

Huntsville, Ala., where a substantial portion of this work was performed.

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### Racemization of Camphor during $\pi$ -Sulfonation. Evidence for Exclusive *exo*-Methyl Migration

Sir:

Camphor-8- $^{14}\text{C}$  (I) was prepared by the following sequence of reactions: carbonation of sodio-3-methylnorbornan-2-one, using  $^{14}\text{C}$ -labeled carbon dioxide, followed by reaction with methylmagnesium iodide to give 2,3-dimethyl-3-hydroxynorbornane-2-carboxylic acid (II), which was separated from nonacidic material and rearranged by 85% sulfuric acid to 1,7-dimethylnorbornane-7-carbo-2-lactone (III, m.p. 192–193°, reported<sup>1</sup> 192–194°); lithium aluminum hydride reduction to 8-hydroxyisoborneol-8- $^{14}\text{C}$  (IV, m.p. 275–276°. *Anal.* Calcd. for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 70.54; H, 10.66. Found<sup>2</sup>: C, 70.35; H, 10.58); Jones oxidation to 8-hydroxycamphor-8- $^{14}\text{C}$  (V, m.p. 232–233°; reported<sup>3</sup> 233°); conversion to 8-bromocamphor-8- $^{14}\text{C}$  (VI, m.p. 120–122°, reported<sup>4</sup> 121.5–122.5°); and hydrogenolysis to I-8- $^{14}\text{C}$ .

Sulfonation of I using chlorosulfonic acid<sup>5</sup> afforded camphor-9-sulfonic acid (VIII)<sup>6</sup> which is virtually completely racemized, even when starting with optically pure (+)-I.

Conversion of VIII to 9-bromocamphor (IX, m.p. 92–93°, reported<sup>5</sup> 93–94°) was accomplished by means of phosphorus pentabromide and heat<sup>5</sup>; IX was converted partly to racemic I and partly to 9-hydroxycamphor (X, m.p. 233–234°, reported<sup>7,8</sup> 233°). Oxidation of X afforded 1,7-dimethylnorbornan-2-one-7-*anti*-carboxylic acid (XI, m.p. 250–251°, reported 249–250°,<sup>7</sup> cf. footnote 6).

Degradation to provide removal of two of the three methyl groups of I (or XI) for determining isotope distribution was carried out on racemic I (from IX) (by reduction to isoborneol, dehydration *via* the phenylurethan to camphene, and isolation of formaldehyde (from original C-10) and dimethylnorcampholide by a previously published procedure<sup>9</sup> and on XI using a modified Hunsdiecker reaction,<sup>10</sup> which provided the original C-9 as carbon dioxide (trapped in phenylmagnesium bromide).

Using a liquid scintillation counter, half of the original radiocarbon was found in C-10 and half in C-8 (none in C-9).

(1) S. Beckmann and H. Geiger, *Ber.*, **92**, 2411 (1959).

(2) Spang Microanalytical Laboratory, Ann Arbor, Mich.

(3) Y. Asahina and M. Ishidate, *Ber.*, **67**, 71 (1934).

(4) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **81**, 6305 (1959).

(5) F. A. Kipping and W. J. Pope, *J. Chem. Soc.*, **63**, 593 (1893); **67**, 155 (1895).

(6) The *anti* configuration is implicit in ref. 3 and 4. Explicitly we have demonstrated this by oxidizing lactone III to 1,7-dimethylnorbornan-2-one-7-*syn*-carboxylic acid (VII, m.p. 273–275°, reported 269–270°)<sup>7</sup> which differs from the *anti* isomer XI.

(7) Y. Asahina and M. Ishidate, *Ber.*, **66**, 1673 (1933).

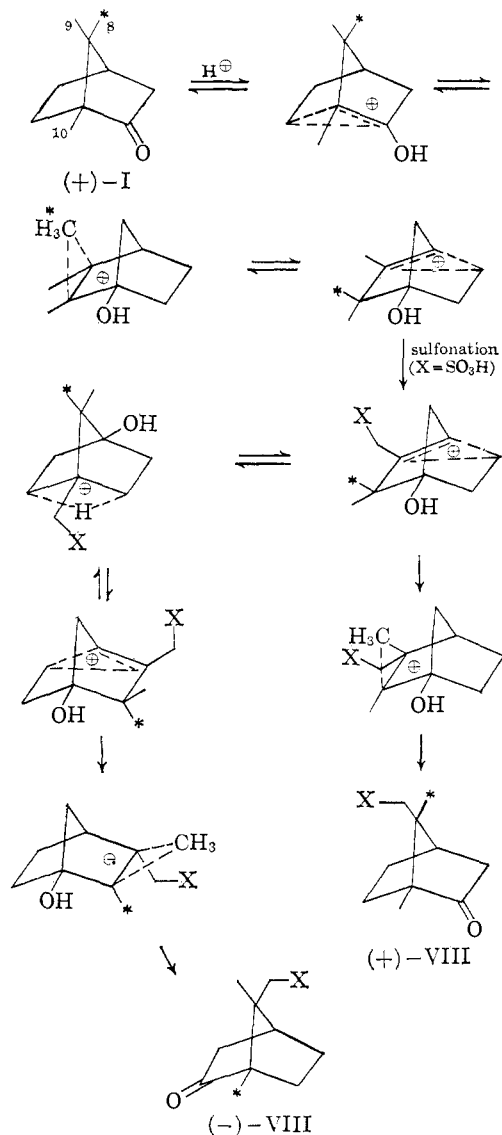
(8) R. C. Guha and S. C. Bhattacharyya, *J. Indian Chem. Soc.*, **21**, 261 (1944).

(9) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Am. Chem. Soc.*, **85**, 2282 (1963).

(10) S. J. Cristol and W. J. Firth, *J. Org. Chem.*, **26**, 280 (1961).

Next, labeled ( $\pm$ )-I was diluted with (+)-I, converted to the menthydrazone,<sup>11</sup> and recrystallized repeatedly until the specific radioactivity fell to slightly more than half the original value. (+)-Camphor-8- $^{14}\text{C}$  was then regenerated<sup>11</sup> and sulfonated, and the sulfonic acid was resolved<sup>12</sup> to give (+)-VIII. Degradation of (+)-VIII by the same procedures as before showed the label to be at C-8.

These data are consistent with a mechanism in which sulfonation is both preceded and followed by migrations involving *exo*-methyl to the exclusion of *endo*-methyl, *e.g.*



Furthermore, recovery of labeled, partially racemized I from an incomplete sulfonation experiment, followed by degradation to dimethylnorcampholide and formaldehyde, showed  $^{14}\text{C}$  distribution consistent with a similar racemization process without sulfonation (*i.e.*, omit sulfonation step and omit X from the structures). This, therefore, is also in keeping with exclusive *exo*-methyl migration.

Berson<sup>13</sup> has recently presented a cogent argument in

(11) R. B. Woodward, T. P. Kohman, and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941).

(12) W. J. Pope and J. Read, *J. Chem. Soc.*, **97**, 992 (1910).

(13) J. A. Berson, R. G. Bergman, J. H. Hammons, A. W. McRowe, A. Remanic, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3246 (1965).

which exclusive *exo*-methyl migration is considered to be compelling evidence for the intervention of non-classical carbonium ions in norbornane system rearrangements. Hence the present rearrangements are assumed to involve such ions.

It should be pointed out that, subsequent to work on camphene racemization<sup>9</sup> in this laboratory, it has been shown that tricyclene intervenes to the extent that our postulate of an *endo*-methyl migration as part of the racemization process may be ruled out.<sup>14</sup> Thus the camphene anomaly cited by Berson, *et al.*,<sup>13</sup> ceases to exist, and exclusive *exo*-methyl migration in this system appears to be the rule.<sup>15</sup>

(14) P. Hirsjärvi, K. Heinonen, and L. Pirlä, *Suomen Kemistilehti*, B37, 77 (1964).

(15) We are indebted to Professor Berson for calling Hirsjärvi's work to our attention.

(16) Partial support, in the form of a predoctoral fellowship for 1964-1965, from American Cancer Society Institutional Research Grant IN-40E, is gratefully acknowledged.

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## Homolytic Aromatic Substitution. VI. Phenylation of Biphenylene<sup>1,2</sup>

Sir:

Localization energies at the two sites of biphenylene have been calculated and indicate that the 2 position should possess the higher reactivity.<sup>3</sup> This prediction has been confirmed for electrophilic aromatic substitution by the isolation of only the 2 isomer from numerous synthetic reactions<sup>3,4</sup> and, more recently,

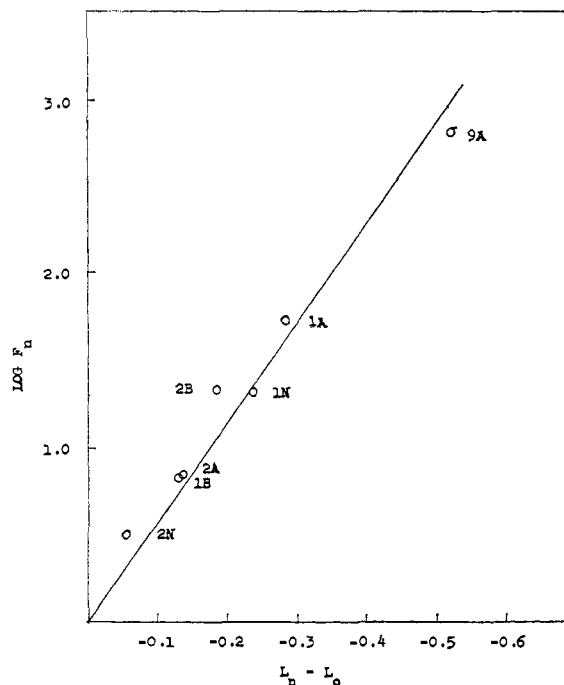


Figure 1. Correlation of partial rate factors for homolytic phenylation of anthracene (A), biphenylene (B), and naphthalene (N) with the respective differences in localization energies ( $L_n - L_0$ ).

phenylations of biphenylene are listed in Table I. The identities of those compounds in the reaction mixtures having the same retention times as authentic samples of 1- and 2-phenylbiphenylenes<sup>8</sup> were confirmed by collection from the gas chromatograph and subsequent comparison of ultraviolet spectra. Meer-

Table I. Homolytic Phenylation of Biphenylene<sup>a</sup>

Runs	Source	Orientation, %		T.r.f.	Rec., % <sup>b</sup>	Yield, % <sup>c</sup>
		1-	2-			
1-9	M <sup>d</sup>	24.3 ± 0.8	75.7 ± 0.8	19.2 ± 0.8	100 ± 3 <sup>f</sup>	2.9 ± 0.1
1-6	NAA <sup>e</sup>	22.6 ± 0.7	77.4 ± 0.7	19.4 ± 0.6	90 ± 3	6.4 ± 0.6

<sup>a</sup> Analyses by g.l.p.c. with internal standards. The uncertainties are average deviations from the mean. <sup>b</sup> Total recovery of biphenylene as unreacted biphenylene and phenylbiphenylenes. <sup>c</sup> Average yields based on biphenylene. <sup>d</sup> M, Meerwein phenylation in aqueous acetone-benzene. <sup>e</sup> NAA, N-nitrosoacetanilide in benzene. <sup>f</sup> Corrected for an 8% loss during the workup prior to analysis.

by studies of rates of tritioderprotonation and detritiation.<sup>5,6</sup> However, almost nothing is known concerning the reactivity of biphenylene in radical reactions.<sup>7</sup> We now report partial rate factors for homolytic aromatic substitution of biphenylene and an evaluation of theoretical predictions concerning the reactivity of this arene.

Percentage compositions, total rate factors, recoveries, and yields for Meerwein and N-nitrosoacetanilide

(1) Part V: S. C. Dickerman and I. Zimmerman, *J. Am. Chem. Soc.*, 86, 5048 (1964).

(2) Supported in part by an Institutional Grant (IN-146) from the American Cancer Society to New York University.

(3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 11.

(4) W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Wiley-Interscience, New York, N. Y., 1959, Chapter 2.

(5) A. Streitwieser, Jr., and I. Schwager, *J. Am. Chem. Soc.*, 85, 2855 (1963).

(6) J. M. Blatchly and R. Taylor, *J. Chem. Soc.*, 4641 (1964).

(7) The reaction of biphenylene with lead tetraacetate has been reported to give 2-hydroxybiphenylene in very low yield: ref. 4, p. 89.

wein and N-nitrosoacetanilide phenylations of biphenylene, like naphthalene,<sup>9</sup> yield essentially identical total rate factors and orientation data. The mechanism of both the Meerwein<sup>10</sup> and N-nitrosoacetanilide<sup>11</sup> methods of arylation have been discussed recently.

Partial rate factors, calculated from the data for Meerwein phenylation in Table I, are 7.0 and 22 for the 1 and 2 positions, respectively. These findings are qualitatively in agreement with the corresponding localization energies but not the free valences.<sup>8</sup> For quantitative evaluation, the partial rate factors for homolytic phenylation of biphenylene, naphthalene,<sup>9</sup>

(8) W. Baker, A. J. Boulton, C. R. Harrison, and J. F. W. McOmie, *Proc. Chem. Soc.*, 414 (1964).

(9) S. C. Dickerman and G. B. Vermont, *J. Am. Chem. Soc.*, 84, 4150 (1962).

(10) S. C. Dickerman, A. M. Felix, and L. B. Levy, *J. Org. Chem.*, 29, 26 (1964).

(11) C. Ruchardt and B. Freudenberg, *Tetrahedron Letters*, 48, 3623 (1964).