Di-, Tri-, and Tetra-cyclopropylethylenes

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Summary The u.v. spectra of 1,1-dicyclopropyl-, *cis*- and *trans*-1,2-dicyclopropyl-, and tricyclopropylethylene, prepared by Wittig reactions, and tetracyclopropylethylene, isolated from decomposition products of dicyclopropyl ketone toluene-*p*-sulphonhydrazone sodium salt in dry diglyme have been studied.

CONSIDERABLE attention has been directed to the electronic spectra of various vinylcyclopropanes in recent years[1-3] and conformational effects on their u.v. absorption have been discussed. We report the preparation and spectral properties of ethylenes with a greater number of cyclopropyl substituents than those reported previously.

1,1 Dicyclopropyl-,[4] *cis*- and *trans*-1,2-dicyclopropyl-,[5] and tricyclopropyl-ethylene were prepared by the reactions of Wittig reagents with appropriate carbonyl compounds. For example, the reaction of (cyclopropylmethyl)triphenylphosphonium bromide[6] and phenyl-lithium with dicyclopropyl ketone in anhydrous ether gave tricyclopropylethylene in 44% yield. Purification by v.p.c. gave an analytically pure material (b.p. 102—102·5°/25 mm., n_D^{20} 1·5029). The structure was established by microanalysis, mass spectroscopy, and i.r. and n.m.r. spectroscopy. 1,1-Dicyclopropylethylene† (b.p. 129—130°, n_D^{20} 1·4677; lit.[4] b.p. 133°/758 mm., n_D^{20} 1·4563), *cis*-1,2-dicyclopropylethylene (b.p. 137—138°, n_D^{20} 1·4794), and *trans*-1,2-dicyclopropylethylene (b.p. 135°, n_D^{20} 1·4753) were prepared and purified similarly. 1,1-Dicyclopropylethylene polymerized slowly on standing at room temperature.

Attempts to prepare tetracyclopropylethylene in the

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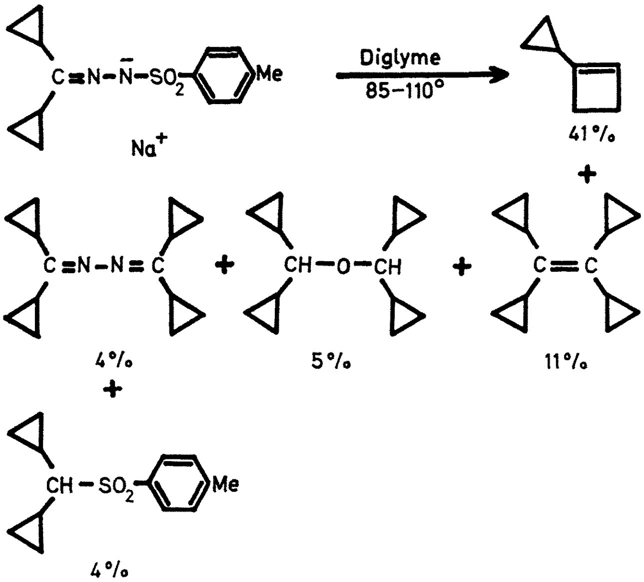
† All compounds which appear hereafter gave satisfactory microanalysis and spectra.

same manner as above were not successful. (Dicyclopropylmethyl)triphenylphosphonium bromide (m.p. 167—168°) was obtained in reasonable yield by Harrison and Lythgoe's procedure.[7] It reacted with benzaldehyde in the presence of phenyl-lithium but did not react with dicyclopropyl ketone under a variety of conditions.



Accordingly, an attempt was made to isolate a dimeric product of dicyclopropylcarbene. Although it has been shown that cyclopropylcarbene forms ring-ruptured products,[8,9] an alkyl substituent, the second cyclopropyl group in the present case, on the carbene, might prevent ring opening, as occurs in carbonium ion reactions.[10] A concentrated solution of the sodium salt of dicyclopropyl ketone toluene-*p*-sulphonhydrazone was made from the hydrazone (66 g.) and sodium hydride in 132 ml. of dry diglyme, and the decomposition was carried out at 85—110°. The reaction product was distilled, giving a low-boiling fraction (*ca.* 60° at 100 mm. Hg.) and a high-boiling fraction (70—90° at 3 mm.). The low-boiling fraction consisted mostly of 1-cyclopropylcyclobutene (41%, b.p. 106—107°, n_D^{20} 1·4665) besides a small amount of unidentified product.

The high-boiling fraction contained three components in a ratio of 1 : 10 : 20, from which the latter two were isolated by v.p.c. Purification by v.p.c. gave analytically pure samples of both components. The major one was a hydrocarbon of a molecular formula $C_{14}H_{20}$ (microanalysis and mass spectroscopy). The n.m.r. spectrum of this compound is distinctive; it shows only two multiplets, at 8·3—8·9 and 9·0—9·9 p.p.m., in a ratio of 1 : 4. These two multiplets are characteristic of the cyclopropyl group attached to an olefin,‡ confirming that the compound is tetracyclopropylethylene (11%, b.p. 88—91° at 2·6 mm., n_D^{20} 1·5149). It decolourized potassium permanganate solution and bromine in carbon tetrachloride.

The second component in the high-boiling fraction was bisdicyclopropylmethyl ether (5%, b.p. 108—109° at 8 mm., n_D^{20} 1·4732). From the distillation residue, the ketone azine (4%, m.p. 91—92°) and dicyclopropylmethyl *p*-tolyl sulphoxide (4%, m.p. 109·5—111°) were isolated.

In the u.v. region, the polycyclopropyl-substituted ethylenes absorbed at considerably longer wavelength than various alkyl substituted vinylcyclopropanes.[1] Dicyclopropylethylenes absorb from 201·5 to 205 nm., 1,1-dicyclopropylethylene absorbing at the shortest wavelength, the *cis*-1,2-isomer the next, and the *trans*-isomer absorbing at the longest wavelength. An auxochromic effect of the cyclopropyl group is manifest in tri- and tetra-cyclopropylethylenes. The third and fourth cyclopropyl groups each cause an additional 7 nm. bathochromic shift. Thus, tetracyclopropylethylene absorbs at 219 nm., which is unusual for an alkene.

U.v. spectral data of some cyclopropylethylenes§

Ethylene	λ_{max} (n-hexane) nm.	ϵ
1-Methyl-1-cyclopropyl-	196	9200
1,1-Dicyclopropyl-	201·5	8700
cis-1,2-Dicyclopropyl-	203·5	16,500
trans-1,2-Dicyclopropyl-	205	14,500
Tricyclopropyl-	212·5	12,400
Tetracyclopropyl-	219	12,000

§ Spectra were recorded with a Hitachi EPS-3T Recording Spectrophotometer.

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‡ Similar patterns were observed in various cyclopropylethylenes and phenylcyclopropanes.[11]

[1] C. H. Heathcock and S. R. Poulter, *J. Amer. Chem. Soc.*, 1968, **90**, 3766; and references cited therein.

[2] M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, 1968, **90**, 3769.

[3] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, 1967, **89**, 3449.

[4] A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, 1965, **30**, 940.

[5] W. Lüttke and A. de Meijere, *Angew. Chem.*, 1966, **78**, 544.

[6] A. Maercker, *Angew Chem.*, 1967, **79**, 576.

[7] I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 1958, 843.

[8] J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, 1965, **87**, 659; F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, 1966, **88**, 3870.

[9] K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, 1966, **88**, 365.

[10] M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 3671; M. Vogel and J. D. Roberts, *ibid.*, 1966, **88**, 2262.

[11] S. Nishida, I. Moritani, and T. Sato, *J. Amer. Chem. Soc.*, 1967, **89**, 6885.