acetic anhydride in acetic acid gave *exo*-norbornyl acetate, $n^{25}D$ 1.4565, infrared spectrum identical with that reported.[15]

Partial resolution of the acid phthalate was effected, according to the reported[15] procedure, by recrystallization of the cinchonidine salt from acetone. The salt (40% of the starting salt) obtained after two recrystallizations was converted to the free acid, fractional crystallization of which from dilute acetic acid and from ethyl acetate–pentane finally afforded material of m.p. 73–76°, $[\alpha]^{25}D$ +4.96° (*c* 9.94 in chloroform, *l* 2). The infrared spectrum (in chloroform) was identical with that of the racemate.

Preparation of *exo*-Norbornyl Acid Phthalate Carbonyl-^{14}C.—Phthalic anhydride-*carbonyl*-^{14}C was prepared by a procedure similar to that of Stevens and Holland.[23] Carbon dioxide-^{14}C was collected in liquid nitrogen traps on a vacuum line after having been generated by the action of concentrated sulfuric acid on barium carbonate-^{14}C. The gas was used to carbonate *o*-tolylmagnesium bromide at −20°, affording toluic acid-*carboxyl*-^{14}C, m.p. 101–103°, in 91% yield. Oxidation of this acid with aqueous potassium permanganate gave phthalic acid-*carboxyl*-^{14}C, m.p. 200° dec. in 90% yield. With thionyl chloride, phthalic anhydride-*carbonyl*-^{14}C, m.p. 130–131°, was obtained in 89% yield. It was diluted 47-fold with inactive phthalic anhydride and the whole recrystallized from chloroform to give material of m.p. 131°.

The radioactive acid phthalate was prepared from the above anhydride and pure *exo*-norborneol in pyridine, according to the procedure of Winstein and Trifan,[15] recrystallized from 50% acetic acid, and dried *in vacuo* over potassium hydroxide pellets to give material of m.p. 98.5–100°, infrared spectrum identical with that of an authentic sample. The apparent activity of an "infinitely thick" sample, determined by the method previously described,[40] was 2985 ± 11 c./min., and the m.p. and activity were unchanged by recrystallization. Independent mountings of this material gave apparent activities that agreed to within the reproducibility of counting a single mounting (less than 0.5% average deviation). Coincidence loss was negligible at this level of activity with the equipment used.[40] Reproducibility of the "*Q*"-gas flow rate was simplified by interposing an oil manometer flow-meter between the storage tank and the detector.

Isotope Dilution Analysis of (+)-*exo*-Norbornyl Acid Phthalate.—A mixture of 1.611 g. of optically active acid phthalate, $[\alpha]D$ +4.96°, and 2.0030 g. of radioactive acid phthalate was recrystallized twice from ethyl acetate–pentane to give 2.10 g. of racemic acid phthalate, m.p. 99–100.5°, $\alpha^{27}D$ −0.003 ± 0.007° (*c* 9.99 in chloroform, *l* 2), apparent radioactivity 1739 ± 7 cc./min. Recrystallization from ethyl acetate–pentane gave 0.70 g. of material of m.p. 99–100°, apparent radioactivity 1734 ± 6 c./min. The enantiomer content (49.4%) in the starting optically active phthalate was calculated from equation 3 of reference 20. The statistical error was calculated as in reference 20, using 0.5% as the error in an observed activity corrected for background. The sample to background activity ratios and counting times were such as to conform to this error, and reproducibilities of mountings and of activities of a given mounting were always better than 0.5%. The uncertainty in the absolute value of the % enantiomer was 2.7%, *i.e.*, the starting phthalate was 46.7–49.4% optically pure. This gives the values 10.0–10.6° for $[\alpha]D$ of optically pure phthalate. Since phthalate of $[\alpha]D$ 8.45° is of the same optical purity as acetate of αD 10.39° (neat, 1 dcm.),[15] optically pure acetate has αD 12.26–13.03° (neat, 1 dcm.).

Acknowledgment.—We are indebted to Professor S. Winstein for permission to quote data in advance of publication, and to the Air Force Office of Scientific Research and the Alfred P. Sloan Foundation for financial support.

LOS ANGELES 7, CALIF.

---

[40] J. A. Berson and W. M. Jones, THIS JOURNAL, **78**, 6045 (1956); J. A. Berson, R. D. Reynolds and W. M. Jones, *ibid.*, **78**, 6049 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

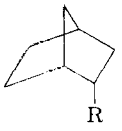
The Reaction of (+)-*endo*-Norbornylamine with Nitrous Acid[1]

BY JEROME A. BERSON AND DAVID A. BEN-EFRAIM

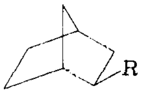
RECEIVED DECEMBER 20, 1958

(−)-*endo*-Norbornanecarboxylic acid, 34–35% optically pure, reacts with hydrazoic acid to give (+)-*endo*-norbornylamine of the same optical purity. In acetic acid, the (+)-amine reacts with sodium nitrite to give *exo*-norbornyl acetate with 23–24% retention of optical purity. The enantiomeric configurations of the amine and product acetate are related on the basis of the stereochemical result and known data on isotope-position rearrangement in this reaction. The optical result is virtually identical with the % retention of skeletal integrity observed in the nitrous acid deamination of *endo*-2-amino-5-norbornene-3-^{14}C. The results suggest that the excess unrearranged portion of the product acetate is derived by direct displacement of solvent on the diazonium ion.

As an adjunct to stereochemical studies in the norbornane series,[2,3] we have prepared optically active *endo*-norbornylamine (Ib) and have examined its reaction with nitrous acid in acetic acid. In addition to its anticipated practical value in providing circumstantial confirmation of the configurational relationship between *exo*-norbornanecarboxylic acid (IIa) and *exo*-norbornyl acetate (IIc), the reaction was of some theoretical interest.



Ia, R = CO_2H; c, R = OBs
b, R = NH_2; d, R = OAc



IIa, R = CO_2H; d, R = OH
b, R = NH_2; e, R = $COCH_3$
c, R = OAc

Diazotization of racemic Ib in aqueous acetic acid[4,5] or in glacial acetic acid[6] occurs with qualitatively predominant inversion of configuration giving *exo*-norborneol and *exo*-norbornyl acetate, respectively. These results are similar to those observed in the acetolysis (and other solvolyses) of *endo*-norbornyl *p*-bromobenzenesulfonate Ic to *exo*-norbornyl derivatives.[7] That the product-determining mechanisms in the amine–nitrous acid

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1544. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] J. A. Berson and D. A. Ben-Efraim, THIS JOURNAL, **81**, 4083 (1959).

[3] J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

[4] G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

[5] K. Alder, G. Stein, E. Rolland and G. Schulze, *ibid.*, **514**, 211 (1934).

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

[7] S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

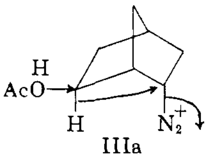
reaction are different (or if the same, at least occur in different proportions) from those in the arenesulfonate solvolyses is evident[6] from the greater extent of isotope-position rearrangement in the solvolysis of Ic-2,3-^{14}C than in the diazotization of Ib-3-^{14}C.

Results.—Racemic *endo*-norbornylamine (Ib) had been prepared by hydrogenation of norcamphoroxime,[8a] by reduction of *endo*-nitronorbornane with iron and acetic acid,[6,8b] and by Curtius degradation of *endo*-norbornanecarboxylic acid (Ia).[4,5] For our purposes, Ib was most conveniently prepared by the Schmidt degradation of Ia. The crystalline amine Ib obtained by this procedure was chemically pure as indicated by titration. High retention of epimeric purity in the Schmidt reaction was expected,[9] and presumptive evidence supporting this was provided by the observation that Ib formed a single acetyl derivative. (The m.p. of Ib itself is a poor criterion of purity; the substance is exceedingly sensitive to moist air, in which it rapidly forms a carbonate, and the m.p. is not reproducible.) For comparison, racemic *exo*-amine IIb was prepared by Hofmann rearrangement of *exo*-2-norbornanecarboxamide. Since this procedure might have led to partial epimerization,[10] the amine was converted to the crystalline, apparently homogeneous, acetyl derivative and regenerated by hydrolysis of the latter. The *exo*-amine IIb obtained in this way was a liquid whose infrared spectrum was unfortunately so similar to that of the *endo*-amine Ib that small amounts of cross-contamination could not be detected. In the optically active series, partially resolved materials were used, and consequently recrystallization of the acetyl derivative of the *endo*-amine could not be used for purification for fear of optical fractionation. Therefore, the epimeric homogeneity of optically active Ib in the sequel was assumed on the basis of the above results with racemic Ib, which was prepared in the same way.

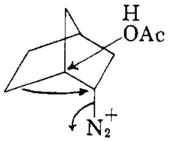
Reaction of (−)-*endo*-norbornanecarboxylic acid (Ia),[2] $[\alpha]_D -10.7°$ (34-35% optically pure[2]) with hydrazoic acid in chloroform gave (+)-amine Ib, $[\alpha]_D + 7.58°$. Since optical fractionation was avoided by purifying the amine by distillation, and since partial racemization or inversion of absolute configuration in the Schmidt reaction in the *endo* series were very unlikely,[12] the absolute configuration and optical purity of the (+)-Ib were identical with those of the starting (−)-Ia.

Under the conditions used by Roberts, Lee and Saunders,[6] (+)-Ib reacted with sodium nitrite in acetic acid to give 65% of a neutral product that consisted mostly of *exo*-norbornyl acetate (IIc) contaminated by 6% of a nitrogenous material which was identified by its infrared spectrum as norbornyl nitrate. (Olefin or nortricyclene, which could also have been formed, were not specifically sought.) Cleavage of the crude product with lithium aluminum hydride gave *exo*-norborneol, which after re-acetylation gave pure *exo*-norbornyl acetate, $\alpha_D -1.048°$ (neat, 1 dcm.), 8.2–8.5% optically pure.[3] Replacement of the diazonium group by acetoxy, therefore, occurred with 23–24% retention of optical purity and 76–77% racemization. That the portion of the reaction that produced optically active acetate was associated with essentially total inversion of epimeric configuration was established by the fact that the product acetate was racemized completely after 3.4 hours at 75° in acetic acid containing 0.759 *M* *p*-toluenesulfonic acid, conditions[7] under which *exo*-acetate IIc racemizes completely but *endo*-acetate Id is optically stable. Assuming that the optical rotations of the *endo*- and *exo*-acetates in acetic acid are about the same[7] (however, *vide infra*), the polarimetric experimental error was small enough to have detected about 7% contamination by *endo*-acetate. Thus, less than 2% of the total amine was converted to active *endo*-acetate.

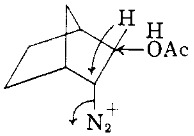
Discussion.—The simplest stereochemical interpretation of these results and those previously[2,3] reported is that (−)-*exo*-norbornanecarboxylic acid (IIa), (−)-*exo*-acetate IIc and (+)-*endo*-amine Ib all belong to the same optically active series, *i.e.*, (1) the Baeyer–Villiger rearrangement[3] of (−)-*exo*-acetylnorbornane (IIe), prepared from (−)-acid IIa, to (−)-acetate IIc, and (2) the diazotization of (+)-amine Ib to (−)-acetate IIc both occur without quasi-inversion[3] at C.4. Net inversion of absolute configuration in reaction 2 would require 23–24% of the product acetate to be formed by some such concerted process as IIIa, IIIb or IIIc. Reactions IIIa and IIIb are improbable on steric grounds and, further, do not fit the data[6] on isotope-position rearrangement. Thus the portion (76–77%) of the product acetate from *endo*-norbornylamine-3-C^{14} that corresponds to the racemic portion of the product acetate from the optically active amine must show at least 50% isotope-position rearrangement,[13a] since it is derived from the 2-fold symmetrical ion IV[7] and/or the 3-fold symmetrical ion V.[6,7,13b] Since reactions IIIa and IIIb both involve 100% isotope-position rearrange-



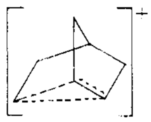
IIIa



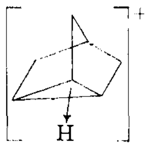
IIIb



IIIc



IV



V

---

[8] (a) K. Alder, G. Stein, S. Schneider, M. Liebmann, E. Rolland and G. Schulze, *Ann.*, **525**, 183 (1936), (b) K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).

[9] *Cf.* A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946).

[10] (+)-Hydratropamide is converted to (−)-α-phenylethylamine under Hofmann conditions with *ca.* 4% racemization.[9,11]

[11] C. L. Arcus and J. Kenyon, *J. Chem. Soc.*, 916 (1936).

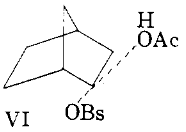
[12] In principle, racemization *is* conceivable in the *exo* series, but now[3] also unlikely.

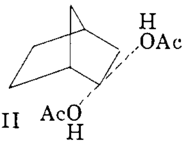
[13] (a) Defined[6] as 100 (activity of the cyclopentane-1,3-diamine)/(activity of the cyclopentane-1,3-dicarboxylic acid) in the degradation scheme.[6] (b) The calculations that follow are based only on the experimental fact[6] that isotope-position rearrangement accompanies racemization; the specific assumption of ions IV and V is not necessary for our purposes.

ment, the minimum amount of isotope-position rearrangement that could be observed is (0.5) (76) + (1)(24) or 62%. But *endo*-amine on diazotization in acetic acid gives only 41.6–44.9% rearrangement.[6] Neither IIIa nor IIIb, therefore, can account for the optical activity of the product acetate. Reaction IIIc cannot directly be eliminated as a possibility on such grounds. However, it seems unlikely. Thus, diazotization of ethylamine-1-^{14}C in aqueous solution produces[14a] ethanol containing only about 1.5% of ethanol-2-^{14}C. If a reaction analogous to IIIc could occur, it would be expected to be more significant in this case, since it would involve attack of water, a more nucleophilic solvent, upon a primary carbon, a sterically more favorable center. These arguments constitute an example of a configurational correlation of starting material and product by means of isotope-position labeling.[14b]

Mechanistically, it is conceivable that the retention of optical activity in the diazotization of Ib could arise from formation of 2-norbornanone without carbon-skeleton rearrangement. In fact, this ketone is observed[6] as a product in the aqueous fluoroboric acid diazotization of Ib. However, it did not seem to be formed in significant amounts in the acetic acid diazotization. The infrared spectrum was of no particular value in establishing the absence of 2-norbornanone in the crude acetate product, since the ketone carbonyl absorption (5.72 μ[15]) occurs very close to that of the acetate (5.74 μ). However, the purification procedure, involving hydride reduction and re-acetylation, would have been expected[16] to give a substantial amount of *endo*-acetate, which has been shown to be absent.

Acetolysis of *endo*-norbornyl *p*-bromobenzenesulfonate (Ic) is reported[7] to produce *exo*-acetate IIc with 7–8% retention of optical purity, under conditions (0.12-0.409 *M* potassium acetate) where the product acetate is optically stable and the amount of optical purity retained is independent of the acetate ion concentration. There is some quantitative uncertainty in this result because of experimental difficulties in the attempted complete resolutions[7] of *endo*- and *exo*-norbornyl acid phthalates. Thus, the *exo*-acid phthalate shows the conventional criteria of optical purity[7] when it is only 85% resolved.[3] Nevertheless, although an accurate value for the maximum rotation of *endo-p*-bromobenzenesulfonate Ic is not available, it is clear that the material considered[7] to be optically pure is at least at an advanced stage of resolution. In order for the result 7–8% retention to be in error by a factor of about 3, which would make the stereochemical result comparable to that obtained (23–24% retention of activity) in the *endo*-amine–nitrous acid reaction, the material originally thought to be optically pure would have to be not more than about 27% resolved. This is unlikely, and it seems safe to conclude that the replacement of the diazonium group proceeds with considerably higher retention of activity than does the solvolysis of the *p*-bromobenzenesulfonate. This result is out of line with the few available comparisons in the literature. Acetolysis of 1-butyl 1-*d*-*p*-nitrobenzenesulfonate occurs with 85% retention of optical activity (net inversion),[17] whereas the reaction of 1-aminobutane-1-*d* with nitrous acid in acetic acid gives 69% net inversion.[18] In the 2-butyl system, the amine–nitrous acid reaction in acetic acid gives 28% inversion,[19] but acetolyses[20] of 2-octyl or 2-butyl *p*-toluenesulfonates give about 80% inversion. Acetolysis of α-phenylethyl chloride proceeds with about 16% net inversion[21a] and diazotization of α-phenylethylamine in water (a reaction expected[18] to show minor sensitivity to solvent change) gives α-phenylethyl alcohol with 14.8% net inversion.[21b] The departure of the *endo*-norbornyl system from this pattern can be understood if it is assumed[7] that optically active acetate in the acetolysis of the *p*-bromobenzenesulfonate arises by collapse of either of the carbonium ion-type intermediates VI or VII. Survival of optical activity is low because conversions of VI or VII to products compete only poorly with the intervention of carbon bridging. This results in diversion of most of the VI and VII to the symmetrical ions IV and V and ultimately to racemic product.[7] In the acetolysis of the acyclic secondary derivatives, the unsymmetrically solvated species or ion-pair analogous to VI can collapse to inverted, optically active product. This process is apparently faster relative to conversion to a symmetrically solvated intermediate than are the conversions of VI or VII to products relative to conversion to IV and V.[7] The situation is analogous in some respects to that observed[22] in solvolyses of the diastereomeric 4-*t*-butylcyclohexyl-*p*-toluenesulfonates. The *equatorial* (*trans*)-isomer solvolyzes to give olefin and exclusively *axial* (*cis*)-acetate, but the *axial* (*cis*)-isomer gives olefin and a mixture of *trans*- and *cis*-acetates, with the amount of *cis*-acetate (retention) increasing along the solvent series 60% acetone <acetic acid <formic acid. This is probably attributable[22] to the intervention of a hydrogen-bridged intermediate when the solvolysis of the *cis*-*p*-toluenesulfonate has proceeded as far as the intimate ion-pair (analogous to VI). Hydrogen-bridging in this case would be mechanistically analogous to carbon-bridging in the case of VI.


VI


VII

---

[14] (a) J. D. Roberts and J. A. Yancey, THIS JOURNAL, **74**, 5943 (1952); (b) B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *ibid.*, **79**, 6160 (1957), have used isotope position labeling to demonstrate stereospecificity in diastereomer formation.

[15] C. J. Norton, Dissertation, Harvard University, 1955.

[16] J. A. Berson and S. Suzuki, THIS JOURNAL, **80**, 4341 (1958).

[17] A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 6233 (1957).

[18] A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957).

[19] K. B. Wiberg, Dissertation, Columbia University, 1950, as quoted in ref. 18.

[20] A. Streitwieser, Jr., paper presented at the Seventh Reaction Mechanisms Conference, Chicago, Ill., Sept. 3–6, 1958.

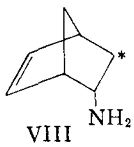
[21] (a) J. Steigman and L. P. Hammett, THIS JOURNAL, **59**, 2536 (1937); (b) A. Campbell and J. Kenyon, unpublished results, quoted by J. Kenyon, *Bull. soc. chim. France*, c. 65 (1951).

[22] S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

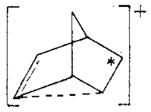
Optically active acetate from the amine–nitrous acid reaction could arise from direct displacement on the diazonium ion by solvent,[23] from a "normal," *i.e.*, solvated (but un-bridged) carbonium ion, *e.g.*, VII,[23] or from a "hot," unsolvated carbonium ion.[6,24] In view of the fact that decomposition of a diazonium ion releases molecular nitrogen, an exceptionally stable entity, it is probable that little solvation of the developing carbonium ion is required.[18] Consequently, the *initial* carbonium ion derived from an amine–nitrous acid reaction is probably more energetic than that derived from halide or sulfonate solvolysis. The crucial point at issue in the debate[23,24] between the advocates of "hot" and "normal" or "cool" carbonium ions, it seems to us, is whether a "hot" carbonium ion could react with solvent without passing through a "cool" or solvated state. The amount of activity surviving in the acetolysis of the *endo-p*-bromobenzenesulfonate is of little help in estimating how much survival of activity to expect in the amine–nitrous acid reaction even if it is assumed that all of the active acetate in the latter reaction arises from a "cool" ion (VII), since the 7–8% of optically active product in the former reaction presumably can arise from VII and/or the intimate ion-pair VI, with an unknown relative contribution from each. Likewise, it is difficult to estimate how much survival of activity to expect from the direct displacement process. Streitwieser[23] has argued that direct displacement should not be invoked as an explanation for the observed[25] high proportion of inversion in diazotizations of *axial* cyclohexylamines because of the low reactivity of cyclohexyl systems in S_N2 reactions. Data are not available for S_N2 reactivities of *endo*-norbornyl derivatives. The fact that the *endo*-norbornylamine and 2-butylamine diazotizations give about the same amount of inversion suggests that, if optically active acetate is derived by direct displacement, the *endo*-norbornyl and 2-butyl systems are about equal in S_N2 reactivity. The agreement could be fortuitous, however, and, in the absence of further data, speculation is unwarranted.

One further point hinders comparison of amine diazotizations and sulfonate solvolyses in acetic acid. The amine diazotization is unavoidably accompanied by the generation of water, both in the reaction itself and in the spontaneous decomposition of nitrous acid. In our experiment, this resulted in a medium change, during a run, from acetic acid to at least about 1.16 *M* (2%) water in acetic acid. The consequences of this are unknown.

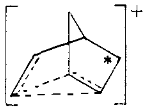
A comparison of the results reported here with the isotope-position rearrangement data for the case of *endo*-2-amino-5-norbornene (VIII) is of interest. Nitrous acid deamination of VIII-3-^{14}C in acetic acid gives[26] a mixture of nortricyclyl acetate and *exo*-5-norbornenyl-2-acetate, the latter being formed with 38.5% isotope-position rearrangement.[13] Since a 3-fold symmetrical ion analogous to V cannot be formed in this system, all of the rearrangement is attributable to the occurrence of the 2-fold symmetrical ion X.[27]



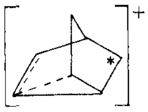
VIII



IX



X



XI

The observed % rearrangement means, therefore, that an excess of 23% of the *exo*-5-norbornenyl acetate is formed without rearrangement, a result that is in precise agreement with the observed retention of skeletal identity (% optical purity) in the case of *endo*-norbornylamine (Ib). It seems unlikely that the "cool," solvated carbonium ions VII and IX would give the same proportions of unrearranged product. In fact, the % isotope-position rearrangement in the acetolysis of norbornyl *p*-bromobenzenesulfonates is considerably more than that of the corresponding 5-norbornenyl derivatives,[6,26] even when correction is made for the contribution of the 3-fold symmetrical ion V to the former reaction. In other words, the partitioning of the solvated ion VII seems to favor rearrangement over direct collapse to unrearranged product to a greater extent than does that of IX. This is understandable if the activation energy for converting the relatively stable[28] homoallylic ion IX to the carbon-bridged ion X is greater than that for the change VII → IV. A simple but perhaps not unique interpretation of the results is that at least some of the excess unrearranged portion of the product acetate from Ib arises from direct displacement by solvent or acetate ion on the diazonium salt. Direct displacement may also be a mechanism for formation of unrearranged acetate from VIII. The observed precise correspondence in retention of skeletal integrity in the deaminations of Ib and VIII could well be fortuitous, since unrearranged acetate from the latter could also arise from the ion IX.

Alternatively, if the results obtained with Ib are to be interpreted on the basis of carbonium ion intermediates as the immediate precursors of the excess unrearranged acetate, these ions must be assigned very special properties, which would be better described as "warm" rather than "hot." Thus the ion from Ib must be sufficiently more energetic and less selective than the corresponding "cool" ion to increase the proportion of product

[23] A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

[24] See, *inter alia*, (a) D. J. Cram and J. E. McCarty, This Journal, **79**, 2866 (1957); (b) L. S. Ciereszko and J. G. Burr, *ibid.*, **74**, 145 (1952); (c) D. Semenow, C. H. Shih and W. G. Young, *ibid.*, **80**, 5472 (1958); (d) a diazoalkane intermediate seems unlikely (refs. 18, 24c, and literature therein cited).

[25] (a) A. K. Bose, *Experientia*, **9**, 256 (1953); (b) J. A. Mills, *J. Chem. Soc.*, 260 (1953); (c) W. G. Dauben, R. C. Tweit and C. Mannerskantz, This Journal, **76**, 4420 (1954); (d) see, however, C. W. Shoppee, D. E. Evans and G. H. R. Summers, *J. Chem. Soc.*, 97 (1957).

[26] J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., This Journal, **77**, 3034 (1955).

[27] The occurrence of the ion XI[26] as a discrete species in combination with its enantiomer, the first-formed ion IX, is indistinguishable isotopically or polarimetrically from the combination IX plus X.

[28] M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

arising from direct collapse and to eliminate the gap in tendency toward rearrangement that exists between the "cool" ions derived from Ib and VIII, but still must be apparently just as selective sterically in its reaction with acetic acid—to give exclusively *exo*-acetate—as the "cool" ion. A "hot" ion interpretation would require the additional hypothesis that the deaminatively produced ion is in fact sterically less selective than the solvolytically produced ion, but that the difference is experimentally undetectable, *i.e.*, the *exo/endo* product ratio from the former is smaller than that from the latter, but both ratios are large (> *ca.* 13). Thus, the general preference for *exo*-addition to unsaturated norbornyl systems would be required to control completely the steric result, even with the "hot" ion. While the "hot" ion interpretation can be adjusted to accommodate the present results, a simpler interpretation is afforded by the hypothesis of a direct displacement mechanism as the path that produces optically active acetate.

The precise details of the hypothetical "direct displacement" process remain to be elucidated. Thus, it is not clear whether (i) an *intermediate* VI (N_2 instead of OBs) is partitioned between, on the one hand VII and/or IV and V, and on the other non-rearranging collapse to product, or (ii) the branching point occurs earlier in the mechanism,[23] and *two* processes—one with VI (N_2 instead of OBs) as a *transition state* and another leading to carbonium ions VII and/or IV and V—compete with each other. At present, we are inclined to favor (ii) as the proper description of "direct displacement" on the grounds that the intermediate of (i) would be expected to be extremely unstable, since covalent interaction between N_2 and carbon would be weak, and charge–charge attraction would be absent. This would make the "intermediate" operationally indistinguishable from a transition state.

The relative contributions of the 2-fold (IV) and 3-fold (V) symmetrical ions to the product acetate in the nitrous acid deamination of Ib can be calculated by combining the stereochemical result with the isotope-position rearrangement data of Roberts.[6] Assuming that 76% (representing racemic material) of the product acetate arises from IV and/or V, the requirement that IV and V produce 50 and 66.7% isotope-position rearrangement, respectively, and the observation[6] of 41.6 and 44.9% rearrangement require that 28–54% of the racemic product (22–41% of the total product) be formed from the 3-fold symmetrical ion V. The quantitative significance of these conclusions may be doubted, however, since the % contribution of V is derived as a small difference between large numbers in the calculation, and especially since the % rearrangement for two presumably identical runs with isotopically labeled amine differ by an amount that seems to be greater than the experimental error of the degradation and isotope analysis. It is conceivable that this is due to sight irreproducibilities in the diazotization reaction conditions. It is therefore uncertain whether the observed isotope-position rearrangement figures differ significantly from 38%, a value that would imply 0% contribution from V.

Experimental[29]

***exo*-Norbornylamine (IIb).**—A solution of 4.5 ml. of bromine and 13.5 g. of sodium hydroxide in 100 ml. of water was cooled to 0°, stirred, and treated with 9.2 g. of pure powdered *exo*-norbornanecarboxamide.[3] An additional 30 ml. of water was added, and the mixture was stirred for two hours, filtered from a small quantity of insoluble material and slowly heated during 30 minutes to 70°, whereupon an oil separated. The temperature was raised to 90°, and after one hour the mixture was cooled, extracted with ether, the ether was washed with water and dried over potassium carbonate. Evaporation of the ether left 8.6 g. of an oil, which after bulb-to-bulb distillation gave 5.6 g. of oily product. This material was boiled with 4 *N* sulfuric acid for 24 hours, the reaction mixture washed with chloroform, made basic with sodium hydroxide and extracted with ether. The ether extract, after having been washed with water and dried over potassium carbonate, was evaporated, and the residue was distilled to give 3.6 g. of liquid amine. A sample of this material (3.2 g.) in 100 ml. of ether containing 4.5 ml. of acetic anhydride was heated at reflux for one hour and then evaporated to give 2.9 g. of crystalline material. Recrystallization from ether gave three crops of crystalline ***exo*-N-acetylnorbornylamine:** (1) 1.5 g., m.p. 143–144°; (2) 0.65 g., m.p. 142.5–143.5°; (3) 0.27 g., m.p. 143–145°. Alder[5] reports m.p. 139°.

Crops 1–3 were combined and boiled with 2 *N* sulfuric acid for 24 hours. The amine was isolated from the basified solution by extraction with ether. After being washed with water and dried with potassium carbonate, the ether was removed with the aid of a Vigreux column and the residue was distilled *in vacuo* (bulb-to-bulb, at 60–75° (48 mm.)) to give 1.0 g. of a colorless liquid. This material set to a waxy solid at *ca.* −50°. Samples for titration were withdrawn and weighed with minimum exposure to air, immediately dissolved in excess standard hydrochloric acid, and back-titrated with sodium hydroxide.

Anal. Calcd. for $C_7H_{13}N$: neut. equiv., 131. Found: neut. equiv., 132, 128.

The amine rapidly forms a solid carbonate, m.p. *ca.* 80–90°, on exposure to moist air. The infrared spectrum of the pure amine in bromoform was quite similar to that of the *endo*-amine.

Racemic *endo*-Norbornylamine (Ib). A. Hofmann Method.—A solution of 8.94 g. of pure *endo*-norbornanecarboxamide[3] in 530 ml. of warm absolute methanol containing sodium methoxide (from 2.90 g. of sodium) was treated with 3.90 g. of bromine. The reaction mixture was stirred and heated at gentle reflux for 45 minutes and the methanol was removed by distillation. The resulting crystalline residue was taken up in 75 ml. of water and boiled for 5.5 hours. Then a solution of 20 g. of sodium hydroxide in 30 ml. of water was added and the mixture was boiled for 20 hours. More water was added, the mixture was distilled and the distillate was made acidic with sulfuric acid and concentrated to a small volume. Basification, isolation with ether in the usual manner, evaporation of the ether and drying of the residue afforded 1.90 g. of crude amine, which softened at 50° and had m.p. 78–84°. Bulb-to-bulb distillation (70–95° (55 mm.)) gave white crystals, which softened at 65° and had m.p. 80–84°. The infrared spectrum in bromoform was identical with that of a sample prepared by the Schmidt method (see B).

Anal. Calcd. for $C_7H_{13}N$: neut. equiv., 131. Found: neut. equiv., 142.

B. Schmidt Method.—A solution of 10.0 g. of pure *endo*-norbornanecarboxylic acid[2] in 40 ml. of chloroform was treated with a solution of 5.5 g. of hydrazoic acid in 100 ml. of chloroform. The mixture was cooled and treated dropwise during 20 minutes with 32 ml. of concentrated sulfuric acid. Gas was evolved. The mixture was warmed to reflux and boiled for two hours (after which time gas evolution ceased), and poured onto ice. The aqueous layer after being washed with fresh chloroform, was made basic, extracted with ether, washed with water and dried over potassium carbonate. Evaporation and distillation through a Vigreux column gave 5.3 g. of distillate, b.p. 80–90° (50 mm.), which solidified to waxy crystals, m.p. 89–90° (soft at 83°). Titration indicated that this material was 96.5% pure (neut. equiv. 136).

---

[29] Melting points are corrected.

The amine rapidly formed an amorphous carbonate, m.p. *ca.* 97–103°, on exposure to moist air.

The acetyl derivative, prepared with ether and acetic anhydride and recrystallized from heptane, had m.p. 131–132°, reported[5] m.p. 124°.

***endo*-Norbornylurea**, prepared from the amine hydrochloride and potassium cyanate, had m.p. 197–198° (from methanol), reported[4] m.p. 196–197°.

Regeneration of pure ***endo*-norbornylamine** from the acetyl derivative was accomplished by 25 hours boiling with dilute sulfuric acid. Isolation in the usual manner and bulb-to-bulb distillation gave material of m.p. 75–85° (soft at 65°), reported[4] m.p. 75–80°.

Anal. Calcd. for $C_7H_{13}N$: neut. equiv., 131. Found: neut. equiv., 131.

(+)-*endo*-Norbornylamine was prepared by the action of hydrazoic acid on (−)-*endo*-norbornanecarboxylic acid.[2] The acid used had m.p. 58–61°, $[\alpha]^{25}_{D}$ −10.7° (*c* 2.7 in 95% ethanol, *l* 4) and was processed exactly as for the racemic acid (see B above) in three batches of 43 g. each, using proportional quantities of the other reagents. Distillation of the combined crude amine through a Vigreux column gave 62.0 g. (51%) of material, b.p. 87–88° (40 mm.), which set to a waxy solid, m.p. 73–80°, soft at 55°. A small sample removed for polarimetry showed $[\alpha]^{25}_{D}$ +7.58° (*c* 2.7 in 95% ethanol, *l* 4). The exact magnitude of the rotation of the amine should be treated with reserve, since the large sample was optically impure and it was not remelted to homogeneity before the polarimetric sample was removed.

Anal. Calcd. for $C_7H_{13}N$: neut. equiv., 131. Found: neut. equiv., 131.

Reaction of (+)-*endo*-Norbornylamine with Sodium Nitrite in Acetic Acid.—A solution of 61.5 g. of the above dextrorotatory amine in 430 ml. of glacial acetic acid was cooled, stirred, and treated portionwise with 61.5 g. of sodium nitrite during 1.5 hours. The mixture was kept cold an additional hour and then allowed to stand overnight at room temperature. More sodium nitrite (15.2 g.) was added during 15 minutes and the mixture, after being stirred one hour was diluted with 150 ml. of water and poured into 1500 ml. of ice-cold 20% sodium hydroxide. The mixture was extracted with ether, the ether layer was washed carefully with *N* hydrochloric acid and water, dried over calcium sulfate, and evaporated. Distillation of the residue through a Vigreux column gave (1) 2.0 g. of colorless liquid, b.p. 103° (38 mm.); (2) 53.4 g. of colorless liquid, b.p. 102° (36 mm.). The yield of crude acetate was thus 65%. This material had n^{27}_{D} 1.4601, α^{30}_{D} −0.772° (neat, 1 dcm.). It did not react with permanganate in acetone. The infrared spectrum was virtually identical with that of pure *exo*-norbornyl acetate[7] except for a strong, sharp band at 6.15 μ which is absent in the latter. This was attributable to the presence of a small amount of norbornyl nitrate.[30,18] The nitrogen content (0.51%)[31] indicated 5.8% contamination by nitrate. That the other most likely nitrogenous contaminant, norbornyl nitrite, was probably absent was suggested by the presence of only one extraneous band in the 6.0–6.2 μ region, rather than the two that would be expected for nitrite.[32]

Twenty-five grams of the above crude acetate in 250 ml. of anhydrous ether were added dropwise during one hour to a stirred solution of 12.5 g. of lithium aluminum hydride in 350 ml. of ether. The mixture was boiled under reflux for 2.5 hours and then treated with 85 ml. of water. The resulting sludge was shaken with five 400-ml. portions of ether, the ether solutions were filtered, dried with calcium sulfate and evaporated under a Vigreux column, leaving 22.6 g. of crude *exo*-norborneol. This material was heated at reflux for 16 hours with 70 ml. of acetic anhydride and 220 ml. of glacial acetic acid, poured into ice-water, the mixture saturated with sodium chloride and extracted with ether. The ether extract was washed with dilute cold sodium hydroxide and with water, dried over calcium sulfate and evaporated under a Vigreux column, leaving 24.5 g. of crude acetate. Careful fractionation in a Vigreux column gave (1) a small forerun of acetic anhydride, b.p. 40–55° (35 mm.); (2) 12.4 g. of colorless liquid, b.p. 95–98° (33 mm.), n^{25}_{D} 1.4558 (*exo*-norbornyl acetate containing *ca.* 1% acetic anhydride); (3) 9.2 g. of pure *exo*-norbornyl acetate, b.p. 96° (32 mm.), n^{26}_{D} 1.4560, n^{25}_{D} 1.4564, reported[7] n^{25}_{D} 1.4565. Fraction 3 showed α^{25}_{D} −1.048° (neat, 1 dcm.); its infrared spectrum was identical in all details with that of authentic[7] *exo*-norbornyl acetate.

A solution of a portion of fraction 3 in glacial acetic acid showed $[\alpha]^{29}_{D}$ −1.30° (*c* 10.42, *l* 4). This polarimetry solution was used to make up to 10.00 ml. a sample of 1.4420 g. of *p*-toluenesulfonic acid monohydrate (0.759 *M*). After the resulting solution was heated at 75° for 3.4 hours, it was optically inactive, α^{25}_{D} +0.003 ± 0.01°.

Acknowledgment.—We are indebted to the Office of Scientific Research, Air Research and Development Command, for financial support.

---

(30) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 251.

(31) Analysis by Dr. Adalbert Elek, Elek Microanalytical Laboratories.

(32) Reference 30, p. 253.

LOS ANGELES 7, CALIF.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Formation and Preferential β-Alkylation of the Dicarbanion of 2,3,3-Triphenylpropionitrile by Means of Potassium Amide in Liquid Ammonia[1,2]

BY CHARLES R. HAUSER, THOMAS M. HARRIS[3] AND T. GLENN LEDFORD[4]

RECEIVED SEPTEMBER 8, 1958

2,3,3-Triphenylpropionitrile was converted by one equivalent of potassium amide in liquid ammonia to the pale green monocarbanion, and by two equivalents of this base to the dark red dicarbanion. This twofold ionization involved the α- and β-hydrogens, respectively. The red dicarbanion reacted with an equivalent of benzyl chloride to give exclusively the β-benzyl derivative and with an equivalent of methylene chloride to produce apparently the corresponding cyclopropane derivative.

It is well known that the amide ion in liquid ammonia can effect the essentially complete ionization of a methylene hydrogen of phenylacetonitrile or diphenylmethane to form the corresponding anions which may be formulated as carbanion I[5] and II,[6] respectively.

$C_6H_5\bar{C}HCN$	$(C_6H_5)_2\bar{C}H$
I (pale green)	II (red)

It therefore seemed possible that the amide ion could effect the essentially complete ionizations of

---

(1) Reported before the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14–16, 1957, and the 133rd National Meeting of the American Chemical Society at San Francisco, Calif., Apr. 13–18, 1958.

(2) Preliminary results were reported in a communication by C. R. Hauser and T. M. Harris, THIS JOURNAL, **79**, 6342 (1957).

(3) National Science Foundation Predoctoral Fellow, 1956–1958.

(4) Deceased; Eastman Kodak Co. Fellow, 1955–1956.

(5) See C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).

(6) See C. R. Hauser and P. J. Hamrick, Jr., *ibid.*, **79**, 3142 (1957).