

(DNP) in the usual manner.<sup>21</sup> The bulk of the material was distilled from the same column, and two fractions were collected: (1) 0.347 g., b.p. 120–159.5°; and (2) 0.498 g., b.p. 159.5–160.0°. Fraction 2 showed only a weak carbonyl absorption at 5.83  $\mu$ , and formed a 2,4-DNP<sup>21</sup> melting at 138.5–139.5° after crystallization from methanol, undepressed on mixed melting with authentic methyl cyclohexyl ketone (m.p. 140°). Column chromatography of the solid 2,4-DNP from the crude reaction mixture on alumina (act. gr. 2) gave three bands which were eluted with benzene (bands 1 and 2) and 1:4 ether–benzene (band 3), respectively. Evaporation and recrystallization from methanol gave

solids which were identified by melting points and mixed melting points as: band 1, methyl cyclohexyl ketone 2,4-DNP, m.p. 138.5–139.5°; band 3, cyclohexanone 2,4-DNP, m.p. 151–156° (reported<sup>21</sup> m.p. 160°). Vapor phase chromatography of the crude reaction mixture on 4-ft. Silicone DC 200 at 151° and 4-ft. dinonyl phthalate at 140° showed four major components, present in approximately equal amounts, but no  $\alpha$ -methylcycloheptanone could be detected. The absence of carbonyl absorption in the distilled product and the isolation of a derivative of methyl cyclohexyl ketone after acid treatment indicates the primary reaction product is the epoxide IV.

[CONTRIBUTION FROM THE CONVERSE LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

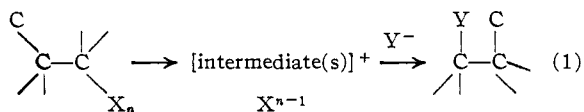
## On the Norbornyl Cation Problem

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RECEIVED AUGUST 2, 1962

Evidence is presented that deamination of *exo*- and *endo*-norbornylamines in acetic acid produces an unsymmetrical, essentially classical carbonium ion, but that the cation from solvolysis of *exo*-norbornyl arenesulfonates is essentially symmetrical.

The determination of structure and chemical properties of the various species which intervene in cationic rearrangements of carbon is central to the detailed understanding of such processes. The present formulations of these reactions, *e.g.* (1), usually include a



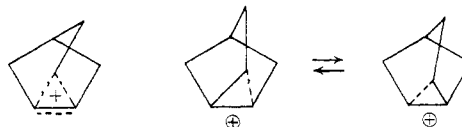
consideration of whether rearrangement occurs *simultaneously* with ionization to give a bridged "non-classical"

action,  $\overset{\text{C}^+}{\text{C}}-\text{C}$  (anchimerically assisted ionization), or *after* ionization to a classical "carbonium ion." In either case there remains a question of whether the structure in which the migrating group forms a bridge across to the carbon atoms is a relatively stable intermediate which leads to product(s) directly by reaction with nucleophile or a transient on the way to a new (rearranged) classical carbonium ion. The intermediacy of such a bridged ion ought to assume increasing chemical significance as the ion becomes more stable than the alternative classical ions and as the energy barrier between these ions is diminished.

The behavior of a system in terms of these considerations might be expected to depend not only on the arrangement of carbon in the molecule but also on the nature of the process for cation generation and the interactions with neighboring solvent and solute molecules. Although it is already clear that the variable of the leaving group X is not trivial in the mechanistic scheme of things, the greater part of present knowledge on intermediates in carbonium ion rearrangements and on related matters, such as interaction of these intermediates with other ions and with solvent, is derived from the study of halide or sulfonate ester solvolysis. The use of other non-solvolytic reactions, *e.g.*, amine deamination, to distinguish between intermediate carbonium ion structures is rather less common for a number of reasons including in the case of amine deamination the inapplicability of kinetic analysis to the steps of interest and the irregularities which have been encountered in attempts to correlate product distribution with that from corresponding sulfonate ester or halide solvolysis in various systems.<sup>2</sup> It now appears

that in the case of deamination the enormous speed of decomposition of the diazonium ion is at least in part responsible for the apparent discrepancies.<sup>3</sup> This, in turn, suggests that the amine reaction, an obviously practical method of carbonium ion generation, may complement the solvolysis approach in the development of a more general understanding of interconverting classical and non-classical cations. Indeed, as will be apparent from what follows, it seems inappropriate to generalize on the basis of solvolysis results *alone*, however quantitative, since the problems of cationic rearrangements of carbon are intrinsically multidimensional as a result of the number and significance of the independent variables. A clear understanding of cation behavior may, in fact, require the study of a spectrum of processes for ion *generation* as well as the variation of carbon structure, stereochemistry and reaction medium.

The present paper deals with some experiments on amine deamination and solvolysis in the 2-norbornyl series which were performed to extend existing knowledge in this remarkably instructive system.<sup>4</sup> Winstein and Trifan have argued convincingly that the considerably greater solvolytic reactivity of *exo*-norbornyl arenesulfonate as compared to the *endo* isomer and the formation of racemic *exo*-acetate from acetolysis of optically active *exo*-sulfonate show that carbon-carbon  $\sigma$ -delocalization accompanies and assists ionization of the *exo* isomer. In addition, they consider that the symmetrical bridged ion is probably both the product of ionization and the direct precursor of *exo*-acetate, but they point out that an alternative formulation, a system of two equilibrated unsymmetrical non-classical ions, is not excluded. In the case of the solvolysis



of the *endo*-norbornyl arenesulfonate the mechanistic evidence is far less clear; it is not yet known, for example, whether *endo*  $\rightarrow$  *exo* sulfonate rearrangement

(2) Cf. H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 93–101, 123–136.

(3) See, for example, the review by J. H. Ridd, *Quart. Revs.*, **15**, 418 (1961), which summarizes recent studies on "conformational control" of rearrangement in deamination reactions of acyclic systems and refs. 10 and 12 given below.

(4) See S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).

(1) (a) U. S. Public Health (N. I. H.) postdoctoral fellow 1959–1961; (b) Research Associate under a grant (G-9999) from the National Science Foundation.

precedes solvolysis. It has been proposed, however, that ionization in acetic acid leads to an unbridged norbornyl cation, possibly coordinated with solvent, which rearranges to the symmetrical cation and which to a much smaller extent associates with acetic acid to produce unrearranged *exo*-acetate. At 75° the unrearranged acetate amounts to 7–8% of the total reaction product as measured by the retention of optical activity. Apropos of the problem of formulating this reaction and the present work is the observation of Berson and Ben-Efraim<sup>5</sup> that the deamination of (+)-*endo*-norbornylamine in acetic acid affords *exo*-norbornyl acetate with *ca.* 23% retention of optical purity. This result was reconciled with the findings of Winstein and Trifan<sup>4</sup> by considering "that the excess unrearranged portion of the product acetate is derived by direct displacement of the solvent on the diazonium ion."<sup>5</sup> This hypothesis is inconsistent with the reasonable expectation that a concerted backside displacement reaction with solvent as nucleophile should be far less likely for amine deamination than for sulfonate solvolysis (*vide infra*). It seemed to us more likely that a classical carbonium ion is produced by loss of nitrogen from the *endo* diazonium cation and that this ion either reacts more rapidly with nucleophile (HOAc or AcO<sup>-</sup>) or rearranges less rapidly than the ion from solvolysis of the *endo*-sulfonate either because of a difference in reaction conditions<sup>6</sup> or a difference between the ions, *e.g.*, in geometry, energy content or environment.<sup>7</sup>

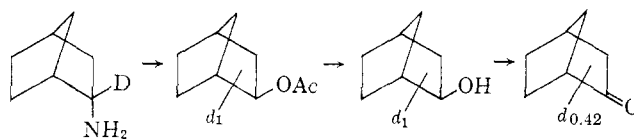
A crucial test of the Berson hypothesis would seem to be the deamination of optically active *exo*-norbornylamine. The *exo*-diazonium ion in this case is clearly not subject to concerted backside displacement for steric reasons and consequently, any retention of optical activity in the product must come from an optically active carbonium ion. We have found that the deamination of the optically active *exo*-amine in acetic acid under the conditions of Berson and Ben-Efraim and isolation of acetate *via* norborneol by their procedure gives acetate with about 15% retention of optical purity, and in addition that the product is a mixture of 96% *exo*-acetate and *ca.* 4% of the *endo*-acetate.<sup>8</sup>

#### Several Inferences Can Be Drawn from This Result.

—First, it seems clear that an optically active carbonium ion must be formed despite the fact that carbon-carbon  $\sigma$ -participation to give a bridged ion is stereo-electronically favorable. Secondly, there must be an energy barrier between this ion and the symmetrically bridged cation. Thirdly, reaction of the unsymmetrical cation with solvent probably gives both *exo*- and *endo*-acetate with the former predominating heavily.<sup>9</sup> Whether the optically active cation formed in the deamination of the *exo*-amine originally possesses a shorter C<sub>2</sub>–C<sub>6</sub> distance than the undistorted classical ion, with a commensurate increase in C<sub>2</sub>–C<sub>6</sub> delocalization, cannot be decided at present. However, for the time being we prefer to consider that this intermediate

holds approximately to the geometry of the classical ion, essentially for the reasons given below and summarized in a general way in the recent excellent discussion of Martin and Bentrude.<sup>10</sup> In the highly exothermic,<sup>11</sup> direct loss of nitrogen from the norbornyl diazonium ion only a small activation energy is required (perhaps on the order of 5 kcal./mole) and only one mode of vibration is involved (C–N stretching). In the alternative C–C participation process simultaneous excitation of C–C bending modes and the C–N stretching mode is demanded, so that this route is disfavored on probability, *i.e.*, entropy, grounds to a degree which could well be critical in a system with low energy barriers.<sup>12</sup>

This view which leads to the conclusion that the retention of optical activity in deamination of *exo* norbornylamine is due to the formation of the classical norbornyl cation, also suggests the possibility that the classical cation may be a common intermediate for both rearranged and unrearranged products. If this were the case for the *exo*-amine it should also hold for the *endo* isomer and, in fact, the product analysis from *endo* and *exo* isomers should be about the same. In view of the reported 23% excess retention of optical activity in the deamination of optically active *endo*-norbornylamine, we have carried out an independent product analysis for the *endo* case using a different but essentially equivalent technique. This involved the deamination of *endo*-2-norbornylamine-2*d*<sub>1</sub> in acetic acid under the standard conditions. The acetates produced were converted to norborneol (LiAlH<sub>4</sub>) which was subsequently oxidized to norcamphor (RuO<sub>4</sub>–Freon). Deuterium analyses were performed by mass spectral measurements. Starting from amine containing 1.00 deuterium per molecule the norborneol and norcamphor which were obtained contained 1.00 and 0.42 atom deuterium per molecule, respectively.<sup>13</sup> The absence of 1,2-hydrogen shifting in the deamination was shown by



the fact that the deuterated norcamphor did not lose deuterium when treated with excess sodium methoxide-methanol under equilibrating conditions.<sup>14</sup> These results correspond (for the *exo* product<sup>8</sup>) to 16% excess retention of optical activity in the stereochemical experiment and as such are in close agreement with our results from *exo*-norbornylamine if both *exo*- and *endo*-amines are assumed to be converted essentially completely to a classical cation which serves as a common intermediate for both rearranged and unrearranged products.<sup>15</sup> This comparison of deuterium labeling

(10) J. C. Martin and W. G. Bentrude, *J. Org. Chem.*, **24**, 1902 (1959).

(11) A rough value  $\Delta H = -3.6$  ev. (gas phase) can be estimated for the reaction  $RN_2^+ \rightarrow R^+ + N_2$  from (1) the first ionization potential of N<sub>2</sub> (15.6 ev.) [F. H. Field and T. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 62], (2) the ionization potential for a *sec*-alkyl radical (8 ev.) [J. J. Kaufman and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3262 (1960)], and (3) the homolytic dissociation energy for C–N<sub>2</sub><sup>+</sup> (estimated at *ca.* 4 ev. from the known value of 4.5 ev. for *d* CH<sub>3</sub>–CN). Assuming that the difference in solvation energies of R<sup>+</sup> and RN<sub>2</sub><sup>+</sup> is not large, it follows that diazonium ion decomposition is also highly exothermic in solution.

(12) See (a) D. J. Cram and J. E. McCarthy, *J. Am. Chem. Soc.*, **79**, 2866 (1957); (b) B. M. Benjamin, H. S. Schaeffer and D. J. Collins, *ibid.*, **79**, 6160 (1957); and (c) D. Y. Curtin and M. Wilhelm, *Helv. Chim. Acta*, **40**, 2129 (1957).

(13) The norborneol consisted of  $95 \pm 1\%$  *exo* and  $5 \pm 1\%$  *endo* isomer as determined by vapor phase chromatography.

(14) The possibility of 1,2-shifting of hydrogen does not appear to have been tested previously by direct experiment.

(15) A significant involvement of cation-acetate pairs seems likely on the basis of related deamination studies using acetic acid solvent; E. H. White

(5) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4094 (1959).

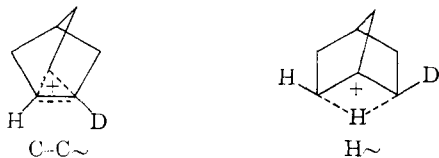
(6) For example, the temperatures used for solvolysis and deamination experiments were 75° and *ca.* 20°, respectively.

(7) The decomposition of diazonium acetate ion pairs to produce (classical) carbonium-acetate ion pairs is a possibility which seems eminently suited to accommodate the experimental data.

(8) Since *exo*- and *endo*-acetates of a given configuration have the same sign and about the same magnitude of optical rotation, the figure given for % retention of optical purity refers to the *exo* isomer. It is quite possible that the retention of optical purity in the *endo* product is very much higher. This interesting point has not been checked chiefly because of obvious experimental difficulties of obtaining pure *endo*-acetate in sufficient quantity for rotation measurements.

(9) Predominance of *exo* attack on the classical cation is expected because of interference to *endo* attack by the *endo*-hydrogen at C<sub>6</sub>. For a summary of related instances, see E. J. Corey, P. A. Vatakencherry and R. Hartmann, *J. Am. Chem. Soc.*, **84**, 2611 (1962).

and optical activity experiments is valid providing it can be assumed that those reaction pathways which lead to rearrangement also lead to inversion. The assumption seems completely justifiable since the two likely rearrangement processes fulfill this condition, *viz.*, rearrangement *via* the structures.



At this point mention should be made of the results of Roberts, *et al.*, which suggest that *ca.* 6% of 1,3-hydrogen rearrangement occurs in the deamination of an *exo-endo*-norbornylamine mixture (70:30) in water.<sup>16</sup> It is entirely possible that a small amount of such rearrangement might have occurred under the conditions of our experiment; we estimate that such a process could amount to *ca.* 5% of total reaction (at most) on the basis of n.m.r. spectrum of the partly deuteriated norcamphor from *endo*-2-norbornylamine-2*d*<sub>1</sub> in which the bridgehead protons (7.43 and 7.62  $\tau$ ) are downfield from the remaining protons in the molecule and almost completely separated (see Experimental section). The ratio of these peaks is 1.0:1.0 in norcamphor and 1.0:0.6  $\pm$  0.05 in the deuteriated norcamphor (total 0.42 deuterium per molecule). Obviously the occurrence of minor amounts of 1,3-hydrogen shifting can be interpreted in terms of a classical carbonium intermediate since the geometry of the norbornyl system itself favors such a rearrangement.

It also remains to consider the possibility that the norbornyl cation produced by deamination or the nearest molecules of solvent might be excessively energetic because of the exothermicity of diazonium decomposition. The possibility that part of the energy of reaction may initially be released as excess vibrational energy of the carbonium ion,<sup>17</sup> coupled with the complication that the times required for a vibration leading to rearrangement and collision with solvent are roughly comparable (*ca.*  $10^{-13}$  sec.), makes it extremely difficult to anticipate the chemical consequences of highly exothermic decomposition in solution. Nonetheless, it seems most likely that the dominant effect of exothermic carbonium ion formation would be a higher than normal incidence of internal rearrangement and it is difficult to see how such a factor *per se* would be responsible for excess retention of optical activity in the norbornyl systems.<sup>18</sup>

The above-mentioned experiments on deamination were prompted partially by a related study which seemed to indicate a discrete existence for the classical or "unsymmetrical" norbornyl cation, the reaction of the isomeric norbornane-2-carboxylic acids with lead tetraacetate. In contrast to the anodic oxidation of

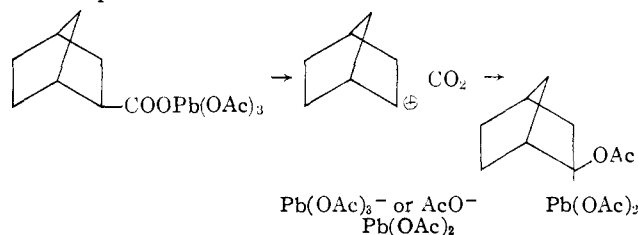
and C. A. Aufdermarsh, *J. Am. Chem. Soc.*, **80**, 2597 (1958); **83**, 1179 (1961). The incidence of ion pairs provides a reasonable explanation (a) for the greater net retention of optical activity in *exo*- or *endo*-amine deamination as compared with *endo*-arenesulfonate solvolysis (*cf.* ref. 7), and (b) for the formation of slightly more *endo*-acetate from *endo*-amine than from *exo*-amine.

(16) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954). These workers prefer to discuss such hydrogen rearrangement in terms of an *ad hoc* non-classical "nortricyclonium" ion.

(17) *Cf.* J. D. Polanyi, *J. Chem. Phys.*, **31**, 1338 (1959), and D. R. Herschbach, G. H. Kwei and J. A. Norris, *ibid.*, **34**, 1842 (1961).

(18) Preliminary experiments by Mr. Richard Atkinson in these laboratories using analytical gas chromatography indicate that no significant amount of *n*-propyl alcohol is formed in the deamination of pure isopropylamine, a possible indication of the unimportance of a vibrationally excited cation. The recent demonstration of "over-all" 1,3-hydride rearrangement in the deamination of *n*-propylamine may however be a consequence of exothermic diazonium ion decomposition (O. A. Reutov and T. N. Shatkins, *Tetrahedron*, **18**, 237 (1962)).

these optically active acids in methanol at high voltages which affords completely racemic *exo*-norbornyl methyl ether *via* a racemized or symmetric cation,<sup>19</sup> it has been found that the optically active *exo*- and *endo*-acids with lead tetraacetate in benzene yield norbornyl acetate (95% *exo* and small amounts of *endo*) with 43% excess retention of optical activity in each case.<sup>20</sup> In acetonitrile as solvent these optically active acids each give *exo*-norbornyl acetate with 34% retention of optical activity. Although the mechanism of oxidative decarboxylation with lead(IV) salts is not known in detail and although the identity of optical result for *exo*- and *endo*-norbornane-2-carboxylic acids in two different solvent systems might be coincidental, the mechanism shown below would seem best suited to accommodate all the facts including the obtention of characteristic carbonium ion rearrangements in other systems.<sup>21-24</sup> It is possible that the norbornyl radical precedes the cation, since the rates of oxidation of *exo*- and *endo*-acids are approximately the same. However, there is ample evidence<sup>25</sup> that the norbornyl radical is not prone to rearrangement at the reaction temperature of oxidation decarboxylation (*ca.* 80°) so that the carbonium ion is required as an intermediate; the assumption that the carbonium ion is a common intermediate for both rearranged and non-rearranged acetate is based on the correspondence of products from *exo*- and *endo*-acids and the rather small change in the fraction of rearrangement in going from benzene to the much more polar acetonitrile as solvent. It should also be noted that the yield and composition of product are not changed in the presence of oxygen at saturation.<sup>19</sup> The high net retention of optical activity as compared with solvolysis and amine deamination may be due to the dominant formation of classical carbonium-acetate ion pairs in non-polar media which favor rapid ion collapse.



In view of the evidence that there is a significant energy barrier between the classical norbornyl cation and the symmetrical bridged ion and the formal possibility that the solvolysis of *exo*-norbornyl bromobenzenesulfonate might involve a pair of unsymmetrical bridged ions which are interconverted at a rapid rate relative to reaction with solvent acetic acid, we have carried out a test for an unsymmetrical intermediate in *exo*-sulfonate solvolysis. In this experiment the arenesulfonate was *m*-carboxybenzenesulfonate in which there is located a nucleophilic group (COO<sup>-</sup> in basic medium) which can interact with the carbonium center *after*, but not *before*, ionization. The *m*-carboxybenzenesulfonate-carbonium ion pair can be expected to have an extremely fleeting existence (especially in media

(19) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(20) E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963).

(21) G. Büchi and J. Marvel (personal communication) have ascertained that cyclobutanecarboxylic acid affords cyclobutyl, cyclopropylcarbonyl and allylcarbonyl acetates corresponding approximately to the mixtures encountered previously in the "bicyclobutonium" cation system; *cf.* R. H. Mazur, *et al.*, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

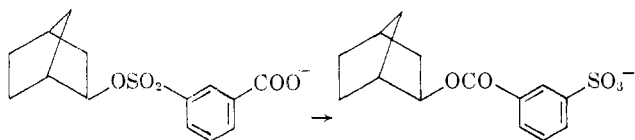
(22) W. A. Mosher and C. L. Kehr, *ibid.*, **75**, 3172 (1953).

(23) L. L. McCoy and A. Zagalo, *J. Org. Chem.*, **25**, 824 (1960).

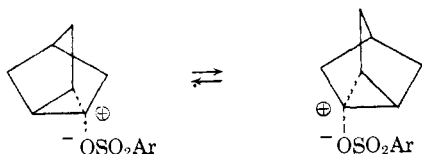
(24) Z. Valenta, *et al.*, *Tetrahedron Letters*, **20**, 25 (1960).

(25) J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960).

of low polarity) since it can recombine with only slight molecular movement to give carboxylate ester; this expectation is reinforced by the results of the oxidative decarboxylation reactions with lead tetraacetate. Thus, if starting from optically active *exo*-norbornyl



ester an unsymmetrical norbornyl cation-carboxylate ion pair were formed, the product resulting from ionization might be the ester of optically active *exo*-norborneol. In practice the experiment was conducted by treating the *p*-nitrophenyl ester of the *m*-carboxybenzenesulfonate with two equivalents of alkali (which saponifies the *p*-nitrophenyl ester essentially instantaneously) and then conducting the ionization reaction in *t*-butyl alcohol or in tetrahydrofuran-water with slow addition of a third equivalent of alkali to maintain a slightly basic reaction solution. After the end of alkali addition no sulfonate ester remained and no *exo*-norborneol could be detected by vapor phase chromatography indicating the formation of carboxylate ester. The ester was saponified with alkali and the liberated *exo*-norborneol was then isolated and characterized. In both *t*-butyl alcohol and in aqueous tetrahydrofuran the *exo*-norborneol obtained was optically inactive within experimental error ( $\pm 0.01^\circ$  in  $[\alpha]_D$ ) in runs starting with optically active *exo*-norborneol of  $[\alpha]^{25}_D -0.305^\circ$  and  $-1.87^\circ$ , respectively. Thus, it would seem that if the solvolysis of *exo*-norbornyl arenesulfonate does not produce the symmetrical ion, but a pair of interconverting unsymmetrical bridged ions, the interconversion rate is so rapid that for chemical purposes the ion may be taken as symmetrical.<sup>28</sup> In connection with this finding and the results reported above for amine deamination, there arises a question of whether the presence of certain neighboring anions (*e.g.*, sulfonate or halide) may facilitate carbonium-ion interconversion or rearrangement. Such an effect might be visualized for the norbornyl system as



Further research on this point is required.

#### Experimental<sup>27,28</sup>

(-)-*exo*-Norbornane-2-carboxylic Acid.—(-)-*endo*-Norbornane-2-carboxylic acid (15.42 g., 0.108 mole), prepared by the method of Berson and Ben-Efraim,<sup>5</sup>  $[\alpha]^{25}_D -14.43 \pm 0.25^\circ$  ( $c$  4.61, 95% ethanol, 1 dm.) calculated optical purity of 47.0  $\pm$  0.9%, and phosphorus tribromide (100 g., 0.37 mole) were mixed and heated in an oil-bath at 160–170° with stirring for 6.5 hours. The red-orange reaction mixture was poured slowly onto *ca.* 500 g. of crushed ice while mixing. After 10 minutes this hydrolysate was extracted with four 50-ml. portions of ether, and the ether was washed with several portions of saturated salt solution. After drying over anhydrous sodium sulfate the ether was removed by distillation and the resulting colorless oil was distilled at 110–114° at 0.7 mm. The distillate crystallized in the receiver and amounted to 11.95 g. (77.5%). The infrared spectrum of this material in carbon disulfide was identical with ( $\pm$ )-*exo*-norbornane-2-carboxylic acid<sup>6</sup> and did not show contamination by the *endo* isomer. The optical rotation of this

(26) This type of experiment is clearly of interest for the *endo*-norbornyl arenesulfonate system as well as in other cases where a non-bridged cation may be formed prior to rearrangement. Further studies along these lines are in progress.

(27) Instruments used were: n.m.r. Varian A-60; infrared, Perkin-Elmer Infracord; V.P.C., F and M model 300.

(28) Microanalytical data from C. Daesslé, Montreal, Can.

substance,  $[\alpha]^{25}_D -12.63 \pm 0.20^\circ$  ( $c$  5.53, 95% ethanol, 1 dm.) leads to a calculated value of 45.3  $\pm$  0.7% optical purity for the sample.<sup>29</sup>

(-)-*exo*-Norbornylamine Hydrochloride.—(-)-*exo*-Norbornane-2-carboxylic acid obtained in the previous experiment (11.92 g., 84.0 mmoles) in 50 ml. of chloroform was stirred at ice temperature and treated with 135 ml. of a dried solution contained 163 mmoles of hydrazoic acid in chloroform. To this solution was added 35 ml. (0.63 mole) of concentrated sulfuric acid over a 40-minute period. The cooling bath was removed and the vigorously stirred mixture was warmed carefully. Nitrogen evolution became vigorous above room temperature and subsided after several minutes. The mixture was refluxed for 2 hours then cooled and poured onto 200 g. of crushed ice. The chloroform layer was separated and the aqueous part was made strongly basic with cold concentrated sodium hydroxide (cooling, stirring) and extracted with two 75-ml. portions of ether. The combined ether extracts were dried over solid potassium carbonate and then treated with anhydrous hydrogen chloride. The filtered solid was washed with a small portion of ether and dried in vacuum. There was obtained 7.42 g. (64%) of white solid, m.p. 316–320° (dec.),  $[\alpha]^{25}_D -8.24 \pm 0.18^\circ$  ( $c$  5.04, CHCl<sub>3</sub>, 1 dm.) whose infrared spectrum (CHCl<sub>3</sub>) was entirely consistent with that of an amine hydrochloride.

The mother liquors from hydrochloride precipitation yielded an additional 1.83 g. upon being reprocessed;  $[\alpha]^{25}_D -7.64 \pm 0.49^\circ$  ( $c$  4.69, CHCl<sub>3</sub>, 1 dm.).

Deamination of (-)-*exo*-Norbornylamine Hydrochloride.—A solution of (-)-*exo*-norbornylamine hydrochloride (6.43 g., 47 mmoles) in 50 ml. of glacial acetic acid was stirred and maintained at 17  $\pm$  1° while solid sodium nitrite (6.43 g., 93.1 mmoles) was added in numerous small portions over 90 minutes. The mixture was stirred for an additional hour at this temperature, than overnight at room temperature. An additional 1.58 g. (22 mmoles) of sodium nitrite was added in small portions and stirring was continued for 1 hour more. The reaction mixture was poured onto 150 g. of crushed ice, and treated with 1 mole of sodium hydroxide in 150 ml. of water (stirring, cooling). The oil which separated was extracted into three  $\times$  75-ml. portions of ether, and the ether extracts, washed successively with saturated salt solution, 2 *N* hydrochloric acid, and saturated salt solution. The ether solution was dried over anhydrous magnesium sulfate and concentrated to *ca.* 50 ml. by slow distillation through a 4-foot Vigreux column. A small sample removed at this time was concentrated to remove the remainder of the ether and was analyzed by infrared and gas chromatography (4 ft. Carbowax 20 M, 50 ml. He/min.), and *exo*-norbornyl acetate was identified by comparison with an authentic sample as the major constituent (85.5%). The infrared spectrum differed from *exo*-norbornyl acetate by a strong 6.15  $\mu$  absorption, assigned to the nitrate.<sup>5</sup> The gas chromatogram showed three contaminants: (1) 1.5%, ret. time 1 min. 45 sec.; (2) 4%, ret. time 8 min. 15 sec.; (3) 9%, ret. time 11 min. 25 sec. The first and third of these impurities agreed well in retention time with those of norbornylene or nortricycylene and *exo*-norborneol, respectively.

The bulk of the reaction mixture above was shaken with 0.2 g. of platinum oxide catalyst at 60 p.s.i. in a Parr apparatus for 3 hours. Removal of the catalyst and concentration through a 4' Vigreux column left a colorless oil which exhibited an infrared spectrum identical with *exo*-norbornyl acetate and a gas chromatogram which was consistent with the conversion of norbornylene to norbornane and norbornyl nitrate to norborneol.

A mixture of hydrogenated product, 2.0 g. of acetic anhydride and 5.0 g. of acetic acid was refluxed gently for 3 hours, then distilled very slowly through a Holtzmann column. The fraction boiling at 131.5–132.0° (147 mm.) (1.97 g.) was collected. The infrared spectrum was identical with that of *exo*-norbornyl acetate and the gas chromatogram (4 ft. dinonyl phthalate, 140°) showed a single peak at a retention time of 19 min. 5 sec. The optical rotation of this sample was  $\alpha^{25}_D -0.892 \pm 0.011^\circ$  (neat, 1 dm.), leading to a calculated<sup>30</sup> optical purity of 7.07  $\pm$  0.29% and a net retention of optical purity in the reaction of 15%. Treatment with lithium aluminum hydride and analysis of the norborneols so produced by V.P.C. on a 20% Ucon 50 HB 280 x on Celite 545 column<sup>31</sup> at 160° showed a composition of 96  $\pm$  1% *exo*- and 4  $\pm$  1% *endo*-norborneol.

N-Acetyl-*endo*-norbornylamine-2-*d*.—Norcamphor oxime (17.12 g.) was reduced with 6.0 g. of lithium aluminum deuteride (99.8% isotopically pure) in 370 ml. of ether at reflux for 48 hours. After decomposition of the reaction mixture with water and treatment of the ether phase and extracts with dry hydrogen chloride 10 g. of crude amine hydrochloride was obtained. The amine was then acetylated in concentrated aqueous solution containing excess alkali at 0° with acetic anhydride and the N-acetyl deriva-

(29) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959).

(30) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

(31) C. H. Deput and P. R. Storey, *Tet. Letters*, **6**, 20 (1959).

tive was isolated by extraction and purified by chromatography on neutral alumina followed by sublimation to give 2.1 g. of pure *N*-acetyl-*endo*-norbornylamine-2-*d*, m.p. 127–128° (lit.<sup>18</sup> 124°), infrared absorption (in CCl<sub>4</sub>) at 2.95, 6.05, 6.5 and 7.3 $\mu$ ,<sup>22</sup> deuterium content 1.00 atom per molecule (analysis performed by J. Nemeth, Urbana, Ill.).

***endo*-Norbornylamine-2-*d* Hydrochloride.**—The above acetyl derivative (2.0 g.) was hydrolyzed at reflux for 40 hours with 30 ml. of 6 *N* hydrochloric acid. Evaporation under reduced pressure and crystallization of the residue from ether-cyclohexane gave 1.75 g. of the hydrochloride as colorless silky needles, m.p. 295° dec.

**Deamination of *endo*-Norbornylamine-2-*d* in Acetic Acid.**—The conditions of Berson and Ben-Efraim<sup>5</sup> were adhered to exactly using 1.70 g. of the amine hydrochloride, 8.95 ml. of glacial acetic acid, 0.945 g. of sodium acetate and 1.28 g. and 0.32-g. portions of sodium nitrite. Distillation of the crude product gave 947 mg. of acetate, b.p. 170° (bath) at 155 mm. This was converted to norborneol with lithium aluminum hydride-ether; isolation of the product by extraction with ether concentration and sublimation at 130° (155 mm.) gave 567 mg. of norborneol, m.p. 119–121°, which by V.P.C. analysis on a 4-meter tricyanoethoxypropane column (15% on firebrick) at 140° was shown to consist of 95  $\pm$  1% *exo* and 5  $\pm$  1% *endo*-norborneol. Deuterium analysis (performed by Mr. J. Nemeth) showed the presence of 1.00 atom deuterium per molecule.

**Oxidation of Norborneol-*d* to Norcamphor-*d* with Ruthenium Tetroxide.**—To a solution of 37 mg. of the above deuterated norborneol in 2 ml. of Freon 11 (trichlorofluoromethane) at 0° was added a slight excess (over one equivalent) of a bromine-free solution of ruthenium tetroxide<sup>33</sup>—Freon 11. After a few minutes a few drops of ether was added to destroy the excess oxidizing agent and the mixture was kept for 5 minutes, then filtered and concentrated and sublimed to give 23 mg. of norcamphor, m.p. 88–89°; infrared absorption (CCl<sub>4</sub>) at 5.7, 6.9 and 7.1 $\mu$ . Deuterium analysis of this and several check runs by mass spectrometer<sup>34</sup> showed the presence of 0.42  $\pm$  0.003 deuterium atom per molecule.

Treatment of the deuterated norcamphor (20 mg.) with 3 ml. of methanol and 2 ml. of *N* sodium hydroxide at reflux under nitrogen for 6 hours and reisolation gave norcamphor (m.p. 88–89°) of essentially the original deuterium content (0.414  $\pm$  0.003 deuterium per molecule), eliminating the possibility that 3-deuterated 2-norbornyl acetate had been produced in significant amount in the deamination.

The n.m.r. spectrum of the deuterated norcamphor differed from that of unlabeled norcamphor in that the relative intensities of the two peaks downfield (at 7.43 and 7.62 $\tau$ ) were 1.0 to 0.6  $\pm$  0.05 in the former and 1.0 to 1.0 in the latter, the measurements being made in CCl<sub>4</sub> or CS<sub>2</sub> using a Varian A-60 spectrometer with electronic integration of signal. These two peaks can be assigned to the bridgehead positions since deuteration of the  $\alpha$ -methylene group in norcamphor leaves their intensities unchanged and diminishes the upfield peaks.

***p*-Nitrophenyl-(*m*-chlorosulfonyl) Benzoate.**—*p*-Nitrophenol (5.56 g., 40 mmoles) was added all at once to a solution of 9.56

g. (40 mmoles) of *m*-chlorosulfonylbenzoyl chloride<sup>35</sup> and pyridine (3.20 ml., 40 mmoles) in 110 ml. of dry benzene stirred vigorously at ca. 5°. After 10 minutes the mixture was stirred at 40–50° for 0.5 hour, filtered, and the solid washed with ca. 20 ml. of benzene. Combined filtrate and washing were evaporated to 50 ml. in vacuum, heated slightly to redissolve the solid, and cooled at about 5° for 0.5 hour. The white crystalline solid which separated was removed by filtration and dried in vacuum. A 64% yield (8.83 g.) was obtained, m.p. 128.5–132°. Two additional crystallizations from benzene (avoid excess heating) gave a sample for analysis, m.p. 135–136°.

**Anal.** Calcd. for C<sub>13</sub>H<sub>9</sub>O<sub>5</sub> NSCl: C, 45.69; H, 2.36; Cl, 10.38. Found: C, 45.76; H, 2.19; Cl, 10.33.

***exo*-Norbornyl-(*m*-carbo-(*p*-nitrophenoxy)) Benzenesulfonate.**—A mixture of 0.4487 g. (4.0 mmoles) of *exo*-norborneol and 1.0251 g. (3.0 mmoles) of *p*-nitrophenyl-(*m*-chlorosulfonyl) benzoate at 5–10° was stirred and treated with 2.0 ml. (30 mmoles) of dry pyridine. The mixture was stirred at 15–20° for 2.5 hours, then filtered. The precipitate was washed with a small portion of benzene, and the combined filtrate and washing were evaporated at reduced pressure without heat. The residual oil was treated with about 5 ml. of toluene, filtered and the precipitate was washed with a small amount of toluene. The solution was then evaporated in vacuum. This process was repeated three times. The residual oil was triturated with pentane, dried at 1 mm. pressure and then used immediately in the solvolysis reaction; it is designated as XI below.

**Solvolysis of Sulfonate XI in Tetrahydrofuran-Water.**—A solution of 1.459 g. of oil XI (2.85 mmoles) in 59.64 ml. of 0.09885 *N* sodium hydroxide (5.70 mmoles) and 40 ml. of tetrahydrofuran was heated at 60°. A third mole (29.82 ml.) of sodium hydroxide was added over the next 7 minutes to maintain neutrality. After 1 hour the solution was cooled, made strongly basic with sodium hydroxide, and extracted with 2  $\times$  30 ml. of pentane. The pentane was washed with 4  $\times$  15 ml. of water, dried over sodium sulfate, and evaporated through a 4-foot Vigreux column. The residue crystallized on brief evacuation, and was essentially pure *exo*-norborneol (87 mg.) by V.P.C. on 2-ft. silicone gum rubber and TCEP.

Another reaction employing essentially identical conditions but starting with (–)-*exo*-norborneol ( $[\alpha]^{25D} - 1.87 \pm 0.14^\circ$ ) gave pure *exo*-norborneol ( $[\alpha]^{25D} - 0.007 \pm 0.014^\circ$ ). This material showed a single peak when subjected to V.P.C. on a silicone rubber column.

**Solvolysis of Sulfonate XI in *t*-Butanol.**—A solution of 3.648 g. (8.75 mmoles) of oily XI in ca. 50 ml. of *t*-butyl alcohol (distilled from calcium hydride) was treated with 0.579 *N* benzyltrimethylammonium hydroxide (29.38 ml.) in *t*-butyl alcohol. The volume was made up to 100 ml., and the solution was thermostated at 75°. One-fourth of an additional equivalent of base was added over 2 hours. After about 12 hours the *t*-butyl alcohol was removed by slow distillation through a 4-foot Vigreux column. A V.P.C. analysis of the distillate showed no norborneol but substantial norbornene. The residue was refluxed for 6 hours with 20 ml. of 6 *N* potassium hydroxide, and the hydrolysate was extracted with 3  $\times$  30 ml. of pentane. Washing of the pentane with 3  $\times$  4 ml. of water, concentration through a 4-foot Vigreux column and distillation of the residual oil (2.35 g.) through a Craig micro-still gave a fraction, b.p. 150–180°, which was purified further by V.P.C. *exo*-Norborneol obtained by collection from V.P.C. showed a rotation  $[\alpha]^{25D} - 0.08 \pm 0.08^\circ$ , starting with *exo*-norborneol of rotation  $[\alpha]^{25D} - 0.305^\circ$ .

(35) H. Limpricht and L. V. Uslar, *Ann.*, **102**, 250 (1857).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

## The Synthesis of *o*-Di-*t*-butylbenzene by Classical Reaction Methods<sup>1</sup>

BY ALBERT W. BURGSTAHLER<sup>2</sup> AND M. O. ABDEL-RAHMAN

RECEIVED AUGUST 10, 1962

The synthesis of *o*-di-*t*-butylbenzene (I), *o*-*t*-amylcumene (Vd) and a number of related compounds by stepwise reactions from 1,1,4,4-tetramethyl-2-tetralone (III) is described.

In the course of their extensive studies on the nature and effects of steric strains in organic molecules, Brown

(1) Portions of this work are taken from the M.S. thesis of M. O. Abdel-Rahman, The University of Kansas, June, 1961, and were also presented by one of us at the Twelfth Annual Kansas City Chemistry Conference, Nov. 18, 1960, and at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(2) Alfred P. Sloan Research Fellow, 1961–1963.

and co-workers<sup>3</sup> drew attention to the difficulty of synthesizing the highly strained hydrocarbon *o*-di-*t*-butylbenzene (I) and its homomorphs. From their findings, they concluded that the strain energy associated with I is of the order of 25 kcal./mole, and on this basis pre-

(3) (a) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 24 (1953); (b) H. C. Brown, D. Gintis and L. Domash, *ibid.*, **78**, 5387 (1956).