1,2-Diphenylcyclobutene

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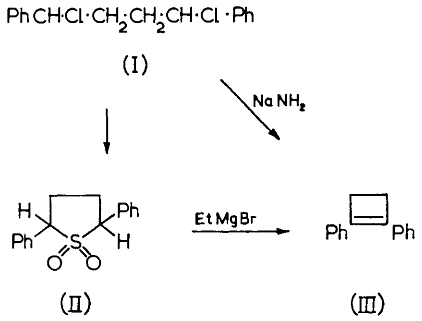
IN a previous communication,[1] we have reported the conversion of sulphones into olefins by treatment with Grignard reagents. Here, we report the application of the concepts developed in that communication to the preparation of 1,2-diphenylcyclobutene.

2,5-Diphenyltetrahydrothiophen dioxide (II), m.p. 165—167°, was prepared from 1,4-dichloro-1,4-diphenylbutane (I), m.p. 35—37°, by reaction with sodium sulphide in dimethylformamide, and oxidation of the resultant 2,5-diphenyltetrahydrothiophen with hydrogen peroxide in formic acid–carbon tetrachloride mixture. Treatment of this cyclic sulphone (II) with ethylmagnesium bromide[2] in ether–benzene mixture produced 1,2-diphenylcyclobutene, m.p. 51·5—52·5° (37% pure; 47% crude yield, m.p. 40–50°). This same compound could be produced in 89% yield by treatment of 1,4-diphenyl-1,4-dichlorobutane (I), m.p. 112·5–113·5°, or a mixture of its stereoisomers, with sodium amide in liquid ammonia.[3]

The structure of the 1,2-diphenylcyclobutene (III) was established by analysis and by comparison of its ultraviolet absorption spectrum, λ_{max} (ethanol) 227·5 mμ (ϵ 23,100) 297·5 mμ (ϵ 17,800), λ_{sh} 309 mμ (ϵ 16,800), with that of



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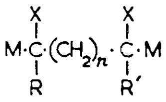
[1] R. M. Dodson, P. P. Schlangen, and E. L. Mutsch, accompanying communication.

[2] We have previously shown that reaction of either *cis*- or *trans*-2,4-diphenylthietan dioxide with ethylmagnesium bromide produces *trans*-1,2-diphenylcyclopropanesulphinic acid. R. M. Dodson and G. Klose, *Chem. and Ind.*, 1963, 1203.

[3] For similar reactions producing acyclic stilbenes see W. R. Brasen, S. W. Kantor, P. S. Skell, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1957, **79**, 397.

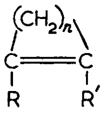
related compounds;[4] and from its n.m.r. spectrum, $\tau 2{\cdot}33$—$2{\cdot}95$ (complex multiplet, integrated for 9·83 H-atoms) and $\tau 7{\cdot}27$ (singlet, integrated for 4·17 H-atoms). Oxidation of (II) with potassium permanganate and sodium metaperiodate in t-butyl alcohol[5] produced dibenzoylethane, m.p. 146—148·5°, (30% yield) identical in all respects with an authentic sample.[6]

The mass spectrum of (III) also confirmed its structure. The most intense peak in the spectrum was that of the molecular ion at *m/e* 206. Peaks corresponding to the diphenylcyclobutenium ion (*m/e* 205, 60% *M*),[7] the diphenylcyclopropenium ion (*m/e* 191, 30% *M*), the positive ion of phenylacetylene (*m/e* 178, 17% *M*), the phenylcyclobutenium ion (*m/e* 129, 15% *M*), and the phenylcyclopropenium ion (*m/e* 115, 19% *M*), as well as the expected peaks at *m/e* 91 (68% *M*), 77 (28%M), and 51 (22% *M*) were present. A moderately intense peak (*m/e* 128, 27% *M*) corresponding to the positive ion of phenylcyclobutadiene or naphthalene was also present.



$$\mathrm{M\cdot\overset{X}{\underset{R}{C}}\cdot(CH_2)_n\cdot\overset{X}{\underset{R'}{C}}\cdot M}$$

(IV)



(V)

Recently Miller and Whalen[8] have shown that trichloromethyl-lithium is stable at −115°. Consequently, the dimetallo-derivatives of dihalides (IV, X = halide), similar in structure to the dimetallo-derivatives of sulphones (IV; M = MgBr; X,X = SO_2), should be moderately stable at low temperatures and should form cyclic olefins on warming.[9] Detailed studies on the generality of such a synthesis of cyclic olefins are in progress.

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[4] (*a*) 1,1-Difluoro-2,3,4-triphenylcyclobutene, $\lambda_{\max}$ 294 mμ (ϵ 17,000), 220 mμ (ϵ28,900). K. Nagarajan, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 449.

(*b*) 1,2-Diphenyl-3,3,4,4-tetrafluorocyclobutene, $\lambda_{\max}$ (ethanol) 293 mμ (ϵ 17,750), 224 (ϵ 8,600) 230 (ϵ 8,000). A. T. Blomquist and E. A. LaLancette, *ibid.*, 1961, **83**, 1387.

(*c*) 3,4-Diphenyl-2-cyclobutenol, $\lambda_{\max}$ 295 mμ. R. Breslow, J. Lockhart, and A. Small, *ibid.*, 1962, **84**, 2793.

(*d*) 1,2,3,4-Tetraphenylcyclobutene, $\lambda_{\max}$ (ethanol) 303 mμ (ϵ 19,500). H. H. Freedman and A. M. Frantz, Jr., *ibid.*, 1962, **84**, 4165. H. H. Freedman, [*ibid.*, 1961, **83**, 2194] had previously reported a compound believed to be a mixture of *cis-* and *trans*-tetraphenylcyclobutene, m.p. 122—123°, $\lambda_{\max}$ (heptane) 293 mμ (ϵ 26,000).

[5] J. T. Edward, D. Holder, W. H. Lunn and I. Puskas, *Canad. J. Chem.*, 1961, **39**, 599.

[6] J. B. Conant and R. E. Lutz, *J. Amer. Soc.*, 1923, **45**, 1303.

[7] H. H. Freedman and A. M. Frantz (ref. 4d) have reported the preparation of 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate. See R. F. Bryan, *ibid.*, 1964, **86**, 733, for structure.

[8] W. T. Miller, Jr. and D. M. Whalen, *J. Amer. Chem. Soc.*, 1964, **86**, 2089.

[9] The above statemen tdoes not necessarily imply that (I) is converted into (III) *via* a disodio-derivative, when treated with sodium amide, or that a stable compound of structure (IV) would have to be formed, at low temperature, in order to obtain the cyclic olefin. For a discussion of the mechanism of formation of stilbenes from benzyl halides and base see W. Kirmse, "Carbene Chemistry," Academic Press, N.Y., 1964, p. 80, and the references contained therein.