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A NEW SYNTHESIS AND ENE REACTION OF 1,2-DIPHENYLCYCLOPROPENE

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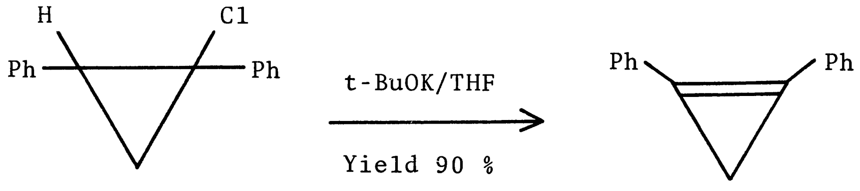
A new worthwhile synthesis of 1,2-diphenylcyclopropene (1) by the dehydrochlorination of cis- and trans-1-chloro-1,2-diphenylcyclopropanes has been found. The isolation of two dimers and ene reactions of 1 have also been described.

The cyclopropene system having a methylene group as the ring member, especially 1,2-diphenylcyclopropene (1) is significant as a probe for the investigation of physical and chemical properties of highly strained double bond. Although we recently encounter only one paper$^{1)}$ dealing with the preparation of 1, its preparation method does not seem to be straightforward and worthwhile, because diphenylcyclopropenyl cation is used as the starting system. From this reason, we have investigated a straightforward and worthwhile synthesis of 1 due to the dehydrochlorination of cis- and trans-1-chloro-1,2-diphenylcyclopropanes, being so far reported to be unsuccessful.$^{2)}$

Here, we wish to report such a new synthesis of 1. A large excess of powdered potassium tert-butoxide was added to the solution of cis-1-chloro-1,2-diphenylcyclopropane (2)$^{3)}$ in tetrahydrofuran (THF) at room temperature under nitrogen, and the mixture was stirred for 24 hours. Ordinary workup afforded 1 in 90 % yield, $C_{15}H_{12}$, mp 50-51°C, (lit.$^{1)}$ mp 42-47°C). Same treatments of the trans-isomer ((4), bp 190°C/1 mm Hg) and of the mixture of both isomers (2 and 4) also aforded 1 in 90 % yield, respectively. Hydrogenation of 1 on Pd-C gave cis-1,2-diphenylcyclopropane, mp 37°C, in quantitative yield. It is to note that the reaction of the trans-isomer (4) with potassium amide in dimethoxyethane for 24 hours at room temperature has afforded 1 in 60 % yield contrast to the case$^{3)}$ of the reaction of 2 (product; 3). As the synthetic method of 1 by dehydrochlorination of 2, t-BuOK-THF gave a best result.



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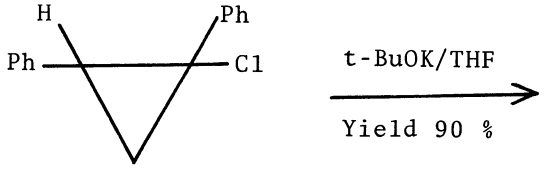

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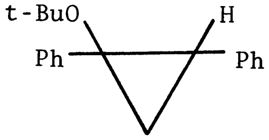
When t-BuOK-dimethylformamide was used as the dehydrochlorinating agent, the mixture of several products containing a minor amount of 1 was obtained. For instance, at around 80°C a major product was 5, $C_{19}H_{22}O$, bp 190°C/1 mm Hg; nmr ($CDCl_3$), three multiplets at τ 2.50-3.10, 7.40 and 8.22 (10H, 1H, and 2H respectively), one singlet at 8.85 (9H); uv (CH_2Cl_2) showed only end absorption, and at 0-20°C major products were polymeric, two of which corresponded to the dimer A (yield 20 %) and B (yield 10 %) of 1. The dimer A, $C_{30}H_{24}$, (yellow viscous oil)$^{8)}$, mass spectrum, m/e 384 (M^+), was also quantitatively produced after standing the solution of 1 for several days at room temperature.$^{4,5)}$ The dimer B (mp 260-261°C) was assigned to 2,3,5,6-tetraphenylcyclohexa-1,3-diene (6) from the elemental analysis$^{8)}$ and the following spectral data; nmr ($CDCl_3$), multiplets at τ 2.40-3.20 (22H) and a singlet at 6.30 (2H); uv, λ_{max} (CH_2Cl_2) mμ(log ε) 255 (4.3), 288 (sh, 3.9); mass spectrum m/e 384 (M^+ 10 %), 382 (100 %).



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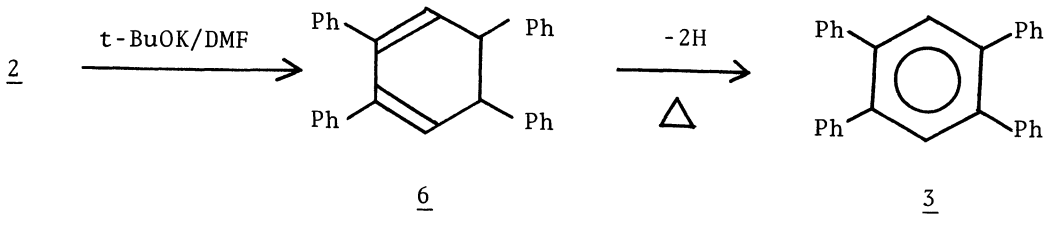
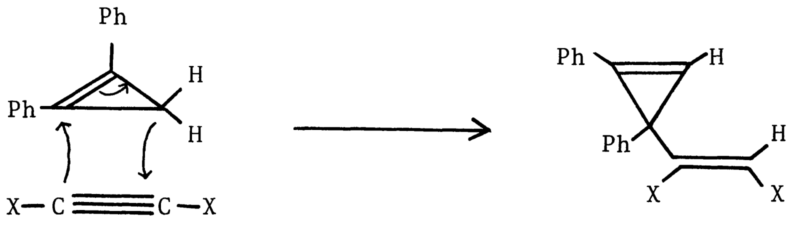
Although 1,4-cycloaddition of 6 has not yet been attempted, the quantitative transformation of 6 to 3 on heating in refluxing toluene for three days is well understood from the assigned structures and mass spectrum of 6.



An attempted reaction of 1 with equimolar amount of dibenzoylacetylene in benzene at room temperature was found to afford an ene reaction product 7, $C_{31}H_{22}O_2$, in 90 % yield, mp 166-167°C; nmr ($CDCl_3$) only complicated multiplets at τ 2.0-3.0, ir (KBr), 1780 cm^{-1} (cyclopropene double bond), 1660 cm^{-1} and 1580 cm^{-1}; uv, λ_{max} (CH_2Cl_2) 260 mμ (log ε 4.2). A similar ene reaction product 8 was also obtained in 40 % yield by the reaction of 1 with excess diethyl acetylenedicarboxylate, $C_{23}H_{22}O_4$ (unstable oil); nmr ($CDCl_3$), multiplets at τ 2.0-2.9 (10 H, phenyl H), two singlets at 3.13 (1 H, cyclopropene H) and 4.27 (1 H, vinyl H), double quartets at τ 5.9 (4 H) and double triplets at τ 8.9 (6 H) due to two ethyls; uv, λ_{max} (CH_2Cl_2) 250 mμ (log ε 4.0); mass spectrum, m/e 362 (M^+, 80 %), 289 (80 %), 244 (50 %), 217 (80 %), 216 (70 %), 215 (100 %), 105 (70 %), 77 (30 %). The cis configuration of 7 and 8 is presumed by analogy with the ene reaction product between 1-methylcyclopropene and hexafluorobutyne-2.[4c)]



7; X = COPh

8; X = CO_2Et

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2) See references cited in Ref. 1.

3) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, J. Amer. Chem. Soc., 87, 5139 (1965). The cis configuration of phenyls of 2 was established by treating with n-BuLi followed by water⁶⁾, because of the exclusive generation of cis-1,2-diphenylcyclopropane.

4) Thermal ene-type dimerization reactions of some cyclopropenes are known⁷⁾: (a) R. Breslow and P. Dowd, ibid., 85, 2729 (1963), (b) P. Dowd and A. Gold, Tetrahedron Lett. 1969, 85, (c) F. J. Weigert, R. L. Baird, and J. R. Shapley, J. Amer. Chem. Soc., 92, 6630 (1970).

5) The structure of this dimer is not yet determined.

6) H. M. Walborsky, F. J. Impastate, and A. E. Young, J. Amer. Chem. Soc., 86, 3283 (1964).

7) Cf. A. J. Schipperijn and J. Lukas, Tetrahedron Lett. 1972, 231.

8) All new compounds described gave satisfactory elemental analyses.

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