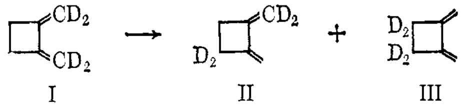
The 1,2-Bis(methylene)cyclobutane Rearrangement

Sir:

The demonstration by Doering and Gilbert[1] of the existence of the degenerate rearrangement of methylenecyclobutane suggested by Chesick[2] led to the idea that 1,2-bis(methylene)cyclobutane might also undergo a thermal degenerate rearrangement. One had dared hope that the apparent allylic assistance to the rearrangement of methylenecyclobutane ($E_a = 49.5$ kcal/mole compared with $E_a = 63.2$ kcal/mole for the opening of cyclobutane[3]) might appear in twofold measure, that is, might lead to an observed $E_a = 63.2 - 2(13.7) = 35.8$ kcal/mole. In close parallel to the investigation of methylenecyclobutane, 1,2-bis(dideuteriomethylene)cyclobutane was synthesized and heated to reveal the hypothesized rearrangement. The results to date are now published parallel with the independent investigation of Gajewski and Shih.[4]



I II III

The synthesis involved the following steps starting from 1,2-dicyanocyclobutane: (a) saponification to the dicarboxylic acid (87%); (b) conversion with thionyl chloride (9 molar excess) to the bis(carbonyl chloride) (80%); (c) addition to a tenfold excess of ethereal dimethylamine (91%); (d) reduction of the $\mathrm{N,N,N^1,N^1}$-tetramethyl-1,2-cyclobutanedicarboxamide with lithium aluminum deuteride to 1,2-bis(dimethylaminodideuteriomethyl)cyclobutane, bp 96–101° (19 mm) (58%); (e) oxidation with hydrogen peroxide to the bis(amine oxide); and (f) pyrolysis up to 200° in a Claisen distillation flask connected to a series of traps (dilute HCl–$CaCl_2$; three traps at −70°) to give 1,2-bis(dideuteriomethylene)cyclobutane (35%), exhibiting a sharp singlet in the nmr at δ 2.58 ppm (>1% absorption in the vinyl region); bands in the infrared (gas at 20.6 mm) at 2990, 2980 (very sharp), 2949–2955, 2318, 2220, 1628, 1420, 880 (very sharp), and 701 (very sharp) cm^{-1}. Undeuterated 1,2-bis(methylene)cyclobutane has slightly broadened singlets at δ 2.58 (4 H), 4.62 (2 H), and 5.06 (2 H) ppm; in the infrared (gas at 18.6 mm) absorptions at 3078–3093, 2990, 2979 (very sharp), and 862 cm^{-1}; and peaks at m/e 84 (45%) and 83 (55%) in the 15-v mass spectrum.

1,2-Bis(dideuteriomethylene)cyclobutane rearranges smoothly at 250–300° as evidenced by the appearance of the vinylic nmr signals at 4.62 and 5.06 ppm and a decrease in the allylic signal at 2.58 ppm. At equilibrium (160 sec at 299.0°), the product showed equal areas in the vinylic and allylic regions, had *inter alia* very sharp bands in the infrared (gas) at 2991, 2981, 2251, 890, 851, 849, and 701 cm^{-1}. The yield, determined with *n*-heptane as internal standard, was >80%; small amounts of dimer were produced; no allene was formed, even at 450°; allene did not dimerize at 250–300°;[5] the rate remained unchanged on addition of large amounts of broken Pyrex or of diphenylamine; recovery after purification by glpc was 70–80% of theory.

The kinetics were determined at 3–5 mm employing unexceptional vacuum techniques in a 5000-cc flask maintained in an air thermostat.[6] Analysis of the extent of rearrangement depended on integration of nmr spectra. Rates were precisely fitted by the theoretical equation for a reversible, first-order reaction: $(k + k_{-1}) = \ln[(A_0 - A_e)/(A - A_e)]/t$ (sec). Rate constants were determined from three runs each at four different temperatures constant to ±0.1°: 261.5 ($k + k_{-1} = 2.14 \pm 0.04 \times 10^{-5}$ sec^{-1}), 274.1 (5.86 ± 0.16), 286.9 (16.0 ± 0.2), and 299.0° (38.6 ± 0.6).

An Arrhenius plot gives $E_a = 46.8 \pm 0.9$ kcal/mole and $\log A = 14.45$ at 274.1°, from which values of $\Delta H^{\ddagger} = 45.7$ kcal/mole and $\Delta S^{\ddagger} = 2.4$ cal/deg can be calculated.

Whether the product is a mixture of I and III in equal parts or of I, II, and III in the ratio 1:2:1 is not known. This important question can be resolved by degradation or perhaps by synthesis of authentic samples of II and III. Until this structural feature has been revealed, the further questions of stereochemistry, mechanism, rationalization of the unexpectedly high activation energy, and relevance of orbital symmetry considerations[7] may profitably be postponed.

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[1] W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, 7, 397 (1966).

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[3] R. W. Vreeland and D. F. Swinehart, *J. Am. Chem. Soc.*, 85, 3349 (1963).

[4] J. J. Gajewski and C. N. Shih, *ibid.*, 89, 4532 (1967), to whom we express warmest thanks for their courteous and generous invitation to publish simultaneously.

[5] Y. Slobin and A. P. Khitrov, *J. Gen. Chem. USSR*, 3, 146, 2748 (1963).

[6] The air thermostat was constructed by Glenn Beasley, Yale University, according to the specifications of W. D. Clarke, Ph.D. Dissertation, University of Oregon, 1958.

[7] Professor R. Hoffmann, Cornell University, has carried through a thorough theoretical analysis of the various possible modes of reaction (privately communicated).

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Hydrogenation by *cis*-9,10-Dihydronaphthalene

Sir:

cis-9,10-Dihydronaphthalene (I) was reported to give naphthalene when heated to high temperatures,[1] but the fate of the hydrogen was not elaborated. Since then it was found, during a vain attempt to detect a temperature dependence of the nmr spectrum, that naphthalene was being produced at temperatures as low as 100°, along with other substances. In fact, when I (1.00 g) was heated in cyclohexane (1 cc) for 20 hr at 95° in a sealed ampoule, four products were isolated in the following ratios (total yield 710 mg): naphthalene (1.00); II (0.56); III (0.23); and IV (0.067).

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[1] W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, 88, 2078 (1966).