.

¹¹⁰ S. A. G. De Graaf and U. K. Pandit, *Tetrahedron*, 1974, **30**, 1115.

¹¹¹ R. H. Prager and H. C. Brown, *Synthesis*, 1974, 736.

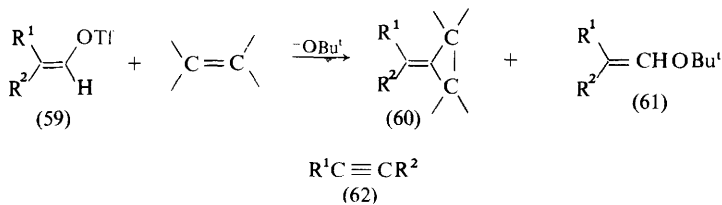


Reaction of 1-bromo-1-alkynes with alkoxide ion allows the generation of vinylidene carbenes (Scheme 5).¹¹²



Scheme 5

The synthetic utility of triflate as a good leaving group has recently begun to be recognized, *e.g.* in the generation of unsaturated carbenes by elimination from the vinyl triflates (59). Good yields of the methylenecyclopropanes (60) were obtained, along with small amounts of the products of substitution (61) for $\text{R}^1, \text{R}^2 = \text{Ph}, \text{Ph}; \text{Me}, \text{Ph};$ or H, Pr^n , only the acetylenes (62) were formed, in quantitative yield.¹¹³



The phase-transfer-catalysed (PTC) or Makosza method grows increasingly popular for the generation of carbenes, and a timely review of its applications to preparative organic chemistry has appeared.¹¹⁴ Further details have been published for the PTC addition of dichlorocarbene to cyclo-octatetraene¹¹⁵ and azepines.^{115, 116} Makosza

¹¹² C. D. Beard, J. C. Craig, and M. D. Solomon, *J. Amer. Chem. Soc.*, 1974, **96**, 7944.

¹¹³ P. J. Strong, M. G. Magnum, D. P. Fox, and P. Haak, *J. Amer. Chem. Soc.*, 1974, **96**, 4562.

¹¹⁴ E. V. Dehmow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 170.

¹¹⁵ T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Org. Chem.*, 1974, **39**, 455.

¹¹⁶ K. Kawashima, T. Saraie, Y. Kawano, and T. Ishiguro, *Ger. Offen.*, 2,404744 (*Chem. Abs.*, 1974, **81**, 135997).