2,3-Diphenyl-4,5-dihydrofuran-5-spirodiphenylcyclopropene

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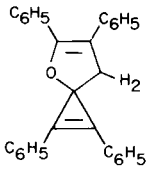
Cyclopropenes can be cleaved to provide three carbon moieties for intermolecular and intramolecular addition reactions. In this manner have been formed 3-methyldihydrofuran-2-one-5-spiromethylcyclopropene from two mole equivalents of methylcyclopropenone (2) and 3-methyldihydrofuran-2-one-5-spirodimethylcyclopropene from one mole equivalent each of dimethylcyclopropenone and methylcyclopropenone (2). It has been proposed that intermolecular self addition of diphenylcyclopropenone led to a dimer, 3,4-diphenyldihydrofuran-2-one-5-spirodiphenylcyclopropene (3). Intramolecular addition of a three carbon species across a phenyl bond was used in rationalization of the formation of 1,2,3-triphenylindene and of 1,4,6-trimethyl-1,2,3-triphenylindene from tetraphenylcyclopropene and 3-mesityl-1,2,3-triphenylcyclopropene, respectively (4). This note describes further exploration of the synthetic possibilities of addition reactions with three carbon moieties derived from cyclopropenes.

Bis=(Δ^2-2,3-diphenylcyclopropenyl) ether heated at about 115° in a glacial acetic acid and pyridine solution in the presence of malononitrile yielded solid which had an elemental analysis correct for an isomer of the cyclopropenyl reactant. The isomer, obtained in 50% of the theoretical yield based on the cyclopropenyl reactant, exhibited spectra consonant with assignment to the structure of 2,3-diphenyl-4,5-dihydrofuran-5-spirodiphenylcyclopropene (I). The nuclear magnetic resonance spectrum of the new isomer showed multiplets attributable to eight *o*-hydrogens on phenyl rings (at τ 2.21), twelve *m*- and *p*-hydrogens on phenyl rings (at τ 2.61), and one methylene unit (at τ 7.03). The last value is at a higher field than has been found for oxymethylene units of tetrahydrofuran (5) and some other cyclic ethers (5); therefore, the white solid is not 3,4-diphenyl-2,5-dihydrofuran-2-spirodiphenylcyclopropene. Included in the infrared absorption spectrum were ν [(chloroform) 2858 (a methylene unit), 1817 (a cyclopropene), 1598 (a conjugated aromatic ring), 1467 (a methylene unit), 1437 (a vinylmethylene unit), 1230 (possibly, a vinyl ether), 1226 (possibly, a vinyl ether), 1197 (possibly, a vinyl ether), and 676 cm^{-1} (a monosubstituted benzene). The 1124 and 1063 cm^{-1} bands of the starting material, bis-(Δ^2-2,3-diphenylcyclopropenyl) ether, were not present in the infrared absorption spectrum of the white reaction product. The relative locations and intensities of peaks in the ultraviolet spectrum assigned to I are in agreement with those characteristic of 1,2-diphenylcyclopropenes. Portions of representative ultraviolet spectra are listed in Table I.

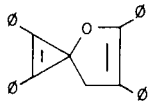
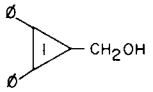
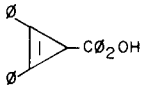
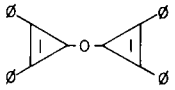
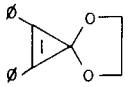
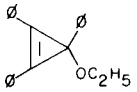
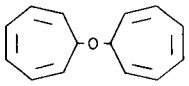
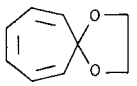


(I)

Compound I is rigid and is constrained in a conformation which can be inspected for homoconjugation, exchange interaction between p orbitals of the alkenoid linkage and of oxygen. The significance of homoconjugation in I can be analyzed by comparison of ultraviolet spectra given in Table I. Reference systems which did not exhibit homoconjugation are (Δ^2-2,3-diphenylcyclopropenyl)-carbinol, diphenyl-(Δ^2-2,3-diphenylcyclopropenyl)-carbinol, and 1,2,3-triphenylcyclopropene. For bis-(Δ^2-2,3-diphenylcyclopropenyl) ether and 3-ethoxy-1,2,3-triphenylcyclopropene interaction between oxy and olefinic units resulted in hypsochromic shifts away from peaks in the appropriate reference compounds (9). Increased exchange interaction, spiroconjugation (9), occurs in the ethylene ketal of diphenylcyclopropenone and this system exhibited large hypsochromic shifts away from peaks of the reference compounds. In the tropilidene series ultraviolet absorption at essentially the same wavelength for both ditropyl ether and the ethylene ketal of tropone was attributed to poor overlap of the alkenoid and both oxygen moieties owing to the nonplanarity of the tropilidene system. The probe for exchange interaction in I indicates that insignificant homoconjugation is

TABLE I

Portions of Ultraviolet Spectra of Some
1,2-Diphenylcycloprop-1-enes and Some Cycloheptatrienes

Compound	Solvent	Values for λ max (in mμ)	Literature Reference
 (I)	CH_2Cl_2	331 (O.D. 0.445), 313 (0.609), 306 (sh, 0.509), 298 (sh, 0.434)	
		332 (ε, 17.4 x 10^3), 316 (23.4 x 10^3)	(6)
		335 (ε 17 x 10^3), 319 (27.5 x 10^3)	(7)
	CH_3CN	318 (ε 44.0 x 10^3), 302 (59.0 x 10^3), 288 (sh, 46.0 x 10^3)	(8)
	i-C_8H_{18}	305 (ε 17.2 x 10^3), 290 (23.6 x 10^3), 278 (22.3 x 10^3)	(9)
		334 (ε 22.8 x 10^3), 318 (28 x 10^3)	(10)
	CH_3OH	316 (ε 24 x 10^3), 300 (29 x 10^3), 286 (23 x 10^3)	(11)
	i-C_8H_{18}	256-260 (ε 10.5 x 10^3)	(12)
	i-C_8H_{18}	258 (ε 4.90 x 10^3)	(9)

observed for the geometry of I; the positions of the long wavelength absorption bands of I are comparable to those of its reference systems [(Δ^2-2,3-diphenylcyclopropenyl)-carbinol and diphenyl-(Δ^2-2,3-diphenylcyclopropenyl)-carbinol].

Two processes necessary to formation of I from bis-(Δ^2-2,3-diphenylcyclopropenyl) ether are cleavage of a carbon to oxygen bond of the starting material and destruction of one cyclopropenyl ring system. A variety of mechanisms can be written to complete the necessary rearrangement. The role of malononitrile in this reaction is, as yet, undefined.

EXPERIMENTAL (13)

2,3-Diphenyl-4,5-dihydrofuran-5-spirodiphenylcyclopropene (I).

A solution of bis-(Δ^2-2,3-diphenylcyclopropenyl) ether (14), glacial acetic acid, pyridine, and malononitrile in the amounts of 2.5 x 10^{-4}, 7.5 x 10^{-2}, 7.5 x 10^{-3}, and 5.0 x 10^{-4} mole, respectively, was kept under a dry nitrogen atmosphere; heated from 26 to 117°; and maintained at 112-117° about one half hour. The reaction mixture was cooled to obtain white needles in 50% of the theoretical yield based on an isomer of the starting ether. When malononitrile was excluded from the reaction mixture solid did not separate from the cooled mixture. The solid, recrystallized from benzene and *n*-hexane or *n*-pentane, melted at 172.8-173.0° with browning and was insoluble in *n*-hexane and soluble in benzene, ether, and

chloroform; infrared absorption spectrum: ν (chloroform) 3063(s), 3014(s), 2965(s), 2931(s), 2925(s), 2858(w), 1817(w), 1674(w), 1598(w), 1517(w), 1497(m), 1487(m), 1467(m), 1447(s), 1437(sh,m), 1429(m), 1373(w), 1345(w), 1315(m), 1230(sh,s), 1226(s), 1197(s), 1109(m), 1096(m), 1072(m), 1052(m), 1035 (sh,m), 1023(s), 1017(s), 924(sh,m), 915(m), 902(sh,w), 801(sh,m), 706(sh,s), 695(sh,s), 686(sh,s), 676(s), and 666(sh,s) cm^{-1}; nuclear magnetic resonance spectrum (deuteriochloroform with tetramethylsilane as an internal standard) τ 2.21 (multiplet, 8 hydrogens), τ 2.61 (multiplet, 12 hydrogens), and τ 7.03 (sharp singlet, 2 hydrogens); ultraviolet absorption spectrum: λ max (dichloromethane) 231(sh, O.D. 0.424), 233(sh, 0.424), 236 (0.430), 298(sh, 0.434), 306(sh, 0.509), 313 (0.609), and 331 mμ (0.445); λ min (dichloromethane) 251 (O.D. 0.053) and 326 mμ (0.393).

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.36; H, 5.68.

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(13) The melting point is uncorrected; sample was inserted at 24.7°. The instruments used for spectral measurements were a Beckman IR-8, a Varian Associates A-60, and a Beckman DB equipped with a linear Varicord model 43 recorder (Photovolt Corp.).

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