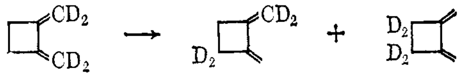
The 1,2-Bis(methylene)cyclobutane Rearrangement

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 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.

Acknowledgment. We express our warm gratitude to the Upjohn Company–Carwin Research and Development, North Haven, Conn., for the gift of a postdoctoral fellowship and our thanks to the National Science Foundation for its grants to Yale University for the purchase of a Varian A-60 nmr spectrometer (G-22689), a Consolidated mass spectrometer (GP-1442), and a research grant (GP-6127X) in support of this work.

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[2] J. P. Chesick, *J. Phys. Chem.*, 65, 2170 (1961).

[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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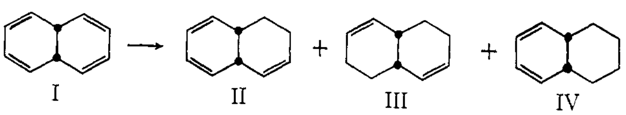
Hydrogenation by *cis*-9,10-Dihydronaphthalene

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).

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

II showed the following signals in the nmr: δ 5.63 (6 H), 3.00 (1 H), 2.34 (1 H), 1.90 (2 H), and 1.58 (2 H) ppm. Among many peaks in the infrared the following are mentioned: 3050 (m), 3025 (s), 3015 (s), 1650 (w), 1575 (w), 1492–1480 (doublet, m), 1075 (m), and 1050 (m) cm^{-1}. The ultraviolet spectrum revealed λ_{max} 262 mμ (ε 4.38 × 10^3; pentane) with a shoulder at 269.5 mμ (ε 4.21 × 10^3). The parent mass was 132.[2] On catalytic hydrogenation II, as well as III and IV, gave only *cis*-decahydronaphthalene and may be assigned the structure *cis*-1,2,9,10-tetrahydronaphthalene.



I II III IV

III showed no absorption in the ultraviolet and an nmr spectrum consisting of signals at δ 5.53 (4 H, multiplet), 2.70 (2 H), 1.87 (4 H), and 1.64 (4 H) ppm. The infrared showed characteristic absorptions at 3015 (s), 1650 (w), 1450–1430 (doublet, m), 1050 (m), and 970 (m) cm^{-1}. The parent mass was at *m/e* 134. III is accordingly assigned the structure *cis*-1,2,5,6,9,10-hexahydronaphthalene.

The structure of IV (*m/e* 134; λ_{max} 264 mμ (ethanol); infrared absorption at 1650 cm^{-1}) is tentatively believed to be *cis*-5,6,7,8,9,10-hexahydronaphthalene. It is concluded from the relative quantities of the three products that the cyclohexadiene type of double bond undergoes 1,2-hydrogenation more readily than does the isolated cyclohexene type.

When I (110 mg) was heated with cyclohexene (740 mg) for 20 hr at 95°, cyclohexane (41 mg) was obtained in 57% of theory. The simultaneous formation of naphthalene, II, III, and IV points to an effective competition between I and cyclohexene as hydrogen acceptors. Determination of competition factors will be undertaken.

To determine the stereochemistry of the hydrogenation, the reaction of I (100 mg) with 1,2-dimethylcyclohexene[3] (1.70 g) was effected at 150° for 48 hr. The resulting 1,2-dimethylcyclohexane, obtained in low yield (5.6 mg; 6.6%), was entirely the *cis* isomer (identified by infrared[4]) and was unaccompanied by *trans* isomer.

The analogy between this hydrogen transfer and that of diimide is particularly strong since both reactions appear to be stereospecifically *cis* hydrogenations.[5] We have incidentally also reduced 1,2-dimethylcyclohexene with diimide and find only *cis*-1,2-dimethylcyclohexane.

As the driving force in the hydrogenation by diimide is very probably associated with the contribution of the heat of formation of nitrogen to the transition state,[5] so the driving force in the transfer of hydrogen from *cis*-9,10-dihydronaphthalene may be dependent on the unique possibility of contributing a part of the full resonance energy of naphthalene (61 kcal/mole)[6] to the transition state. This speculation would be considerably strengthened by further evidence in support of a concerted transfer. At the moment only the *cis* stereospecificity points to this type of mechanism.

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[2] We wish to thank D. J. Friedland, Yale University, for measurements of mass spectra.

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Phosphorus-31 Chemical Shifts of Isostructural and Isoelectronic Trialkyl Phosphite Metal Complexes[1]

Sir:

Recently it was established for the ligands $P(OCH_3)_3$, $P(OCH_2)_3CR$ (where R = C_2H_5 or *n*-C_3H_7), and $P(OCH)_3(CH_2)_3$[2] that the series of complexes shown in Table I parallel one another in stoichiometry as well as in spectral and magnetic properties.[3,4] Furthermore, the *Dq* values for these ligands in the $[CoL_6]^{+3}$ cation are similar.[3] In view of the small differences in ligand properties of these phosphites, it was thought not unreasonable to expect parallels in any trends observed in the P^{31} chemical shifts of their complexes. We show here that correlation of metal oxidation states with the P^{31} resonances for the complexes is shown to be valid only for systems which are both isoelectronic and isostructural.

Table I. P^{31} Chemical Shifts of Trialkyl Phosphite (L) Complexes with Respect to 85% H_3PO_4 as External Standard

Compound	$P(OCH_3)_3$	$P(OCH_2)_3CR^a$	$P(OCH)_3$-$(CH_2)_3$
L	-141^b	-92^c (R = C_2H_5) -93^c (R = *n*-C_3H_7)	-137^d
$[NiL_5](ClO_4)_2$	-110^e	-108^f	-125^g
$[AgL_4]ClO_4$	-132^e		
$[AgL_4]NO_3$		-99^f	-134^d
$[CuL_4]ClO_4$	$-125^{e,h}$	. . .^{i}	. . .^{i}
$[CoL_5]ClO_4$		-138^f	-157^f
$[CoL_5]NO_3$	-147^a		
$[NiL_4]$	-163^j	-128^k	-153^c

^{a} R = C_2H_5 in all cases except $[CoL_5]ClO_4$ and $[NiL_4]$ where R = *n*-C_3H_7. ^{b} Neat. ^{c} CH_3CN. ^{d} Dimethyl sulfoxide. ^{e} Acetone. ^{f} CH_2Cl_2. ^{g} Dimethylformamide. ^{h} The P^{31} absorption was reported to consist of two overlapping four-line patterns due to Cu^{63}–P^{31} and Cu^{65}–P^{31} spin–spin coupling: R. W. King, T. J. Huttemann, and J. G. Verkade, *Chem. Commun.*, 561 (1965). Although only six of the eight lines were observed, we have since achieved sufficient resolution in the spectrum of the nitrate salt in acetone to identify all eight lines. ^{i} Insolubility prevented observation of the P^{31} signal. ^{j} C_6H_6. ^{k} $CHCl_3$.

P^{31} chemical shifts for the $[NiL_5]^{+2}$, $[CoL_5]^+$, and $[CuL_4]^+$ complexes of all three phosphite ligands as well as those for the $[NiL_4]$ complexes of $P(OCH_2)_3CR$

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[1] We thank the National Science Foundation for generous suppor of this work.

[2] 2,8,9-Trioxa-1-phosphaadamantane.

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