

**Acknowledgment.**—This investigation was supported in part by Public Health Service Research Grant HE-07503 from the National Heart Institute.

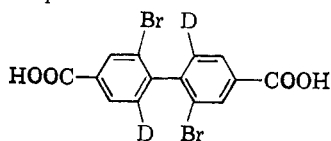
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RECEIVED NOVEMBER 12, 1963

**Steric Isotope Effects. The Isotope Effect on the Racemization of 2,2'-Dibromo-4,4'-dicarboxybiphenyl**  
*Sir:*

Experiments with sterically hindered biphenyl derivatives specifically designed to test the theory of steric isotope effects proposed by Bartell<sup>1</sup> have recently been reported by Mislow and his co-workers.<sup>2,3</sup> However, a quantitative comparison between the experimental observations and theoretical predictions has not been attempted, due to a lack of information about the detailed conformation of the transition state.

We have now prepared a hindered biphenyl system for the appraisal of the importance of steric factors in secondary deuterium isotope effects which allows a comparison between theory and experiment, *viz.* optically active 2,2'-dibromo-4,4'-dicarboxybiphenyl specifically deuterated in the 6 and 6' positions. The deuterium isotope effect on the racemization of this



compound should clearly reflect any effective size difference between protium and deuterium. Since it is known that in 2,2'-dihalobiphenyls the conformation with the two halogen atoms in van der Waals contact is energetically favored,<sup>4</sup> there is little reason to believe that steric crowding involving the isotope has any appreciable effect on the ground state. Accordingly, it is plausible to ascribe the entire steric isotope effect to crowding in the transition state.

Theoretical evaluations of the activation energy for the racemization of the protium compound by Westheimer<sup>5</sup> (18 kcal./mole) and by Howlett<sup>6</sup> (21.9 kcal./mole) are in good agreement with the experimental value<sup>7</sup> (19.0 kcal./mole). These calculations also provide a detailed picture of the equilibrium conformation of the transition state, which is assumed to be planar, and thus afford the input data necessary for the computation of the isotope effect according to Bartell.<sup>1</sup>

We have prepared the specifically deuterated compound in  $\geq 97\%$  isotopic purity (according to n.m.r. analysis). The introduction of deuterium was accomplished *via* reduction of tetrazotized 2,2'-dibromo-4,4'-dicarbomethoxy-6,6'-diaminobiphenyl with  $D_3PO_2$  prepared by repeated exchange of  $H_3PO_2$  with 99.8%  $D_2O$ . The complete synthetic procedure is reserved for a forthcoming detailed paper.

The kinetics were followed on a Perkin-Elmer 141 automatic reading polarimeter, using the mercury lines

- (1) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).
- (2) K. Mislow, E. Simon, and H. B. Hopps, *Tetrahedron Letters*, 1011 (1962).
- (3) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Am. Chem. Soc.*, **85**, 1199 (1963).
- (4) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).
- (5) F. H. Westheimer, *J. Chem. Phys.*, **15**, 252 (1947).
- (6) K. E. Howlett, *J. Chem. Soc.*, 1055 (1960).
- (7) M. M. Harris and R. K. Mitchell, *ibid.*, 1905 (1960).

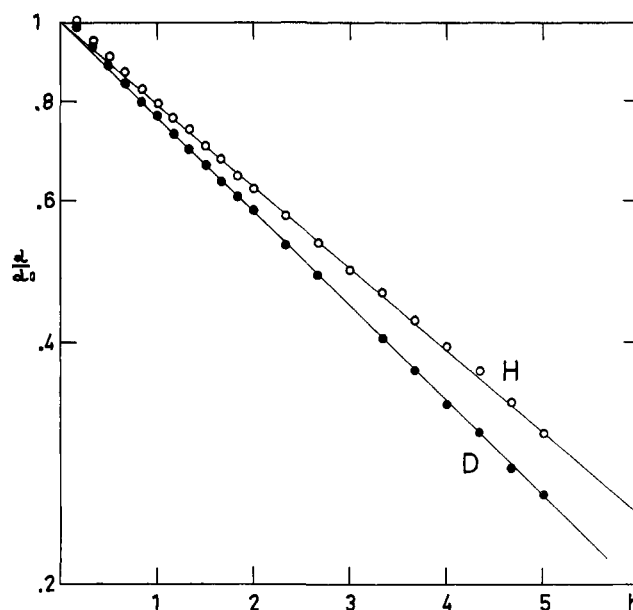


Fig. 1.—Semilogarithmic plot of relative optical rotation *vs.* time for runs 9 (H) and 14 (D) (see Table I).

at 436 and 546  $m\mu$  and the sodium D line. Due to the optical lability of these biphenyls, the measurements had to be made below  $0^\circ$ , and the results here reported were obtained at  $-19.8 \pm 0.1^\circ$  in ethanol solution. Difficulties due to the formation of frost were overcome by blowing streams of nitrogen through specially constructed brass mouthpieces onto the polarimeter cell windows. A comparison plot of representative kinetic runs (no. 9 and 14 in Table I) for the protium and deuterium compounds is shown in Fig. 1. Specific rates were obtained graphically from such plots. The results, together with the maximum deviation of four separate determinations for each compound, are given in Table I. The isotope effect ratio ( $k_D/k_H$ ) calculated from these data is 1.19.

TABLE I  
RACEMIZATION RATES OF 2,2'-DIBROMO-4,4'-DICARBOXYBIPHENYL AND ITS 6,6'-DIDEUTERIO DERIVATIVE AT  $-19.8 \pm 0.1^\circ$  IN ETHANOL

Run	Isotope	Concn., mg./ml. EtOH	Rate constant, $10^6 k$ sec. <sup>-1</sup>	Av. and max. dev., sec. <sup>-1</sup>
4	H	27.2	6.31	
7	H	19.4	6.74	
9	H	21.4	6.53	
11	H	19.2	6.35	
				$6.48 \pm 0.26 \times 10^{-6}$
14	D	21.4	7.62	
15	D	20.0	7.58	
16	D	21.9	8.02	
17	D	21.7	7.60	
				$7.71 \pm 0.31 \times 10^{-6}$

In the absence of a study of the temperature dependence of the isotope effect, it is impossible to separate the observed effect into entropy and enthalpy components. However, if it is assumed that the observed effect is entirely due to a difference in enthalpy,  $\Delta H_H^* - \Delta H_D^*$  would be equal to about 90 cal./mole. The data of Westheimer<sup>5</sup> combined with the computational procedure of Bartell<sup>1</sup> lead to a value of 506 cal./mole for this difference, whereas the data of Howlett<sup>6</sup> lead to a value of 100 cal./mole. The discrepancy arises mainly from the widely different nonbonded  $H \cdots Br$  repulsion potentials used by these authors. Finally, it should be pointed out that the magnitude

of a possible inductive effect caused by the difference in hydrogen mass can hardly be estimated at the present stage, but such an effect is probably of minor importance in this case.<sup>8</sup>

Temperature dependence studies are in progress.

**Acknowledgments.**—We are indebted to Dr. Sture Forsén of the Royal Institute of Technology for recording, interpreting, and discussing n.m.r. spectra. We wish to thank Prof. Bengt Lindberg and Dr. Olof Theander at the Swedish Forest Products Research Laboratory for permission to use the Perkin-Elmer 141 polarimeter and other facilities. This investigation was supported in part by a Public Health Service Postdoctoral Fellowship (GM-11,563) to R. E. Carter from the National Institutes of Health, Division of General Medical Sciences.

(8) See, for example, H. S. Klein and A. Streitwieser, Jr., *Chem. Ind.* (London), 180 (1961); E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

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RECEIVED SEPTEMBER 23, 1963

### Photoreduction of 2,2-Diphenyl-1-picrylhydrazyl (DPPH) in Hydrocarbons

Sir:

The chemistry of 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been studied by several authors<sup>1-3</sup> while the stability of the radical has been of special interest in the field of paramagnetic resonance. However, little is known about the photochemical reactivity of this important stable radical.<sup>4</sup> A few papers<sup>5-7</sup> have

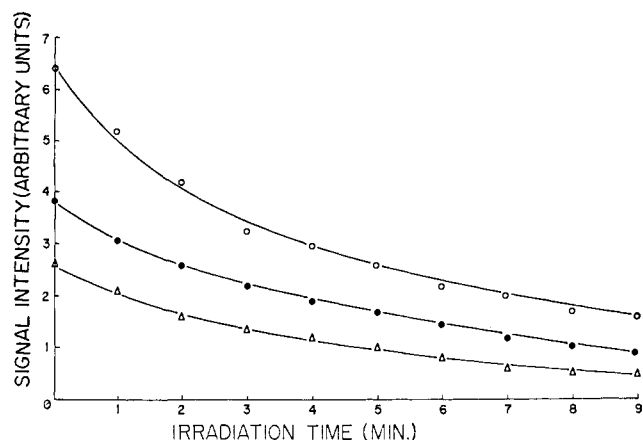


Fig. 1.—Rate of photoreduction of DPPH at various initial concentrations in cumene at 25°, initial concentration of DPPH: ○,  $2 \times 10^{-4}$  mole/l.; ●,  $5 \times 10^{-5}$  mole/l.; △,  $2 \times 10^{-5}$  mole/l.

demonstrated the photo-induced fading of DPPH in aromatic disulfides. However, the disappearance of the DPPH is due to the scavenging reaction of sulfide radicals which are generated in the presence of light.

(1) R. H. Poirier, E. J. Kahler, and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952); R. H. Poirier and F. Benington, *ibid.*, **19**, 1157 (1954).

(2) K. E. Russell, *J. Phys. Chem.*, **58**, 1437 (1954); J. S. Hogg, D. H. Lohman, and K. E. Russell, *Can. J. Chem.*, **39**, 1394, 1588 (1961); P. Venker and H. Herzmann, *Naturwiss.*, **47**, 133 (1960).

(3) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1932).

(4) An investigation concurrent with ours but dealing primarily with the kinetics of the photolysis of DPPH in CCl<sub>4</sub> followed spectrophotometrically has recently been reported: A. Suzuki, M. Takahashi, and K. Shiomi, *Bull. Chem. Soc. Japan*, **36**, 644 (1963).

(5) M. Calvin and J. A. Balltrop, *J. Am. Chem. Soc.*, **74**, 6153 (1952).

(6) K. E. Russell and A. V. Tobolsky, *ibid.*, **76**, 395 (1954).

(7) Y. Schaafsma, A. F. Bickell, and E. C. Kooyman, *Tetrahedron*, **10**, 78 (1960).

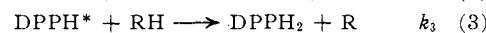
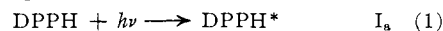
We report here the results of a preliminary e.p.r. investigation of the photo-induced abstraction of hydrogen atoms from hydrocarbons by DPPH. The photochemical reaction was carried out at room temperature within the microwave cavity of a Varian e.p.r. spectrometer with 100-kc. field modulation. The light source was a PEK mercury medium-pressure lamp with suitable filters placed at a distance of 100 cm. from the cavity. Solutions to be studied were degassed under vacuum and filled with purified nitrogen at atmospheric pressure. The determination of the approximate amount of light absorbed by DPPH solutions at 3130 Å. was carried out using the photochemical disappearance of benzophenone and the formation of acetone in isopropyl alcohol as an actinometer.<sup>8,9</sup> The benzophenone concentration was adjusted so that the fraction of light absorbed at 3130 Å. matched that absorbed by the DPPH solution.

Although DPPH has absorption maxima at 520 and 330 mμ, we observed that the photoreaction proceeds rapidly enough for e.p.r. measurement only on irradiation in the shorter wave length band. The rates of the photoreduction were followed by recording the relative spin concentration as a function of time at a constant magnetic field, the latter being adjusted to give maximum response. In the dark no diminution in e.p.r. signal intensity was observed; however, during irradiation the e.p.r. signal decreased according to the first-order rate law. A typical curve for the disappearance of DPPH in isopropylbenzene is shown in Fig. 1.

It has been reported that the e.p.r. signal of DPPH in impure isopropylbenzene solution gives a triplet spectrum instead of a quintet.<sup>10</sup> We observed the same triplet spectrum when the isopropylbenzene used was not carefully purified. However, when chromatographically purified isopropylbenzene was used, the ordinary five-line spectrum was obtained. In addition, we also observed a triplet spectrum when DPPH was dissolved in solvents such as hexene and cyclohexene. In the ultraviolet absorption spectrum of these solutions the maximum at 330 mμ was shifted to 345 mμ, suggesting some probable complex formation.

The kinetics of the disappearance of DPPH were also checked by following the reaction colorimetrically; the results agree within about 5%.

The experimental data obtained to date are insufficient to establish the entire reaction mechanism, but seem to fit the sequence



In the experiment the hydrocarbon RH is the solvent so that its concentration is practically constant. If reaction 4 is assumed to be rapid, reaction 3 is slow and rate-determining, and fluorescence is negligible, the following kinetic expression is obtained

$$k_2/k_3 = (2/\phi) - 1 \quad (5)$$

where  $\phi$  is the quantum yield of the disappearance of DPPH. If  $\phi$  is measured the values of  $k_2/k_3$  can be calculated for different solvents. A summary of the experimental results is given in Table I.

We have also briefly studied the photochemical reaction of DPPH in the solid state with infrared spectrometry. The DPPH was mixed with KBr powder and a pellet was formed. The reaction was carried out with the pellet in a Perkin-Elmer 221 infrared spectro-

(8) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Pecktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

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(10) H. Ueda, E. Kuri, and S. Shida, *J. Chem. Phys.*, **36**, 1676 (1962)