the three halogen molecules with $[BrCl]^2/[Br_2][Cl_2] = 12$ (compared to a reported[5] value of 8 at 300°K). These observations did not establish the kinetics of BrCl formation but suggest that $k_3 \simeq k_1/150$.

Reactions 1 and 2 are so rapid that homogeneous atomic chain mechanisms are ruled out. As a further test, it was observed that no dark reaction occurred when HBr was replaced by H_2, but illumination with visible light led to a rapid reaction. Substitution of air for nitrogen as carrier gas also had no noticeable effect on the rate.

The kinetic data and the independence of reaction rate on cell diameter indicate that reactions 1 and 2 are indeed elementary bimolecular processes. If usually accepted values are used for collision frequencies, the activation energies are about 10 to 15 kcal/mol; these low values demonstrate that the mechanism[1] of the $H_2 + I_2$ reaction does not apply in this system.

The much slower reaction 3 has not yet been studied in detail, and Christie, Roy, and Thrush[6] thought it to be heterogeneous in another system. Our present data merely set an upper limit for the rate of the homogeneous reaction, but even that upper limit is at least two orders of magnitude slower than the rate in supposedly "inert" solvents like carbon tetrachloride, carbon disulfide, and perfluoroalkanes.[7]

The apparatus used for these exploratory measurements will not permit really reliable measurements of rate constants and activation energies; apparatus for such quantitative studies is now being constructed. Calculations indicate that self-heating during reaction (Draper effect[8]) will not seriously interfere with such measurements.

Acknowledgment. This research was supported in part by a grant from the U. S. Army Research Office (Durham) on reactions of small molecules. The participation of Paul Goldfinger was made possible by a National Science Foundation Senior Postdoctoral Fellowship.

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(5) W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Res. Natl. Bur. Stand.*, **55**, 147 (1955).

(6) M. I. Christie, R. S. Roy, and B. A. Thrush, *Trans. Faraday Soc.*, **55**, 1139 (1959).

(7) B. L. McKinney, observations at the University of Oregon.

(8) P. Goldfinger, G. Huybrechts, A. M. Mathieu-Van der Auwera, and D. Van der Auwera, *J. Phys. Chem.*, **64**, 468 (1960).

(9) Université Libre de Bruxelles, Brussels, Belgium.

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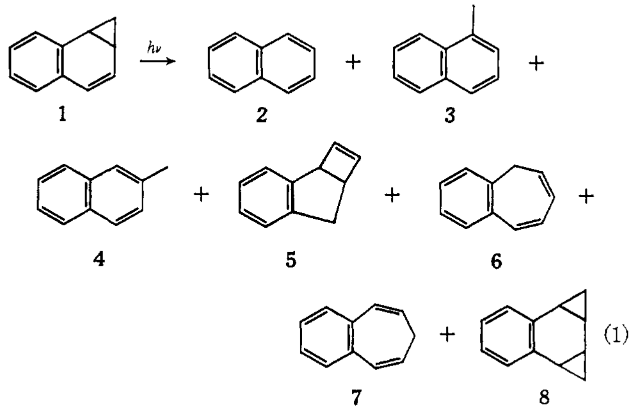
A Photochemical Berson-Willcott Bones Rearrangement[1]

Sir:

Recent interest in the photochemical reactivity of benzonorcaradienes[2] prompts us to report our work with the parent hydrocarbon.[3] Irradiation of a dilute, outgassed solution of benzonorcaradiene (**1**) in pentane with a 400-W GE mercury lamp through a Pyrex filter for 2 hr resulted in the formation of naphthalene (**2**, 46%), 1-methylnaphthalene (**3**, 7%), 2-methylnaphthalene (**4**, 4%), benzobicyclo[3.2.0]hepta-2,6-diene (**5**, 2%), 1,2-benzotropilidene (**6**, 2%), 3,4-benzotropilidene (**7**, *ca.* 2%), and bismethanonaphthalene (**8**, trace, eq 1). Recovered **1** represented 36% of the reaction mixture under these conditions.



(1)

Compounds **2**, **3**, **5**, and **6** were isolated pure by preparative glpc,[4a] while **7** was obtained admixed with **1** and **4**. After extended irradiation **4** could be isolated in pure form, since **1** and **7** ultimately rearranged. **2**, **3**, **4**, and **6**[3b] were identified by comparison of their nmr spectra and glpc retention times[4a] with those of authentic samples, while **8** was identified as reported previously.[3a] The presence of **7**, in the mixture with **1** and **4**, was deduced from its nmr spectrum by comparison with a known mixture of **1**, **4**, and **7**. In addition, its glpc retention time was identical with that of an authentic sample[3a] of **7**.[4b] **5** was characterized by comparison with an authentic sample prepared by the benzophenone-sensitized photolysis of indene and maleic anhydride,[5a] followed by $Pb(OAc)_4$ oxidative bisdecarboxylation.[5b,6]

The formation of **2** and **8** has been discussed previously.[3a] Swenton and Krubsack have recently provided analogy for the formation of **3** and **4**,[2a] and discussed the formation of this type of compound.

The formation of **6** can be rationalized by two different types of mechanisms. The first would be the reverse of the photochemical hydrogen migration by which **6** rearranges to **1**.[3b] The alternative possibility would employ a carbon skeletal rearrangement and no hydrogen shift. When 7,7-dideuteriobenzonorcaradiene (**9**)[7] was briefly irradiated[8] with uv light (5–10 min), it could be shown by nmr spectroscopy that the 1,2-benzotropilidene formed retained the CD_2 group. Thus, this result is inconsistent with a hydrogen

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(1) (a) E. Vogel in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967; (b) J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).

(2) (a) J. S. Swenton and A. J. Krubsack, *ibid.*, **91**, 786 (1969); (b) E. Ciganek, *ibid.*, **89**, 1458 (1967).

(3) (a) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6798 (1967); (b) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6799 (1967).

(4) (a) A 10 ft × 0.25 in. column packed with 20% Carbowax 20 M on 60–80 mesh Chromosorb P, operated at 180°, was employed. (b) **7** could be partially separated from **1** and **4** with a 10 ft × 0.25 in. column packed with 20% TCEP on 60–80 mesh Chromosorb P operated at 175°.

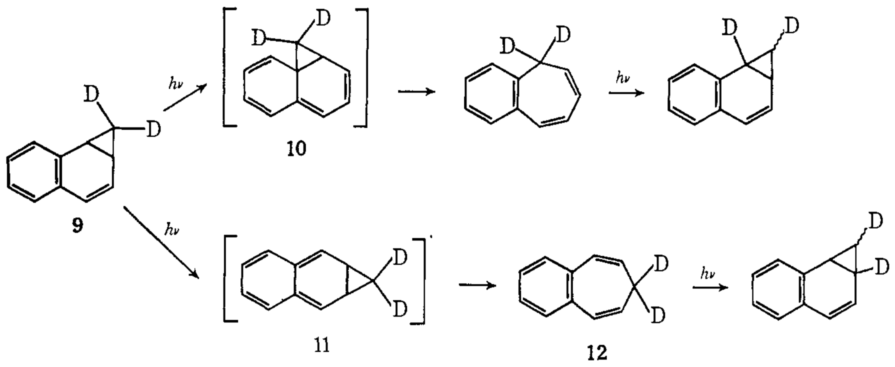
(5) (a) W. Metzner, H. Partale, and C. H. Krauch, *Chem. Ber.*, **100**, 3160 (1967); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(6) An independent preparation has since appeared: (a) W. Metzner and K. K. Morgenstern, *Angew. Chem. Intern. Ed. Engl.*, **7**, 379 (1968); (b) W. Metzner and W. Hartmann, *Chem. Ber.*, **101**, 4099 (1968).

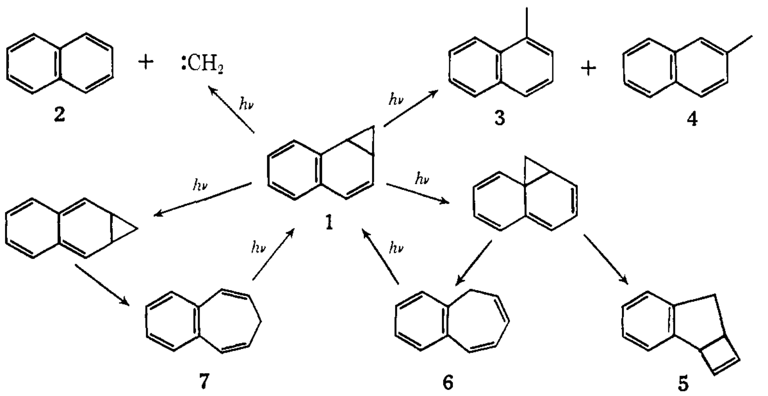
(7) M. Pomerantz and G. W. Gruber, *J. Org. Chem.*, **33**, 4501 (1968).

(8) Irradiations of 5–10-min duration produced *ca.* 5% of **2** and 90–95% of starting material (**1** or **9**). After 30 min there was *ca.* 27% of **2** and *ca.* 53% of **1** or **9**. Deuterium scrambling in the starting material in the former case was <5%. Thus the products, **5**-d_2 and **6**-d_2 would not, within experimental error, have shown scrambling.

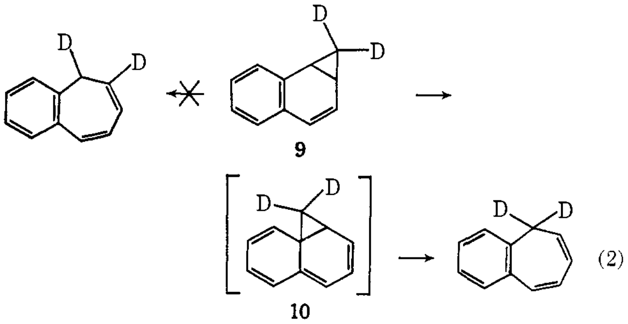
Scheme I



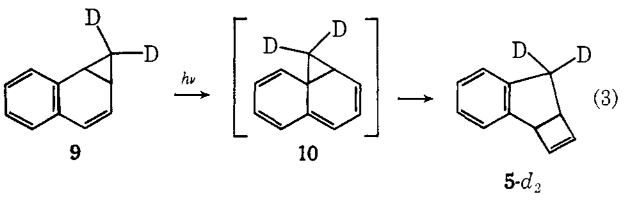
Scheme II

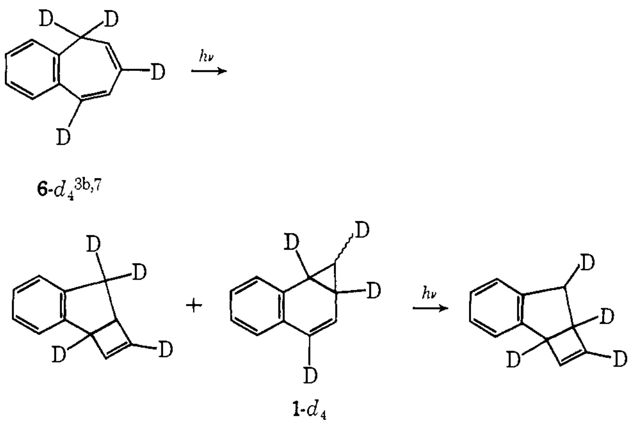


(deuterium) shift mechanism, and suggests a Berson–Willcott Bones molecular reorganization involving cleavage of the 6–7 bond, and formation of a bond between carbons 2 and 7, followed by the appropriate valence tautomerization (eq 2).[1] The rearrangement might be viewed as a concerted, suprafacial [1,5] carbon migration,[9] requiring inversion of the C-7 configuration, although a stepwise process cannot be ruled out.



Further support for an intermediate such as **10** comes from the labeling pattern in **5**-d_2 from the photochemical reorganization of **9**. The nmr spectrum of **5** has been interpreted very recently by Metzner.[10,11] With these assignments it was possible to show that the **5**-d_2 produced from **9** upon very short irradiation (5–10 min)[8] retains the CD_2 group, thus supporting the intermediacy of **10** (eq 3).[13] These results are consistent with the 7,7-dicyanobenzonorcaradiene to 2,2-dicyanobenzobicyclo[3.2.0]hepta-3,6-diene rearrangement observed by Ciganek.[2b] In our case, however, 1,2-benzotropilidene is not the precursor for **5** since **5** forms more rapidly from **1** than from **6**. When **9** was irradiated to partial completion (30 min)[8] and reisolated





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[9] For similar interpretations see: J. A. Berson, *Accounts Chem Res.*, **1**, 152 (1968); H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 756 (1969).

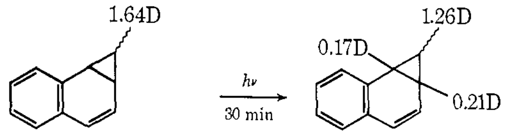
(10) D. Wendisch and W. Metzner, *Chem. Ber.*, **101**, 4106 (1968).

(11) Additional support for the nmr assignments of **5** comes from deuterium-labeled **5** formed as a minor product (<1 %) by electrocyclic ring closure of 3,5,7,7-tetradeuterio-1,2-benzotropilidene (**6**-d_4)[3b] upon irradiation.[12] Furthermore, when **1**-d_4 is irradiated yet another differently labeled **5**-d_4 is produced whose nmr spectrum is also consistent with the assignments.

(12) M. Pomerantz and G. W. Gruber, results to be published.

(13) A similar sequence has been suggested previously; see H. Hart and R. K. Murray, Jr., *Tetrahedron Lett.*, 4995 (1968); 379 (1969).

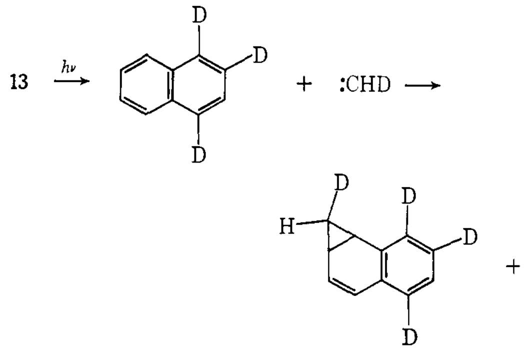
it was observed to have undergone deuterium scrambling into the two remaining cyclopropyl positions (eq 4). This result can be rationalized by invoking two



9 (4)

Berson–Willcott Bones rearrangement isomers, **10** and **11** (Scheme I). In support of the intermediacy of **12**, and therefore of **11**, is the presence of **7** in irradiations of **1** run to partial completion. Furthermore, the 3,4-benzotropilidene-d_2 produced from irradiation (5–10 min)[8] of **9** was shown by nmr spectroscopy (mixture with **9**) to be identical with authentic **12**,[3a] since its nmr spectrum showed two vinyl doublets, one being somewhat broadened. These results, therefore, provide the first direct evidence of a photochemical rearrangement of this type occurring in both directions.[14]

An additional mechanistic interpretation of the above observations deserves consideration. Methylene extrusion–readdition could explain the observed labeling patterns. By employing 1,4,6,7-tetradeuteriobenzonorcaradiene (**13**)[3b,15] such a sequence was eliminated since methylene extrusion–readdition would be expected to lead to products with aromatic deuterium (eq 5). Oxidation (alkaline permanganate) of the reaction mixture from irradiation of **13** followed by esterification



(5)

with diazomethane produced dimethyl phthalate which contained, within experimental error (*ca.* 1%), no deuterium, as determined by low-voltage mass spectroscopy.

The photochemistry of **1** can therefore be summarized as shown in Scheme II.[16]

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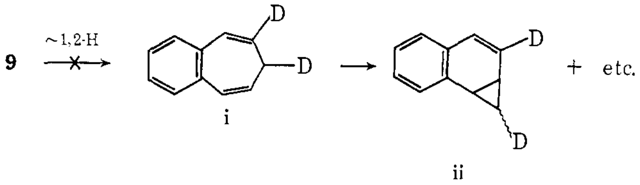
[14] That a hydrogen-shift mechanism is not operative and that **11** and **12** are intermediates in the photorearrangement of **9** can be deduced from additional evidence. If the 3,4-benzotropilidene produced in the reaction came about by a hydrogen-shift mechanism i would be produced. This would in turn lead to a benzonorcaradiene with vinyl deuterium (ii);[3a] this is, however, not observed (eq 4).



[15] The photorearrangement results with 1,4,6,7-tetradeuteriobenzonorcaradiene are consistent with those of **9**.

[16] In a given irradiation of **9**, comparison of the amount of deuterium scrambling to the amount of naphthalene formed indicates that rearrangement occurs more rapidly than methylene extrusion.

Nuclear Magnetic Resonance Studies of Ion Association

Sir:

In recent years the fundamental theories of ion association have undergone continued revision and discussion.[1] Manifestations of solute–solvent interactions as evidenced by the dependence of the ion-pair contact distance on solvent[2] and dielectric constant,[3] and the often observed deviation[1] from linearity of plots of the logarithm of the association constant *vs.* reciprocal dielectric constant have drawn increasing attention to the inadequacy of present theories.[4] With the hope of bringing new information to bear on the problem, we have initiated a study of the association of methyltributylammonium tetraphenylboride (MB) in nonaqueous solvents by nuclear magnetic resonance techniques.

The α-methyl resonance of methyltributylammonium picrate appears 192 Hz downfield from TMS in a 0.05 *M* chloroform solution, and in the limit of infinite dilution approaches a resonance frequency 197 Hz downfield from TMS. In contrast, the α-methyl resonance of a 0.05 *M* chloroform solution of MB appears only 80 Hz downfield from TMS. This unusually large upfield shift (greater than 100 Hz) can only be due to the formation of associated species in which the α-methyl of the cation is in close proximity to the phenyl rings[5] of the anion. It is likely that at these concentrations in a low dielectric solvent such as chloroform highly associated species are present.[6] However, proper choice of higher dielectric solvents and concentration ranges should facilitate the isolation and study of an ion, ion pair equilibrium (*vide infra*).

Rapid exchange between free ions and the associated species results in only one α-methyl resonance, this being a weighted average of the contribution of free and paired ions to the observed resonance frequency, ν_{obsd}.

$$\nu_{\text{obsd}} = \gamma\nu_{\text{free}} + (1 - \gamma)\nu_{\text{paired}} \tag{1}$$

γ is the fraction of free ions, and ν_{paired} and ν_{free} are the resonance frequencies of paired and free ions, respectively. As the picrate anion has only a slight effect on the α-methyl resonance of the cation, ν_{free} can accurately be determined by extrapolation of the α-methyl resonance of methyltributylammonium picrate to infinite dilution.

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(1) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968), and references therein.

(2) (a) R. M. Fuoss and E. Hirsch, *J. Amer. Chem. Soc.*, **82**, 1013 (1960); (b) D. S. Berns and R. M. Fuoss, *ibid.*, **82**, 5585 (1960).

(3) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

(4) (a) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958); (b) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

(5) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, p 140.

(6) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, New York, N. Y., 1959, p 249.