COMMUNICATIONS TO THE EDITOR

DISPLACEMENT REACTIONS ON THE $B_{10}H_{12}$ UNIT

Sir:

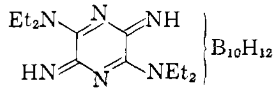
We wish to report two transformations of the compound $B_{10}H_{12}\cdot 2CH_3CN$[1] (I) which indicate that the $B_{10}H_{12}$ unit is transferred from one ligand to another.

Treatment of decaborane with diethylcyanamide in diethyl ether at room temperature produces hydrogen and the air stable and crystalline compound $B_{10}H_{12}\cdot 2(C_2H_5)_2NCN$ (II) which melts at 145° dec. (calcd.: B, 34.17; H, 10.19; C, 37.94; N, 17.70. Found: B, 31.32; H, 10.31; C, 37.89; N, 16.65). Approximately one mole of hydrogen is evolved per mole of product formed. The infrared spectrum of II contains strong C≡N stretching at 2300 cm.$^{-1}$ (C≡N in diethylcyanamide at 2210 cm.$^{-1}$). This indicates that the $B_{10}H_{12}$ unit is attached by the amino nitrogens of the two diethylcyanamide molecules in II. Treatment of I with diethylcyanamide in refluxing benzene produces II in high yield with the displacement of acetonitrile (recovered from run in *p*-xylene).

Decaborane and triphenylphosphine react in diethyl ether at the reflux temperature to produce a crystalline compound $B_{10}H_{12}\cdot 2(C_6H_5)_3P$ (III) (calcd.: B, 16.78; H, 6.56; C, 67.05; P, 9.61. Found: B, 15.78; H, 6.91; C, 64.13; P, 9.56) which is stable without melting to above 300°. Again, approximately one mole of hydrogen is evolved per mole of compound produced. Both II and III are recrystallized easily from polar solvents such as methylene chloride. Treatment of I or II with triphenylphosphine in hot acetonitrile and benzene, respectively, produces pure III. Attempts to convert III to II with excess diethylcyanamide were unsuccessful as were attempts to convert II to I by treatment with acetonitrile. The chart summarizes these transformations.

$$\begin{tikzcd}
B_{10}H_{12}\cdot 2CH_3CN \arrow[dd, "(C_2H_5)_2NCN"'] \arrow[drr, "(C_6H_5)_3P"] & & \\
 & B_{10}H_{14} \arrow[ul, "-H_2"', "CH_3CN"] \arrow[r, "(C_6H_5)_3P", "-H_2"'] \arrow[dl, "-H_2"', "(C_2H_5)_2NCN"] & B_{10}H_{12}\cdot 2(C_6H_5)_3P \\
B_{10}H_{12}\cdot 2(C_2H_5)_2NCN \arrow[urr, "(C_6H_5)_3P"'] & &
\end{tikzcd}$$

Liquid hydrogen cyanide and II react slowly at room temperature to produce the brilliant red, crystalline compound $B_{10}H_{12}\cdot 2(C_2H_5)_2NCN\cdot 2HCN$ (IV). (Calculated: B, 29.22; H, 9.18; C, 38.89; N, 22.69. Found: B, 29.39; H, 9.49; C, 38.51; N, 22.54.) The compound IV is extremely stable toward water and mild oxidizing agents such as acetone. Its infrared spectrum exhibits N–H (3300 cm.$^{-1}$) and N=C (1630 cm.$^{-1}$) stretching. As in I, II and III, B–H stretching is observed at 2500 cm.$^{-1}$. In the ultraviolet λ_{max} 450 mμ, ε 9.5 × 10^3. The partial structure of IV is tentatively formulated as



IV

The relatively great sizes of triphenylphosphine and the postulated ligand of IV place considerable steric limitations upon the possible bonding sites of the $B_{10}H_{12}$ unit. It appears clear, however, that the $B_{10}H_{12}$ unit functions as a discrete electron deficient species.

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[1] R. Schaeffer, This Journal, **79**, 1006 (1957).

PHOTO-γ-TROPOLONE METHYL ETHER

Sir:

Irradiation[1] of an aqueous solution of γ-tropolone methyl ether[2] (IA) gave photo-γ-tropolone methyl ether (II) in good yield. This represents the first instance of photoisomerization in a simple, monocyclic troponoid compound.[3]

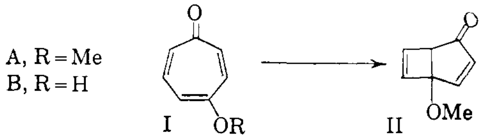


Photo-γ-tropolone methyl ether (b.p. 34° at 0.1 mm.), obtained by fractional distillation of the methylene chloride extract of the filtered aqueous solution from the irradiation, showed an infrared maximum at 5.85 μ (but no intense maximum in the 6.2 μ region) and $\lambda_{max}^{95\%\ EtOH}$ 243 mμ (14,900) and 328 mμ (1780). Hydrogenation of II over platinum gave a dihydro derivative, III, ($\lambda_{max}^{CHCl_3}$ 5.85 μ and $\lambda_{max}^{95\%\ EtOH}$ 215 mμ (3,200)) and a tetrahydro derivative, IV, ($\lambda_{max}^{CHCl_3}$ 5.75 μ; no high intensity absorption in the ultraviolet). The photoisomer II did not show chemical or physical properties characteristic of enol ethers. Dilute acid did not alter II; however, refluxing II in dilute hydrochloric acid for 6–7 hours gave a high yield of γ-tropolone (IB) identified by its characteristic ultraviolet spectra in alcohol and 0.1 *N* sodium hydroxide.[4,5] Similar acid treatment of dihydrophoto-γ-tropolone methyl ether (III) gave 2-cyclohepten-1,4-dione (V). For comparison, 2-cyclohep-

[1] Sunlight and mercury arc sources gave the same product.

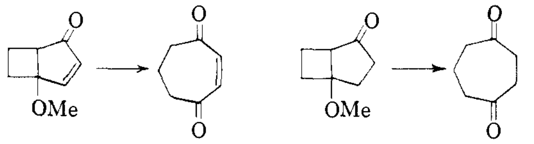
[2] J. Meinwald and O. L. Chapman, This Journal, **80**, 633 (1958).

[3] The naturally occurring alkaloid colchicine has previously been found to yield three photoproducts (R. Grewe and W. Wolf, *Ber.*, **84**, 621 (1951), and F. Šantavý, *Biol. Listy*, **31**, 246 (1950)). The structures of two of the photoproducts are known (E. J. Forbes, *J. Chem. Soc.*, 3864 (1955) and P. D. Gardner, R. L. Brandon and G. R. Haynes, This Journal, **79**, 6334 (1957)).

[4] L. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. and Ind.*, 66 (1955).

[5] R. B. Johns, R. S. Coffey and A. W. Johnson, *ibid.* 658 (1955).

ten-1,4-dione was synthesized by an unequivocal method.[6] Dilute aqueous acid at room temperature rapidly converted IV to cycloheptan-1,4-dione (VI) which was characterized by the bis-2,4-dinitrophenylhydrazone previously reported by Cope.[7] This transformation is so facile that treatment of IV with a solution of 2,4-dinitrophenylhydrazine in cold ethanolic acid gives directly the bis-2,4-dinitrophenylhydrazone of VI. The acid catalyzed openings of the bicyclic system in II, III and IV reported above are in sharp contrast to the reported failure of such reactions in related systems.[8] The success of the reaction in the present cases presumably is due to the strategic location of the methoxyl group.



III V IV VI

Satisfactory analyses have been obtained for all new compounds either directly or for the 2,4-dinitrophenylhydrazones

The anomalous ultraviolet spectrum of II and additional transformations of II will be discussed in a forthcoming paper.

Acknowledgment.—The authors are pleased to acknowledge financial support of this work by the Research Corporation through a Frederick Gardner Cottrell grant.

(6) O. L. Chapman and D. J. Pasto, unpublished results.

(7) A. C. Cope, J. A. Liss and G. W. Wood, THIS JOURNAL, **79**, 6287 (1957).

(8) See the reference in footnote 3 to the work of Forbes.

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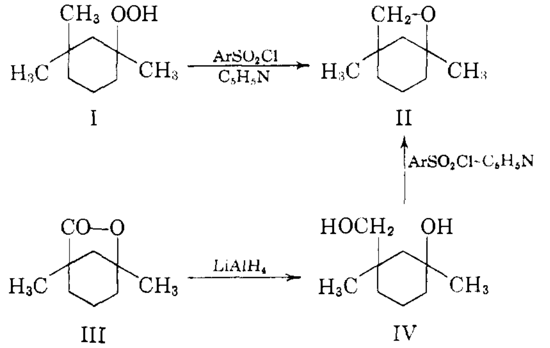
RECEIVED NOVEMBER 14, 1958

CATIONIC DISPLACEMENT OF HYDROGEN BY OXYGEN AT A SATURATED CARBON ATOM

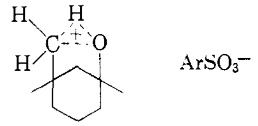
Sir:

Although the oxygenation of paraffinic groups via free radical chain reactions is well known,[1] the replacement of alkyl hydrogen by oxygen using cationic oxygen species does not appear to have been realized. This note reports evidence that such an ionic substitution process can be effected and that intramolecular attack can be directed at a specific carbon atom.

The substance used in this study of oxidation by cationic oxygen was 1,3,3-trimethylcyclohexyl hydroperoxide (I), obtained from 1,3,3-trimethylcyclohexanol[2] using freon—25% hydrogen peroxide in 50% sulfuric acid[3] (70% yield); *p*-nitrobenzoyl derivative, m.p. 113.5–114° (dec.), found: C, 62.53; H, 6.75; infrared max. 1755 cm.$^{-1}$. Reaction of the hydroperoxide I with *p*-nitrobenzenesulfonyl chloride in cold pyridine–methylene chloride produced the *bicyclic ether II*, which was synthesized unambiguously for comparison from the known lactone III[4] by reduction (lithium aluminum hydride) to the diol IV, m.p. 78–78.5°, found: C, 68.41; H, 11.59; followed by cyclization (*p*-toluenesulfonyl chloride); found for II: b.p. 66.5–67° (31 mm.), n^{20}_D 1.4466; C, 77.15; H, 11.66. The identity of the products obtained from the hydroperoxide I and the lactone III was established by identical vapor chromatographic constants on nonyl phthalate and Carbowax columns at six different temperatures and from the correspondence of the characteristic infrared and nuclear magnetic resonance spectra. The latter spectrum exhibits a quartet centered at +48 c.p.s. (at 40 mc., relative to water) due to $-CH_2-O-$, two methyl peaks at +138 and +146 c.p.s. and a peak from the remaining eight protons at +129 c.p.s. The yields of II obtained from the hydroperoxide I have been in the range 5–10%; however, optimum conditions have not yet been determined.



Since O–O cleavage of the *p*-nitrobenzenesulfonyl derivative of I is doubtless heterolytic under the conditions used,[5] we consider the change I → II as proceeding via a cationic transition state such as V, a mechanism intermediate between the extremes for attack of cationic oxygen (1) exclusively on hydrogen and (2) exclusively on carbon. We have not been able to detect II as a product of thermal or photochemical decomposition of I or its *p*-nitrobenzoate.



V

The reaction I → II is particularly interesting as a possible chemical counterpart of enzymatic hydroxylation at a saturated carbon which also appears to involve electrophilic oxygen[6] and which proceeds by frontal displacement as implied by V.[7-9] It also may be related to the ozone–decalin reaction.[10]

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RECEIVED NOVEMBER 10, 1958

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(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 9.

(2) A. W. Crossley and C. Gilling, *J. Chem. Soc.*, **97**, 2220 (1910).

(3) We are indebted to Prof. N. A. Milas for suggesting this procedure.

(4) J. Meinwald and H. C. Huang, THIS JOURNAL, **79**, 2911 (1957).

(5) P. D. Bartlett and B. T. Storey, *ibid.*, **80**, 4954 (1958), have demonstrated that *t*-butyl arylpersulfonates decompose in solution by ionic O-O fission.

(6) B. M. Bloom and G. Shull, *ibid.*, **77**, 5767 (1955).

(7) M. Hayano, *et al.*, *ibid.*, **80**, 2336 (1958).

(8) S. Bergstrom, *et al.*, *ibid.*, **80**, 2337 (1958).

(9) E. J. Corey, G. Gregoriou and D. H. Peterson, *ibid.*, **80**, 2338 (1958).

(10) J. R. Durland and H. Adkins, *ibid.*, **61**, 429 (1939).

(11) National Science Foundation Predoctoral Fellow 1956–58. This work was supported also by U. S. Public Health Grant 4565.