tope must be introduced to at least this extent in the 4 position even if the mechanism of introduction is highly stereospecific. In addition, any kinetic isotope effect shown in reaction (3) will be in favor of further ^{10}B introduction.

(b) As the reaction of hydrogen chloride with sodium triborohydride proceeds, a fraction of the latter is converted to diborane which in this case contains 96% ^{10}B. The ^{11}B isotope content of the original diborane is thus lowered somewhat, depending on the degree of branching of reaction (2).

A more complete report of this work together with an alternate but less selective synthesis and the implications of the work with respect to the mechanisms of interconversion of boranes will be reported in the near future. Work is also in progress on the mechanisms of tetraborane reactions using the labeled material.

Acknowledgments.—Support of this work by National Science Foundation Grant G-6224 is gratefully acknowledged. The initial study of the reaction of sodium triborohydride with hydrogen chloride and diborane was carried out by R. O. Buttlar and will be reported elsewhere.

CONTRIBUTION No.
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THE SYNTHESIS OF HEXAPHENYLPENTALENE

Sir:

In the forty years since Armit and Robinson[1] first suggested that pentalene might be an aromatic hydrocarbon, there has accumulated in the chemical literature a wealth of information concerned with unsuccessful attempts to synthesize[2] and describe theoretically[3] this pseudoaromatic[4] and its derivatives.[5] Reported here is the synthesis of hexaphenylpentalene I, the first derivative of pentalene free of fused rings.[5]

The fluoride-catalyzed (potassium fluoride in dimethyl sulfoxide) condensation[6] of 1,2,3-tri-

(1) J. W. Armit and R. V. Robinson, *J. Chem. Soc.*, **127**, 828 (1922).

(2) For original references see the reviews of: (a) E. D. Bergmann in "Non-benzenoid Aormatic Compounds" (D. Ginsburg editor), Interscience Publishers, New York, N. Y., 1959; (b) M. E. Vol'pin, *Uspekhi Khim.*, **29**, 298 (1960); (c) H. Paul, *Chem. Techn.*, **8**, 189 (1956).

(3) See the reviews in reference 2. Also: (a) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., 1961; (b) H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1962).

(4) For pertinent discussions of pseudoaromaticity see: (a) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); also, see chapter by D. P. Craig in reference 2a; (b) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

(5) Several fused ring derivatives of pentalene have been reported: (a) 5,10-disubstituted dibenzo[a,e]pentalene, K. Brand, *Ber.*, **45**, 3071 (1912); (b) dibenzo[a,e]pentalene, C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952); C. C. Chuen and S. W. Fenton, *J. Org. Chem.*, **23**, 1538 (1958); (c) 3,5-dimethylcyclohepta[c,d]pentalene, K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1952); (d) 1,2,3-triphenyl-benzopentalene, E. Le Goff, *J. Am. Chem. Soc.*, **84**, 1505 (1962).

(6) The ability of F⁻ to form the strongest known hydrogen bond[7] in

HF₂⁻ presumably accounts for its functioning as a Lewis base: HC̈—H

+ 2F⁻ → HC̈⁻ + FHF⁻.

(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 460.
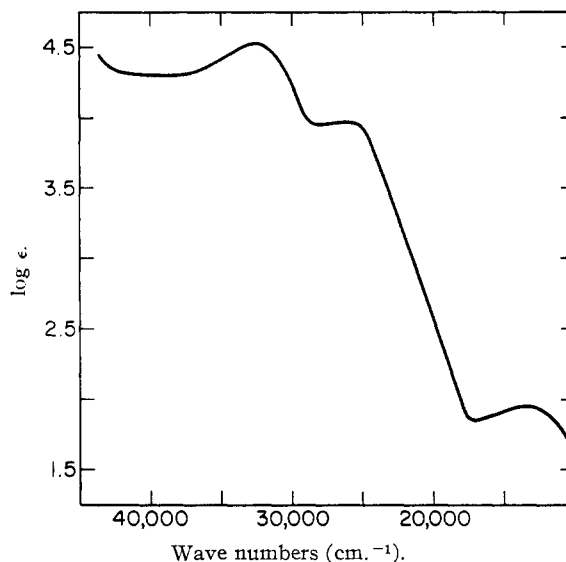

Wave numbers (cm.⁻¹).

Fig. 1.—Ultraviolet, visible, and near-infrared spectrum of hexaphenylpentalene.

phenylcyclopentadiene[8] with 1,2,3-triphenylpropenone[9] *via* a Michael–Knoevenagel dehydration reaction sequence[10] afforded in 53% yield the dihydrohexaphenylpentalene, II [bright yellow needles (methanol–chloroform) m.p. 266–267°. Calcd. for $C_{44}H_{32}$: C, 94.25; H, 5.75; mol. wt., 560.7. Found: C, 94.26, 94.11; H, 5.85, 6.03; mol. wt., 556; ultraviolet (acetonitrile) λ_{max} mμ (log ϵ): 242 (4.39), 296 (4.24), 355 (4.14); infrared (KBr): 3.27, 3.30, 6.24, 6.72, 6.90, 9.30, 9.72, 13.20, 13.65, 14.40 μ].[11]

II undergoes rapid dehydrogenation by N-bromosuccinimide in refluxing deoxygenated carbon tetrachloride to give in 77% yield hexaphenylpentalene, I [green-brown needles (methanol–chloroform), m.p. 273–276°. Calcd. for $C_{44}H_{30}$: C, 94.59; H, 5.41; mol. wt., 558.7. Found: C, 94.53, 94.51; H, 5.51, 5.65; mol. wt., 527. Ultraviolet–visible spectrum (dioxane) λ_{max} mμ (cm.⁻¹, log ϵ): 310 (32,300 cm.⁻¹, 4.52), 380 (26,400 cm.⁻¹, 3.99), 720 (13,900 cm.⁻¹, 1.95) see Fig. 1. Near-infrared (carbon tetrachloride): 800 mμ (12,500 cm.⁻¹) to 1.5 μ (6700 cm.⁻¹) broad tailing of 720 mμ (13,900 cm.⁻¹) peak. Infrared (KBr): 3.27, 6.25, 6.26, 6.27, 6.66, 6.73, 6.91, 9.31, 9.79, 12.81, 12.97, 13.47, 13.88, 14.37].[11]

Hexaphenylpentalene also was prepared in low yields by iodine oxidation of the deep red solution (λ_{max} 489 mμ) resulting from the reaction of II with butyllithium in tetrahydrofuran.

While solutions of I are air sensitive, the crystalline solid appears to be quite stable. Both I and II give deep green solutions with bromine (CCl₄) and

(8) P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 4153 (1961).

(9) A. Dornow and F. Boberg, *Ann.*, **578**, 101 (1952).

(10) Potassium fluoride in ethanol, ether and benzene previously has been reported to catalyze Knoevenagel reactions: A. Sakurai, *Sci. Paper Inst. Phys. Chem. Research (Tokyo)*, **53**, 250 (1959); M. Igarashi, H. Midorikawa and S. Aoyama, *J. Sci. Research Inst. (Tokyo)*, **52**, 151 (1958); H. Baba, H. Midorikawa and S. Aoyama, *ibid.*, **52**, 99–117 (1958).

(11) Melting points are corrected; molecular weight was determined with vapor pressure osmometer; the infrared spectrum, for which the more prominent absorption peaks are recorded, was consistent with the proposed structure.

IIIa, R = Ph, R' = CO₂CH₃
b, R' = Ph, R = CO₂CH₃
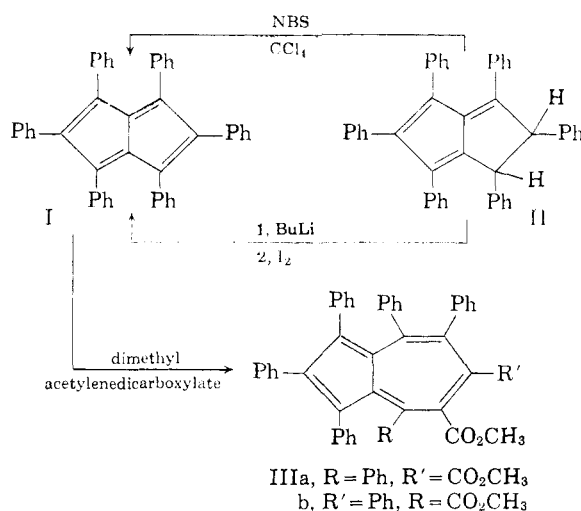
deep blue with antimony pentachloride. Trifluoroacetic acid produces a deep blue color with I and a fluorescent red color with II. Addition of hydroxylic solvents immediately discharges these intense colors.

Heating I with excess dimethyl acetylenedicarboxylate at 160° affords in 63% yield the dicarbomethoxyhexaphenylazulene, III (a or b) [dark greenish-blue crystals, m.p. 247–248°; calcd. for $C_{50}H_{36}O_4$: C, 85.69; H, 5.18; mol. wt., 700.8. Found: C, 85.54; H, 5.10; mol. wt., 664. Ultraviolet-visible spectrum (chloroform) λ_{max} mμ (log ϵ): 265 (4.64), 339 (4.96), 634 (2.80). Infrared (KBr): 3.27, 3.39, 5.75, 6.24, 6.67, 6.91, 7.84, 8.17, 9.25, 9.71, 13.09, 14.32].[11]

Thus, the pentalene structure of I is consistent with: (1) the mode of formation (two routes), (2) the analytical results, (3) the unusual spectral properties, and (4) the unique two carbon ring-expansion to form an azulene.

The author wishes to thank Mr. R. B. La Count for assistance in obtaining the spectral data.

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RECEIVED AUGUST 13, 1962

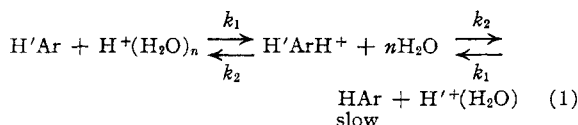## THE ISOTOPE EFFECT ON ACID-CATALYZED SLOW PROTON TRANSFER IN DILUTE AQUEOUS SOLUTION[1]

Sir:

Few examples of slow proton transfer from catalyzing acid to substrate are known, and not many measurements of the isotope effect on this reaction have been made. In the several cases reported so far, the deuterium isotope effect (k_H/k_D) has not been larger than two whenever the catalyzing acid has been the solvated proton in dilute aqueous solution.[2] Since this small isotope effect is in accord with at least one theoretical prediction,[3]

(1) Work supported by the Atomic Energy Commission, in part under USAEC Contract AT(11-1)-1025 and in part by Brookhaven National Laboratory.
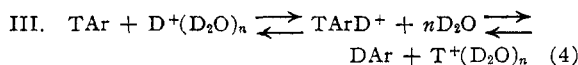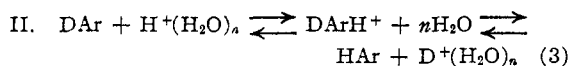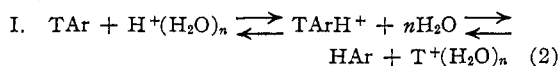
(2) (a) S. H. Maron and V. K. LaMer, J. Am. Chem. Soc., 61, 692 (1939); A. V. Willi, Z. Naturforschg., 13a, 997 (1958); Z. physik. Chem. N. F., 27, 221 (1961); H. G. Kuivila and K. V. Nahabedian, J. Am. Chem. Soc., 83, 2164 (1961); (b) F. A. Long and D. Watson, J. Chem. Soc., 2019 (1958); T. Riley and F. A. Long, J. Am. Chem. Soc., 84, 522 (1962).

the conclusion has been drawn that this isotope effect will always have a value near unity, and this value has been used to deduce the relative acid strengths of the species H_2O and D_2O.[2b] We wish here to report a deuterium isotope effect on rate-determining proton transfer from the solvated proton which is considerably greater than unity.

Acid-catalyzed aromatic hydrogen exchange in 1,3,5-trimethoxybenzene is known to proceed by the two-step reaction sequence[4]

$$H'Ar + H^+(H_2O)_n \underset{k_2}{\overset{k_1}{\rightleftarrows}} H'ArH^+ + nH_2O \underset{k_1}{\overset{k_2}{\rightleftarrows}}$$

$$HAr + H'^+(H_2O) \quad (1)$$
slow

The first forward step in this reaction is a slow proton transfer from catalyzing acid to substrate. The isotope effect on this step ($k_1^{H_2O}/k_1^{D_2O}$) as well as that on the second step (k_2^H/k_2^D) can be obtained by performing the experiments (I), (II) and (III).

I.　$TAr + H^+(H_2O)_n \rightleftarrows TArH^+ + nH_2O \rightleftarrows$
$$HAr + T^+(H_2O)_n \quad (2)$$

II.　$DAr + H^+(H_2O)_n \rightleftarrows DArH^+ + nH_2O \rightleftarrows$
$$HAr + D^+(H_2O)_n \quad (3)$$

III.　$TAr + D^+(D_2O)_n \rightleftarrows TArD^+ + nD_2O \rightleftarrows$
$$DAr + T^+(D_2O)_n \quad (4)$$

These reactions are practically non-reversible, and their observed second order rate constants are related to the rate constants for the individual steps in the following way

$$k_{obs} = \frac{k_1}{1 + k_2^H/k_2^{H'}} \quad (5)$$

With the aid of a relationship between deuterium and tritium isotope effects,[5] equations of the form of (5) for reactions I, II and III can be solved for

$$(k_{obs})_I = \frac{k_1^{H_2O}}{1 + k_2^H/k_2^T} = \frac{k_1^{H_2O}}{1 + (k_2^H/k_2^D)^{1.442}} \quad (6)$$

$$(k_{obs})_{II} = \frac{k_1^{H_2O}}{1 + k_2^H/k_2^D} \quad (7)$$

$$(k_{obs})_{III} = \frac{k_1^{D_2O}}{1 + k_2^D/k_2^T} = \frac{k_1^{D_2O}}{1 + (k_2^H/k_2^D)^{0.442}} \quad (8)$$

the rate ratios $k_1^{H_2O}/k_1^{D_2O}$ and k_2^H/k_2^D. (This treatment neglects secondary isotope effects in the aromatic molecule, but there are both empirical[6] and theoretical[5b,6a] reasons to expect these to be absent.) For 1,3,5-trimethoxybenzene in 0.05 M $HClO_4$, the data (Table I) give the values: $k_1^{H_2O}/k_1^{D_2O} = 2.93$ $\sigma = 0.07$, and $k_2^H/k_2^D = 6.68$, $\sigma = 0.18$ (σ is the standard deviation of the mean value).

The isotope effect k_2^H/k_2^D is near the maximum value for C–H bond-breaking in a methylene group. The predicted rate ratio based on a simple consid-

(3) F. A. Long and J. Bigeleisen, Trans. Faraday Soc., 55, 2077 (1959).

(4) A. J. Kresge and Y. Chiang, J. Am. Chem. Soc., 81, 5509 (1959); 83, 2877 (1961); Proc. Chem. Soc., 81 (1961).

(5) (a) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, J. Am. Chem. Soc., 80, 5885 (1958); L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Company, New York, N. Y., 1960, p. 23; (b) S. Olsson, Arkiv Kemi, 16, 489 (1960).

(6) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, J. Am. Chem. Soc., 80, 2326 (1958); (b) L. Melander, "Isotope Effect, on Reaction Rates," The Ronald Press Company, New York, N. Y. 1960, 107 ff.