Some Derivatives of 2, 3-Diphenylcyclopropenone[1]

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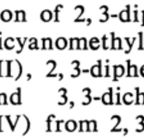
Recently, the aromaticity of the cyclopropenyl system has been investigated theoretically as well as experimentally in several countries.[3] In connection with our studies of the cycloheptatrienyl system, we compared these two systems. This paper will describe the preparation of 2, 3-diphenylcyclopropenethione (I), 3-dicyanomethylene-1, 2-diphenyl-1-cyclopropene (II), 2, 3-diphenylcyclopropenone oxime (III) and 3, 3-dichloro-1, 2-diphenyl-1-cyclopropene (IV) from 2, 3-diphenylcyclopropenone (V).



I : X=S
II : X=C(CN)$_2$
III : X=NOH
IV : X=Cl$_2$
V : X=O

2, 3-Diphenylcyclopropenethione (I). — The reaction of 2, 3-diphenylcyclopropenone[4] (V) with phosphorus pentasulfide in dry benzene at 50~60°C gave 68% of I; m. p. 125~126°C (decomp.), yellow prisms from methanol. Found: C, 81.16; H, 4.70. Calcd. for $C_{15}H_{10}S$: C, 81.06; H, 4.54%. IR (KBr disk) :[5] 1780(m), 1597(m), 1438(m), 1350(vs), 1310(s), 1298(s), 1170(m), 1015(m), 760(s), 682(s), 658(m) cm^{-1}; (in CCl_4) : 3050(m), 1780(m), 1597(m), 1450 (m), 1358(vs), 1311(s), 1298(s), 1172(m), 1020 (m) cm^{-1}. The bands at 1780 and 1350~1358 cm^{-1} may be due to the C=C stretching in a three-membered ring and to C=S stretching[6] respectively. UV λ_{max} mμ (log ε) (in cyclohexane) : 236(4.32), 245(4.52), 268(4.40), 284 (4.28), 298(4.06), 360(3.98) ; (in methanol) : 227(4.17), 234(4.11), 265(4.39), 277(4.36), 336 (4.14). The dipole moment of I in benzene at 30°C is 5.8 D. The hydrolysis of I with 75% sulfuric acid regenerated V.

3-Dicyanomethylene-1, 2-diphenyl-1-cyclopropene (II).—The refluxing of V with malononitrile in freshly-distilled acetic anhydride in the presence of a minute amount of boron trifluoride afforded 23% of II; m. p. 299°C (decomp.), pale yellow prisms from tetrahydrofuran. Found: C, 84.64; H, 3.93; N, 10.88. Calcd. for $C_{18}H_{10}N_2$: C, 85.02; H, 3.96; N, 11.02%. IR (KBr disk) :[5] 2210(s), 2190(s), 1865(m), 1600(m), 1507(s), 1477(s), 1444(s), 1393(s), 1375(s), 769(s), 687(s) cm^{-1}. UV λ_{max} mμ (log ε) (in dioxane) : 244(4.28), 274(4.43), 293(4.45), 306(4.40), 362(4.06). The dipole moment II in dioxane at 30°C is 9.3 D.

2, 3-Diphenylcyclopropenone Oxime (III). — The reaction of V with hydroxylamine hydrochloride in methanol and the neutralization of the resulting mixture with sodium hydrogencarbonate yielded 24% of III, m. p. 99~101°C, colorless prisms. Found: C, 81.35; H, 4.92; N, 6.16. Calcd. for $C_{15}H_{11}ON$: C, 81.43; H, 5.01; N, 6.33%. IR (KBr disk) :[5] 3420 (s), 3250(s), 1875(m), 1850(m), 1593(s), 1450(s), 1360(s), 866(s), 764(vs), 690(vs) cm^{-1}.

3, 3-Dichloro-1, 2-Diphenyl-1-cyclopropene (IV).—When V was allowed to react with phosphorus pentachloride in chloroform, it gave IV,[7] m. p. 123~126°C. IR[5] (in CCl_4) : 1810(w), 1630(m), 1600(w), 1450(s) ; (in CS_2) : 1342(s), 1145(s), 1120(s), 1013(m), 911(m), 760(s), 725(m), 701(s), 680(s) cm^{-1}. The structure of IV was suggested by a comparison of its infrared spectrum with that of tetrachlorocyclopropene,[8] by the quantitative regeneration of V by hydrolysis with water, and by the neutralization equivalent of the hydrogen chloride yielded in the hydrolysis reaction. Details of this report, a comparison with the corresponding cycloheptatrienyl

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[1] A part of this paper was presented as a special lecture at the Symposium on Molecular Structure, Sendai, October 3, 1963. Two other communications[2] prompted us to report in the preliminary form. This investigation was supported in part by a donation from the Sankyo Co., Tokyo.

[2] E. D. Bergmann and I. Agranat, *J. Am. Chem. Soc.*, **86**, 3587 (1964); A. S. Kende and P. T. Izzo, ibid., **86**, 3587 (1964).

[3] J. D. Roberts, A. Streitwieser, Jr. and C. M. Regan, ibid., **74**, 106 (1956); S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959); R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963) and ref. cited therein; A. S. Kende, ibid., **85**, 1882 (1963); M. A. Battiste, ibid., **86**, 944 (1964); M. E. Volpin et al., *Izvest. Akad, Nauk SSSR, otdel, Kim Nauk*, **1959**, 560; *Doklady Akad Nauk SSSR*, **139**, 1107 (1961).

[4] Prepared by the method of R. Breslow (*J. Am. Chem. Soc.*, **85**, 234 (1963)).

[5] Only significant bands are shown.

[6] The ratio between the $\nu_{C=O}$ of cyclopropenone and the $\nu_{C=S}$ of the corresponding thioketone is 1.33~1.37. This obeys Mecke's rule. Cf. R. Mecke, R. Mecke and A. Lüffringhans, *Chem. Ber.*, **90**, 975 (1957).

[7] Microanalysis could not be carried out because of this substance's high hygroscopic property.

[8] S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

system, and the dipole moment⁹⁾ of the compounds will be reported on in the near future.

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9) S. Katagiri, M. Saga, H. Azumi, M. Funamizu and Kitahara, to be published.