Hydrolysis of 1.0 g. of the ester in 20 ml. of 8% sodium hydroxide for one hour and crystallization of the acid from ligroin gave 0.4 g. (85%) of 1-hydroxycyclohexaneacetic acid, m.p. 61° (lit.[31] 62–64°).

Desulfuration of *t*-Butyl 1-Hydroxycyclohexylthiolacetate.—*t*-Butyl 1-hydroxycyclohexylthiolacetate (2.2 g.) was heated for an hour in refluxing *t*-butyl alcohol with 40 g. of Raney nickel which had been washed with *t*-butyl alcohol. Removal of the nickel and alcohol and evaporative distillation (at 140° (12 mm.)) of the residue gave 1.1 g. (80%) of 2-(1-hydroxycyclohexyl)-ethanol, n^{18}_D 1.4900.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.66; H, 11.19. Found: C, 66.31; H, 11.01.

Rate of Reaction of Ethyl Dithiolmalonate with Benzaldehyde.—The ethyl dithiolmalonate[32] was prepared by reaction of malonic acid with thionyl chloride followed (without purification of the acid chloride) by the addition of ethyl mercaptan. Careful fractionation gave a 25% yield of a nearly colorless product, b.p. 110–112° (2 mm.), n^{25}_D 1.5203.

Anal. Calcd. for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29; S, 33.35. Found: C, 43.77; A, 6.32; S, 33.18.

The rate of reaction was determined by using the procedure described by Pratt and Werble.[23] A repetition of their rate determination was made with 500 ml. of benzene solution of 0.25 *M* in benzaldehyde and 0.25 *M* in ethyl malonate containing 64 units[33] of the piperidine–caproic acid catalyst and there was obtained a rate constant of 9.95 × 10^{-3} liters moles^{-1} min.$^{-1}$ which agrees quite well with the value of 9.96 × 10^{-3} obtained by Pratt and Werble.

The reproducibility of the measurements was improved by prior treatment of the inside of the water separator with diphenyldichlorosilane in order to prevent wetting of the glass by the water droplets.

Since the rate of reaction of the thiolester (0.25 *M* in a total volume of 500 ml. with benzaldehyde (0.25 *M*) was found in preliminary experiments to be considerably faster than the malonic ester reaction, the catalyst concentration was halved to 32 units. The plot of log *c vs. t* (Fig. 1) is in good agreement with the assumed first-order dependence of the reaction rate on thiolester concentration and a rate constant of 20.8 × 10^{-3} liters mole^{-1} min.$^{-1}$ was obtained. This gives a relative rate of reaction of about 4:1 for ethyl dithiolmalonate compared with ethyl malonate.

The ethyl benzaldithiolmalonate underwent considerable decomposition during fractionation. There was obtained 24 g. (68%) of the condensation product, b.p. 177–179° (1 mm.), n^{25}_D 1.6180.

Anal. Calcd. for $C_{14}H_{16}O_2S_2$: C, 59.96; H, 5.75; S, 22.87. Found: C, 59.94; H, 5.76; S, 23.02.

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[31] O. Wallach and E. Issac. *Ann.*, **347**, 329 (1906).

[32] J. E. Purvis, H. D. Jones and H. S. Tasker. *J. Chem. Soc.*, **97**, 2287 (1910).

[33] A solution of 16.6 g. of piperidine and 45.4 g. of caproic acid made up to 200 ml. with benzene contains 1 unit catalyst/ml. (9.76 × 10^{-4}) mole/ml. of piperidine and 2(9.76 × 10^{-4}) mole/ml. of caproic acid.

PORTLAND, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

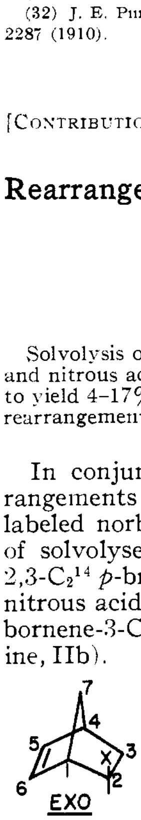
Rearrangements in Carbonium Ion-Type Reactions of C^{14}-Labeled Dehydronorbornyl Derivatives[1]

BY JOHN D. ROBERTS,[2] C. C. LEE AND W. H. SAUNDERS, JR.

RECEIVED OCTOBER 11, 1954

Solvolysis of *exo*- and *endo*-dehydronorbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonates in acetic acid and formic acid solutions and nitrous acid deaminations of *endo*-dehydronorbornyl-3-C^{14}-amine in acetic acid and aqueous fluoboric acid were found to yield 4–17% of dehydronorbornyl derivatives with 30–48% of the C^{14} located at other than the 2,3-positions. The C^{14}-rearrangements are discussed in terms of unsymmetrical "dehydronorbornium" intermediates.

In conjunction with our investigation of rearrangements in carbonium ion-type reactions of C^{14}-labeled norbornyl derivatives,[3] studies were made of solvolyses of *exo*- and *endo*-dehydronorbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonates (Ia and IIa) and nitrous acid deamination of *endo*-2-amino-$\Delta^{5,6}$-norbornene-3-C^{14} (*endo*-dehydronorbornyl-3-C^{14}-amine, IIb).



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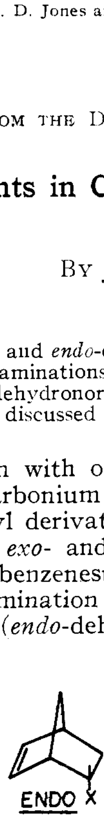

II

Ia, IIa, X = p-$BrC_6H_4SO_3$–
Ib, IIb, X = $-NH_2$
Ic, IIc, X = –OH
Id, IId, X = –OAc
Ie, IIe, X = $-O_2CH$

Synthetic Procedures and Experimental Results

A mixture of *exo*- and *endo*-dehydronorborneols-2,3-C_2^{14} (Ic and IIc) was obtained by the lithium aluminum hydride reduction of mixed labeled dehydronorbornyl acetates (Id and IId) from the Diels–Alder reaction between cyclopentadiene and vinyl-1,2-C_2^{14} acetate.[3] Equilibration of the alcohol mixture in refluxing toluene with sodium and fluorenone effected enrichment in the *exo*-isomer,[3,4] the latter amounting to 47% of the recovered product. With *p*-bromobenzenesulfonyl chloride in pyridine,[5] the alcohols yielded the desired sulfonates Ia and IIa.

The stereoisomeric *p*-bromobenzenesulfonate mixtures were not separated for the solvolysis experiments since the published[6] relative solvolysis rates of Ia and IIa indicated that Ia easily can be solvolyzed preferentially at 45° in the presence of IIa. Acetolysis of Ia or IIa gave principally 3-acetoxynortricyclene (IIIa) with lesser amounts of *exo*-dehydronorbornyl acetate (Id).[6] Conversion of the product mixtures to the corresponding alcohols and hydrogenation gave mixtures of 3-hydroxynortricyclene (IIIb) and *exo*-norborneol (IV). The hydro-

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[1] (a) Supported in part by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission. (b) Presented in part at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951.

[2] Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, Calif.

[3] J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., THIS JOURNAL, **76**, 4501 (1954).

[4] (a) W. v. E. Doering and T. C. Aschner, *ibid.*, **71**, 838 (1949); (b) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950), erroneously infer that the equilibrium product is substantially pure *exo*-dehydronorborneol.

[5] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[6] S. Winstein, H. M. Walborsky and K. Schreiber, THIS JOURNAL, **72**, 5795 (1950).

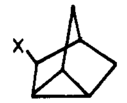
TABLE I

RADIOACTIVITY ANALYSES OF DEGRADATION PRODUCTS OF DEHYDRONORBORNYL COMPOUNDS FROM CARBONIUM ION-TYPE REACTIONS OF DEHYDRONORBORNYL-2,3(OR 3)-C^{14} DERIVATIVES

Reactant	Con-fig.	Solvent	Temp., °C.	Time, hr.	Dehy-dro prod.,[a] %	Acid V, activity Meas.[b]	Cor.[c]	Diamine VI, activity Meas.[b]	Cor.[c]	$BaCO_3$, activity Meas.[b]	Cor.[c]	Rearr., %[d]
p-Bromobenzenesulfonate	*endo*	HOAc	Reflux	48	17	850	2050	358[e]	618	1941	1342	30.1
p-Bromobenzenesulfonate	*exo*	HOAc	45	1.0	11	442	1065	236[e]	407	877	602	38.2
p-Bromobenzenesulfonate	*exo*	HCO_2H	45	1.0	4	530	1278	355[e]	613	937	646	48.0
Amine	*endo*	HOAc	Room	12	17	0.03946[f]		0.01521[f,g]		0.02298[f,h]		38.5
Amine	*endo*	H_2O–HBF_4	Room	48	7	.06905[f]		.02416[f,g]		.04306[f,h]		35.0

[a] As determined by quantitative hydrogenation; remainder of product presumed to be nortricyclyl derivatives. [b] Measured C^{14}-activities in counts/min., determined with a windowless methane-filled counter (Nucleometer), of "infinitely thick" barium carbonate samples of cross-sectional area equal to 2.90 cm.² and prepared as described by J. D. Roberts, W. Bennett, E. W. Holroyd, Jr., and C. H. Fugitt, *Anal. Chem.*, **20**, 904 (1948). The activities are corrected for background and have standard deviations of less than 2%. [c] C^{14}-Activities in dis./min./mg. of barium carbonate, corrected for self absorption and dilution by non-labeled carbon atoms as described by J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950). [d] Figures are for (activity of VI/activity of V) × 100. The $BaCO_3$ activities were used only as a rough check on the activity balance.[3] [e] Determined by combustion of the stannous chloride complex of VI.[3] [f] Activities in microcuries/millimole (μc./min.) determined by the procedure of O. K. Neville, *ibid.*, **70**, 3499 (1948). [g] Combustion of the dibenzoyl derivative of VI.[3] [h] Corrected for a statistical factor of two.

gen absorptions indicated that the product from the acetolysis of Ia contained 11% Id, whereas the acetolysis of IIa, Id amounted to 17% of the total product.

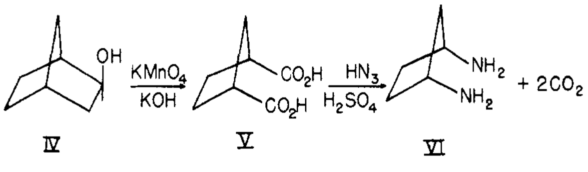


IIIa, X = OAc
IIIb, X = OH
IIIc, X = OCHO

The *exo*-isomer Ia was solvolyzed also in formic acid. Hydrogenation showed the product to contain only 4% unsaturated material, presumably *exo*-dehydronorbornyl formate (Ie), the remainder being nortricyclyl formate (IIIc). Cleavage of the ester mixture with lithium aluminum hydride followed by hydrogenation gave a mixture of IIIb and IV.

endo-Dehydronorbornyl-3-C^{14}-amine (IIb) was prepared by the iron and hydrochloric acid reduction of the Diels–Alder adduct of nitroethylene-2-C^{14} and cyclopentadiene.[3] IIb was treated with nitrous acid in acetic acid and in aqueous fluoboric acid. As in the solvolyses, the products were mixtures of the corresponding nortricyclyl and dehydronorbornyl derivatives[7] which eventually were converted to IIIb and IV. Quantitative hydrogenation showed the proportion of dehydronorbornyl derivatives, Id from the reaction in acetic acid and Ic from the reaction in aqueous fluoboric acid, to be 17 and 7% of the total product, respectively.

The radioactive *exo*-norborneol in the hydrogenated reaction products was degraded by the method previously reported.[3]



IV V VI

Appropriate amounts of non-radioactive norborneol were added as carrier to aid the degradation. Alcohol IIIb appeared to cause no complications in the oxidation of IV to V. The C^{14}-content of the diacid V is equivalent to the total activity of IV, while that of VI represents the C^{14}-activity which migrated from its original location at the 2,3-positions. Consequently, the figures for (activity of VI/activity of V) × 100 are designated as "% rearrangement." Data from the C^{14}-assays and the "% rearrangements" for the reactions studied are given in Table I.

Discussion

As with the norbornyl derivatives,[3] it appears reasonable to assume that the only mechanistic difference between solvolysis reaction of the *p*-bromobenzenesulfonates Ia and IIa is that 6–10% of direct displacement reaction may take place with the *endo*-isomer IIa. With this assumption, the part of the reaction which leads to rearrangement is considered mechanistically independent of the configuration of the starting material. Rearrangement of the C^{14}-activity from carbons 2 and 3 amounted to 38% in the acetolysis of *exo*-sulfonate Ia and 30% rearrangement was found in the acetolysis of the *endo*-isomer IIa (Table I). The 8% difference in rearrangement between the isomers is attributable to the above-mentioned direct non-rearranging displacement reaction between solvent molecules and the *endo*-sulfonate (IIa). The quantitative hydrogenation data also tend to support this interpretation since more Id is formed in the acetolysis of IIa than in the acetolysis of Ia.

Simonetta and Winstein[8] have reviewed the stereochemical and kinetic evidence for important conjugative interaction between a carbonium ion center and an appropriately oriented Π-electron-bearing β-substituent such as the vinyl group in dehydronorbornyl derivatives. A non-classical "dehydronorbornonium" ion with the structure VII has been proposed[1b,9] as a possible reaction intermediate in the solvolyses of dehydronorbornyl halides. To accommodate the observed rearrangements in the carbonium ion-type reactions reported here, it is necessary to postulate also either ion VIII or a relatively slow equilibration of VII with its enantiomorph IX. The failure to achieve complete rearrangement indicates ion VII to be the initial

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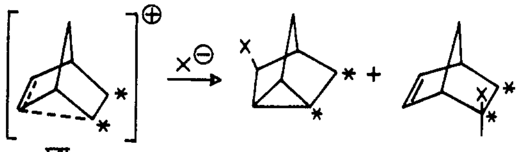
(7) *Cf.* W. E. Parham, W. T. Hunter and R. Hanson, THIS JOURNAL, **73**, 5068 (1951).

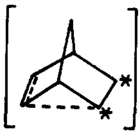
(8) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

(9) J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950).

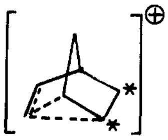
intermediate in the ionization process. Either VII, VIII or IX can react with the conjugate base of the solvent at position 5 to give a nortricyclyl derivative. With VII, the alternative is reaction at position 2, giving rise to an unrearranged dehydronorbornyl derivative.



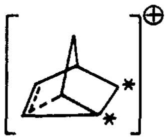
VII



VII

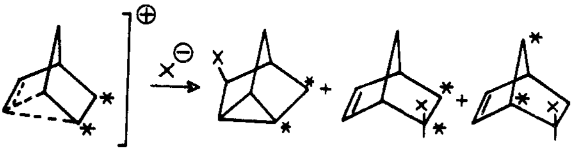


VIII



IX

With VIII, besides position 5, reaction may occur with equal probability at positions 1 and 2, leading to a 50% rearrangement of the labeled atoms in the unsaturated product if isotope effects are neglected. IX can only yield nortricyclyl or rearranged dehydronorbornyl (X) derivatives.



VIII X

Since the system, acetic acid–acetate ion, is more nucleophilic than formic acid–formate ion, the activation energy for the product-controlling reaction between a cationic intermediate and either solvent or anion should be lower with acetic acid than with formic acid. Thus, in the acetolysis of Ia or IIa, the first intermediate VII can react partly with acetate ions to give unrearranged dehydronorbornyl acetate and partly be converted to intermediates VIII or IX. In such circumstances, the product shows less than 50% rearrangement of C^{14} atoms. In formic acid, the activation energy for the product-forming reaction is higher, and a better opportunity is available for the first intermediate to proceed successively through VIII (and/or IX) before giving the final products. The larger observed rearrangement of 48.0% in the formolysis of Ia is in accord with this idea.[10]

Nitrous acid deamination of IIb in acetic acid gave similar extents of rearrangement and dehydronorbornyl acetate formation to those obtained in acetolysis of the *endo*-sulfonate ester IIa. In aqueous fluoboric acid, IIb gave somewhat more rearrangement and a substantially smaller fraction of dehydronorbornyl product. The difference in extent of rearrangement with acetic acid and water as solvents correlates with the behavior of labeled norbornylamines in corresponding reactions[3] but is not yet satisfactorily explicable.

It is of interest to note that, if intermediate VIII is solely responsible for the observed rearrangements as postulated above, complete degradation of the norborneol IV should show no C^{14} in positions 5 and 6. Also, since VII is asymmetric and VIII has a plane of symmetry, acetolysis of optically active Ia may be predicted to lead to only partial loss of optical activity whereas formolysis should give a practically completely racemized product.

The lack of complete isotope-position rearrangement in the acetolysis of dehydronorbornyl-2,3-C_2^{14} sulfonates coupled with the tendency of *exo*-dehydronorbornyl sulfonate to be interconverted with the corresponding nortricyclyl sulfonate ester[11] indicates that either the "internal return" process studied by Winstein and co-workers[12] does not lead to rearranged sulfonate (as X) or else that the actual degree of rearrangement in the solvolyses is substantially less than appears from the C^{14}-data.

Experimental

Dehydronorborneol-2,3-C_2^{14} was prepared in 82% yield by lithium aluminum hydride cleavage of dehydronorbornyl-2,3-C_2^{14} acetate obtained from Diels–Alder addition of vinyl-1,2-C_2^{14} acetate to cyclopentadiene.[3]

Partial Isomerization of *endo*- to *exo*-Dehydronorborneol-2,3-C_2^{14}.—A mixture of 4.5 g. of dehydronorborneol-2,3-C_2^{14} (from Diels–Alder adduct, *exo*-isomer content about 19%), 0.09 g. of fluorenone and 0.045 g. of sodium in 20 ml. of toluene was refluxed for 45 hours. The equilibration product was isolated as previously described.[3] The yield was 3.4 g. (76%). The proportion of *exo*-isomer, as measured by the acid liberated when the *p*-bromobenzenesulfonate was solvolyzed in 75% acetone–25% water at 45° for one hour, was 47%.

Dehydronorbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonates were prepared as described for the norbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonates.[3]

Solvolysis of *exo*-Dehydronorbornyl-2,3-C_2^{14} *p*-Bromobenzenesulfonate in Acetic Acid.—Eight grams (0.024 mole) of a mixture of *exo*- and *endo*-*p*-bromobenzenesulfonates prepared from isomerized dehydronorborneol-2,3-C_2^{14} and 2.5 g. (10% excess) of potassium acetate in 50 ml. of acetic acid were heated at 45° for 1 hour. The resulting solution was worked up as described for the acetolysis of *exo*-norbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonate.[3] The recovery of *endo*-norbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonate, m.p. 88–89°, was 4.1 g. (51%). The yield of mixed acetates (nortricyclyl and dehydronorbornyl), b.p. 70–72° (8 mm.), amounted to 1.3 g. (35%). Treatment of the crude product with lithium aluminum hydride yielded 0.80 g. (85%) of 3-hydroxynortricyclene and *exo*-dehydronorborneol which absorbed 11% of one molar equivalent of hydrogen in ethyl acetate over platinum oxide. The yield of hydrogenated alcohols was 0.71 g. (89%). Non-radioactive norborneol (0.70 g.) was added and the total of 1.41 g. of norborneol and 3-hydroxynortricyclene mixture was oxidized with 5.6 g. of potassium permanganate and 5.6 g. of potassium hydroxide in 56 ml. of water as in the oxidation of pure norborneol.[3] The isolated *cis*-cyclopentane-1,3-dicarboxylic acid amounted to 0.60 g. (55% based on the norborneol present). It melted alone and in admixture with an authentic sample at 119–120°. Its infrared absorption spectrum (Nujol mull) was also identical with that of an authentic sample.

The decarboxylation of the *cis*-cyclopentane-1,3-dicarboxylic acid and the radioactivity assays of the degradation products were carried out as previously described.[3] The results are given in Table I.

Solvolysis of *endo*-Dehydronorbornyl-2,3-C_2^{14} *p*-Bromobenzenesulfonate in Acetic Acid.—A mixture of 4.1 g. (0.012 mole) of *endo*-dehydronorbornyl-2,3-C_2^{14} *p*-bromo-

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(10) The situation in these reactions is very similar to that encountered in carbonium ion reactions of β-phenylethylamines, see J. D. Roberts and C. M. Regan, THIS JOURNAL, **75**, 2069 (1953).

(11) S. Winstein, paper presented at the Organic Reaction Mechanisms Symposium.[11]

(12) (a) See for example, S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2156 (1952); (b) S. Winstein and D. S. Trifan, *ibid.*, **74**, 1154 (1952).

benzenesulfonate and 1.35 g. (10% excess) of potassium acetate in 25 ml. of acetic acid was heated under reflux for 48 hours. The products were isolated as in the acetolysis of *endo*-norbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonate.[3] The yield of the mixture of nortricyclyl and *exo*-dehydronorbornyl acetate was 1.2 g. (63%). The corresponding alcohol mixture (0.76 g.) obtained after lithium aluminum hydride reduction absorbed 17% of a molar equivalent of hydrogen. The hydrogenation product (0.64 g.) was mixed with 0.70 g. of inactive norborneol and the whole was oxidized with potassium permanganate, giving 0.69 g. (60% based on the norborneol present) of *cis*-cyclopentane-1,3-dicarboxylic acid. Results of radioactivity analyses of the degradation products are given in Table I.

Solvolysis of *exo*-Dehydronorbornyl-2,3-C_2^{14} *p*-Bromobenzenesulfonate in Formic Acid.—A mixture of 7.0 g. (0.021 mole) of mixed *p*-bromobenzenesulfonates prepared from the isomerized *exo*- and *endo*-dehydronorborneol-2,3-C_2^{14}, 1.45 g. (0.021 mole) of sodium formate and 40 ml. of anhydrous formic acid was heated at 45 ° for 1 hour. The products were isolated as for the acetolysis experiment. The recovered *endo*-dehydronorbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonate weighed 2.5 g. (36%). The yield of nortricyclyl and *exo*-dehydronorbornyl formate mixture, b.p. 60° (8 mm.), was 1.0 g. (34%). The mixture of formates was converted to the corresponding alcohols which absorbed 4% of a molar equivalent of hydrogen. The hydrogenation product and 0.40 g. of norborneol carrier was oxidized to give 0.40 g. of *cis*-cyclopentane-1,3-dicarboxylic acid. Degradation and radioactivity assays were carried out the usual way.

***endo*-Dehydronorbornyl-3-C^{14}-amine with Nitrous Acid.**—The experiment using acetic acid as solvent was carried out as with *endo*-norbornyl-3-C^{14}-amine.[3] The crude ester from 2.5 g. of *endo*-dehydronorbornyl-3-C^{14}-amine and sodium nitrite in acetic acid was cleaved with lithium aluminum hydride and yielded 0.56 g. of mixed alcohols, m.p. 85–95°. The product absorbed 17% of one molar equivalent of hydrogen. The hydrogenated material was diluted with carrier *exo*-norborneol and degraded as before.

The aqueous fluoboric acid deamination employed the previously described procedure[3] and 2.5 g. of amine afforded 0.60 g. of crude alcohol mixture, m.p. 95–103°. On quantitative hydrogenation, 7% of one molar equivalent of hydrogen was absorbed. The reduction product was degraded in the usual way.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

A Quantitative Treatment of Isomer Distribution in Aromatic Electrophilic Substitution[1,2]

BY CHARLES W. MCGARY, JR.,[3] Y. OKAMOTO[4] AND HERBERT C. BROWN

RECEIVED DECEMBER 20, 1954

An extension of the Hammett relationship to electrophilic substitution reactions is proposed. It has been demonstrated that the usual side-chain σ_p substituent constants are not suitable for such electrophilic reactions. New $\sigma_p{}^+$ values are developed which permit the quantitative treatment of directive effects in aromatic substitutions. Good agreement is obtained for *para/meta* ratios calculated in this way with ratios observed experimentally. *Ortho* and *meta* reactivities in electrophilic substitutions generally follow a relationship similar to that previously proposed for *para* and *meta* substitution. Only in the case of mercuration, chloromethylation and isopropylation are serious deviations observed. It is proposed therefore that the present quantitative treatment can be extended to include *ortho* substituents in many electrophilic aromatic substitutions where the steric factor is either moderate or negligible. The treatment has been extended mathematically to polysubstituted benzene derivatives. It is shown to be identical with the relationship demonstrated previously on an empirical basis for the chlorination and mercuration of the methylbenzenes.

In the development of the theory of aromatic substitution, attention has been directed primarily toward the aromatic component. Thus, orientation and relative rates have been interpreted qualitatively in terms of various electrical and steric effects in the substituent already present.[5] In general, the effect of the activity of the substituting agent upon isomer distribution has been largely ignored. In a few cases where steric and polar explanations fail, such as in diazonium coupling,[6a] such activity has been invoked occasionally to account for *ortho/para* ratios.[6b]

A detailed discussion of the importance of the activity of the attacking species in controlling the *para/meta* isomer distribution has been presented recently.[7,8] Thus, it has been shown that in numerous reactions of aromatic nuclei, including chlorination, chloromethylation, base strength, nitration, mercuration and isopropylation of toluene, the orientation can be correlated with the "activity" or "selectivity" of the attacking species.

It has been demonstrated[7,8] that these reactions obey the relationship

$$\log p_f = c \log (p_f/m_f) \qquad (1)$$

where p_f and m_f are the partial rate factors for substitution in the *para* and *meta* positions of toluene and, presumably, of other monosubstituted benzenes. This expression was developed and tested as an empirical relationship. However, the validity of this relationship argues for the existence of a linear free energy expression for aromatic substitution of the same type as that developed by Hammett for side-chain aromatic derivatives

$$\log (k/k_0) = \rho\sigma^9 \qquad (2)$$

The relationship between the empirical expres-

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[1] Directive Effects in Aromatic Substitution. VII. Previous publications in this series: THIS JOURNAL, **77**, 2300 (1955); **77**, 2306 (1955); **77**, 2310 (1955).

[2] Based upon a thesis submitted by C. W. McGary, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Purdue Research Foundation Fellow, 1952–1953; American Cyanamid Corp. Fellow, 1953–1954. Research assistant on a grant from the National Science Foundation, 1954.

[4] Research assistant on a grant from the Petroleum Research Fund, 1954–1955.

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