Bimolecular Displacement Reactions. I. Reaction of *endo*-Norbornanol and 7-Norbornanol with Triphenylphosphine and Bromine

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Optically active *endo*-norbornanol reacts with triphenylphosphine and bromine to give optically active *exo*-norbornyl bromide. Using mild reaction conditions, the norbornoxytriphenylphosphonium bromide salt was isolated from both *endo*- and 7-norbornanol; thermal decomposition of this salt gave the appropriate alkyl bromide. These data suggest that the course of bromination involves a concerted displacement of the triphenylphosphine oxide moiety by bromide ion to produce an alkyl bromide of opposite configuration from that of the starting alcohol.

To obtain meaningful kinetic data concerning the ionization rates of norbornyl derivatives it is necessary to use optically active compounds to avoid the complications which result from internal return.[3] Brown's[4] hydroboration procedure has provided a convenient route to optically active *exo*-norbornanol, but unfortunately the arenesulfonates of the norbornanols are characterized by low values[3] of $[\alpha]_D$ and were therefore unsuitable for the kinetic studies which we had planned.

A survey of the literature[5] revealed that the magnitude of rotation of alkyl halides is frequently several times that of the corresponding alcohol and this suggested that the norbornyl halides might be more suitable for our purposes. Owing to the propensity of the norbornyl cation to rearrange, it was necessary to choose a preparative method through which the alcohol or a readily accessible derivative could be converted to the halide by a direct displacement process. Although data concerning bimolecular displacement reactions on the norbornyl skeleton are sparse,[6,7] several detailed studies[8,9] on neopentyl compounds, which are also prone to rearrange, have been published and served as a valuable guide.

In 1953 Landauer and Rydon[9] reported that triphenyl phosphite methiodide reacted with neopentyl alcohol to give neopentyl iodide; with triphenyl phosphite benzylochloride, optically active 2-chlorooctane of inverted configuration was obtained from optically active 2-octanol.[9,10] Consequently, we were encouraged to investigate the reaction of the Rydon reagents with the norbornanols.

endo-Norbornanol (**1**) was treated with triphenyl phosphite benzylochloride at room temperature and the product was identified as *exo*-norbornyl chloride (**2**) from its solvolytic rate constant.[11] When optically active **1** was used, the *exo*-norbornyl chloride (**2**) which was formed was also optically active. These results provide additional evidence that the steric course of reaction of alcohols with the Rydon reagents involves a Walden inversion.[10,12]

Shortly after these results were obtained, Wiley and co-workers[13-15] reported that a superior method for converting alcohols or phenols to alkyl or aryl halides involved the use of triphenylphosphine and a halogen. Since we were having difficulty in removing small quantities of benzyl chloride which were present in **2** as a contaminant from the reaction described above, we abandoned this route in favor of the newer alternative.

Wiley[15] has reported that the reactivity of alcohols toward triphenylphosphine dibromide paralleled the general order of reactivity of the particular carbon skeleton in S$_N$2 reactions and that neopentyl alcohol was converted to neopentyl bromide without rearrangement[14]; therefore, it can be concluded that this reaction must involve a highly concerted displacement process at the carbon atom undergoing reaction.

Treatment of **1** with triphenylphosphine and bromine in N,N-dimethylformamide (DMF) gave a norbornyl bromide which was identified as the *exo* isomer by a comparison of its retention time on gas phase chromatography, its infrared spectrum, and its rate of solvolysis with those of an authentic sample.[11] A careful kinetic analysis showed that 98 ± 2% of the bromide present had the *exo* configuration.

When optically active **1** reacted with the same reagents in triglyme, the *exo*-norbornyl bromide (**3**) which formed was again optically active. To determine if any racemization accompanied the conversion of **1** to **3** the Grignard reagent of the bromide was prepared and carbonated and the mixture of optically active *endo*- and *exo*-norbornanecarboxylic acids was isolated. Since the maximum rotations of the *endo* and *exo* acids are 30.6 and 27.8°, respectively,[16] and since the carbonation product contains from 50 to 90%[17] of the *exo* isomer, a separation of the acids was not necessary to obtain a reliable estimate of the optical purity of the product. Examination of the rotation of the acids showed that their optical purity was experimentally indistinguishable from that of the norbornanone

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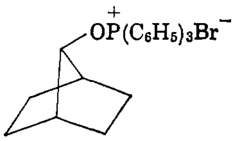
used to prepare the *endo* alcohol. From these data we can conclude that no significant racemization accompanied the conversion of *endo*-norbornanol to *exo*-norbornyl bromide. It also follows that the norbornyl Grignard reagent, which undoubtedly has considerable carbanion character, does not rearrange as does the cation.

Reaction of 7-norbornanol (**4**) with triphenylphosphine and bromine in triglyme gave a very stable intermediate which was isolated and identified as 7-norbornoxytriphenylphosphonium bromide (**5**) on the basis of its equivalent weight, elemental analysis, and behavior on pyrolysis. Decomposition of **5** above its melting point (161–162°) gave 7-norbornyl bromide (**6**) and triphenylphosphine oxide. The bromide was identified by the fact that its retention time on gas phase chromatography was similar to that of **3** and on solvolysis it produced **4** which was isolated and characterized as its *p*-nitrobenzoate ester.



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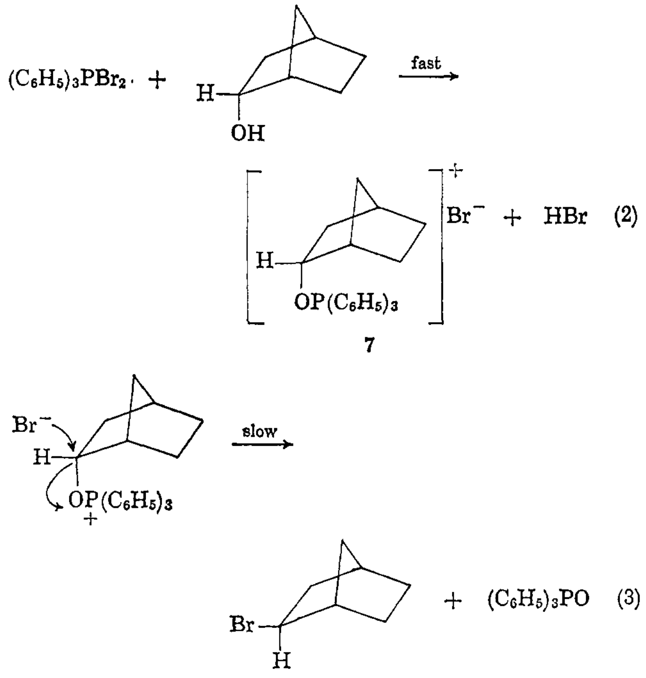
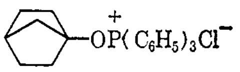
A modification of the experiments with **1** led to the isolation of an analogous intermediate (**7**) with similar physical and chemical properties to those of **5** but which was much less stable. When bromine was added to a solution of triphenylphosphine in triglyme, a precipitate of triphenylphosphine dibromide formed immediately; when a similar experiment was carried out in the presence of **1** no precipitate formed. On the basis of the foregoing data and the chemical and kinetic evidence reported by Wiley and co-workers,[13–15] the following mechanism can be written.

$$(C_6H_5)_3P + Br_2 \xrightarrow{\text{fast}} (C_6H_5)_3PBr_2 \qquad (1)$$



In addition to the stereochemical evidence which favors the formulation of the displacement reaction as we have depicted it in eq. 3, this step is supported by qualitative observations on the relative reactivity of the oxytriphenylphosphonium salts. In a recent study by Denney, *et al.*,[18] on the reaction of hypochlorides with triphenylphosphine, **8** was obtained as the product from 1-norbornyl hypochlorite. Decomposition of **8** to the chloride required pyrolysis at 200° whereas we have found that **5** and **7** decomposed rapidly at 170 and 115°, respectively; this order of stability (**8** > **5** > **7**) is in accord with what would be predicted for displacement reactions on these compounds. In **8**, the norbornyl framework shields the back side of the carbon–oxygen bond from rearward attack and an alternative pathway for decomposition, probably involving dissociation to an ion pair, must be found. In view of the instability of the 1-norbornyl cation, the high temperature required for decomposition is not surprising.



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In the cases of **5** and **7** several factors will influence the relative rates of displacement of the triphenylphosphine oxide moiety, the major ones being relative changes in angle strain, and the relief and development of nonbonded interactions.[19,20] The ratio of rates of solvolysis of the tosylates of **1** and **4** is 1.7 × 10^7; a critical analysis of the solvolytic data suggests that the relative inertness of the tosylate of **4** is due primarily to bond angle strain which is compensated to a small degree through the relief of nonbonded interactions with the C-2 and C-3 *exo* hydrogens. In the bimolecular displacement reaction the same factors will influence the rate of reaction but the development of two new nonbonded interactions between the nucleophile (bromide) and the *exo* hydrogens at C-2 and C-3 will further serve to decrease the reaction rate. In view of these considerations, the reactivity of **5** is quite reasonable.

The evaluation of the parameters which influence the solvolysis rate of *endo*-norbornyl tosylate is more complex. Bond angle strain again is probably the major factor inhibiting carbonium ion formation,[19] but this is largely compensated for by torsional and nonbonded interactions[19] which act to enhance the rate of departure of the tosylate group. In bimolecular displacements of *endo* substituents an extension of these considerations leads to the conclusion that displacements should be facile and comparable in rate to those on cyclohexane itself. Although no quantitative data bearing on this latter point are available, observations by Wiley and ourselves are certainly in qualitative accord. We are currently investigating quantitative aspects of bimolecular displacements on the bicyclo[2.2.1]heptane framework and plan to report on this work in the future.

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(18) D. Z. Denney, A. Appelbaum, and D. B. Denney, *J. Am. Chem. Soc.*, **84**, 4969 (1962).

(19) P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).

(20) C. S. Foote, *ibid.*, **86**, 1853 (1964).

Experimental[21]

exo-**Norbornanol.**—Norbornene (180 g., 1.92 moles) was added to a solution of 600 ml. of 88% formic acid and 20 ml. of concentrated sulfuric acid and the mixture was refluxed for 1.5 hr. The solution was cooled, made basic with aqueous sodium hydroxide, and refluxed for an additional 1.5 hr. The solution was steam distilled, the distillate was extracted with hexane and dried, and the solvent was removed by distillation. The yield of product was 189.0 g. (88%), m.p. 124–127° (lit.[22] m.p. 128–129°).

Norcamphor.—Both the oxidation procedures of Sarett[23] and of Kleinfelter and Schleyer[24,25] were used. The product was further purified through its semicarbazone to give pure ketone, m.p. 92–95° (lit.[22] m.p. 91–92°).

endo-**Norbornanol.**—This alcohol was prepared by the procedure described in detail below for (+)-*endo*-norbornanol. The yield of product varied from 88 to 94%, m.p. 148–150° after sublimation (lit.[22] m.p. 149–150°).

exo-**Norbornyl Chloride.**—*endo*-Norbornanol (3.1 g., 0.027 mole) was added in one portion to a chilled solution of 18 g. (0.041 mole) of triphenyl phosphite benzylochloride and the reaction mixture was allowed to stand overnight. The solution was distilled at 10 mm. and the distillate was washed with 2 *N* sodium hydroxide and water. The alkyl halide was dried over anhydrous magnesium sulfate and filtered; about 0.5 g. of product was obtained but this yield was low due to mechanical loss of product.

The titrimetric rate of solvolysis of the product using Roberts'[11] procedure was $h = 0.16$ hr.$^{-1}$ (lit.[11] *exo*-norbornyl chloride, $h = 0.14$ hr.$^{-1}$; *endo*-norbornyl chloride, $h = 0.002$ hr.$^{-1}$), which indicates that the product must be the *exo* isomer. When optically active *endo* alcohol ($[\alpha]^{25}_{\mathrm{D}}$ +0.34°) was used the *exo* chloride isolated was also optically active ($[\alpha]^{25}_{\mathrm{D}} \approx 2°$), but the presence of small amounts of benzyl chloride as a contaminant places a small uncertainty on the absolute values of the above numbers. In view of this complication this reaction was not investigated further.

exo-**Norbornyl Bromide.**—Addition of hydrobromic acid to norbornene as described by Roberts[26] gave the *exo* halide, b.p. 80° (28 mm.), n^{24}_{D} 1.5149 [lit.[26] b.p. 82° (29 mm.), n^{25}_{D} 1.5226].

(−)-*exo*-**Norbornanol.**—The procedure described is similar to the method of Brown and Zweifel[4] but is more convenient for the preparation of large quantities of alcohol and gives a higher yield of product. Sodium borohydride (72.5 g., 1.88 moles) was dissolved in 1700 ml. of triglyme and T and R brand turpentine, 681 g., 85% α-pinene, $[\alpha]^{30}_{\mathrm{D}}$ +35.4° (neat), was added in one portion. Boron trifluoride etherate (355 g., 2.50 mole) was added dropwise with vigorous stirring to the chilled solution over a 1.5-hr. period and the solution was stirred for an additional 15 min. Norbornene (235 g., 2.50 moles) dissolved in 150 ml. of triglyme was added over a period of 1.5 hr. at 0° and the mixture was then stirred for several hours. An aqueous solution of sodium hydroxide (835 ml. of 3 *N* solution) was added rapidly followed by 775 ml. of 30% hydrogen peroxide at 20°.

The three-phase solution was stirred for 1 hr. at room temperature and the bottom layer was then removed, extracted once with ether, and discarded. The middle layer, which contained isopinocampheol, *exo*-norborneol, water, and triglyme was shaken vigorously with a large amount of anhydrous potassium carbonate until two phases formed; the lower phase was extracted with several portions of ether and discarded. The top layer, the organic portion of the middle layer, and the combined ether extracts were dried separately overnight with anhydrous potassium carbonate.

The ether extracts were filtered and concentrated by distillation through a Vigreux column until the temperature reached 90°; the solution was cooled and the filtrates from the top and middle layers were added. Distillation through a Todd column packed with glass helices gave 227 g. (81.2%) of product which boiled at 170–173° (700 mm.) and solidified in the receiver. Recrystallization from hexane gave 154 g. of purified product, m.p. 123–126° (lit.[3] m.p. 126–126.6°), $[\alpha]^{27}_{\mathrm{D}}$ −0.70 ± 0.03° (*c* 7.99, $CHCl_3$). No impurities could be detected chromatographically. The rotation of the product indicated an optical purity of 23.5–25.6%,[27] but a much higher value can be obtained when pure α-pinene is used.[4]

(+)-**Norcamphor.**—This method is a modification of the general procedure of Sarett.[23] Chromium trioxide (75.0 g., 1.125 moles) was added in portions to 750 ml. of pyridine at 15°. A solution of 28.0 g. (0.25 mole) of (−)-*exo*-norbornanol and 300 ml. of pyridine was added to the yellow suspension over a 45-min. period and the solution was stirred overnight. The reaction mixture was cooled and the unreacted chromium trioxide was reduced with a solution of 91.5 g. (0.89 mole) of sodium bisulfite in 250 ml. of water. Excess concentrated hydrochloric acid was added to the cold reaction mixture and the solution was steam distilled. The distillate was basified with potassium carbonate, saturated with sodium chloride, and extracted with pentane; the extracts were dried with a mixture of anhydrous potassium carbonate and magnesium sulfate. After filtration and removal of the solvent by distillation the crude product was sublimed and gave 24.8 g. (92.8%) of purified ketone, m.p. 90–93° (lit.[3] m.p. 95.5–96.2°), $[\alpha]_{\mathrm{D}}$ 7.53 ± 0.05° (*c* 4.07, $CHCl_3$). The rotation of the ketone indicated that the compound was 25.6–26.8% optically pure[28] and showed that no racemization accompanied the oxidation reaction. If a smaller excess of chromium trioxide was used only partial oxidation of the alcohol occurred under the conditions described.

(+)-*endo*-**Norbornanol.**—A solution of 20.0 g. (0.178 mole) of (+)-norcamphor and 100 ml. of anhydrous ether was added dropwise to a slurry of 3.20 g. (0.0845 mole) of lithium aluminum hydride and 100 ml. of ether. The reaction mixture was stirred at room temperature for several hours and then decomposed with excess 3 *N* hydrochloric acid. The suspension was saturated with sodium chloride and extracted with ether, which was dried and concentrated to give 18.6 g. (91.2%) of (+)-*endo*-norbornanol, m.p. 148–150° after sublimation (lit.[3] m.p. 151.2–152.5°), $[\alpha]^{25}_{\mathrm{D}}$ +0.34 ± 0.10° (*c* 4.08, $CHCl_3$). Since the maximum rotations of *exo*-norbornanol and *endo*-norbornanol in the same series are −2.85 and +2.07°, respectively,[27,29] the low rotation of the alcohol which we have observed required that about 10–20% of the alcohol is the *exo* isomer; this is in excellent agreement with the direct analysis recently carried out by Wilcox.[30]

(+)-*exo*-**Norbornyl Bromide.**—Triphenylphosphine (37.4 g., 0.143 mole) and 15.5 g. [0.138 mole, $[\alpha]_{\mathrm{D}}$ 0.34° (*c* 4.08, $CHCl_3$)] of (+)-*endo*-norbornanol were added to 100 ml. of triglyme and the suspension was stirred until the solution was homogeneous. The solution was cooled and 22.8 g. (0.143 mole) of bromine dissolved in 50 ml. of cold triglyme was added as the temperature was maintained between 30 and 40°; the intermediate *endo*-norbornoxytriphenylphosphonium bromide began to precipitate soon after addition was started. A pressure of 4.5 mm. was applied and the solution was slowly warmed to drive off the hydrogen bromide present; the solution was then distilled until all of the solvent and product had been collected (ice water was circulated through the condenser and the receiver was placed in a Dry Ice–acetone bath). The distillate was added to 2 l. of ice–water and the organic phase was separated. The aqueous phase was extracted with 10-ml. portions of chloroform and discarded; the combined organic extracts were washed with

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(21) Boiling points and melting points (taken in sealed capillary tubes) are uncorrected. Optical rotations were measured with a Rudolph Model 80 high-precision polarimeter. The vapor chromatograms were taken using a 10-ft. 20% Carbowax 20M on firebrick column in a Wilkins Instrument and Research, Inc., Aerograph gas chromatographic instrument or on a similar 5-ft. column in an F and M Scientific Corp. Model 609 flame ionization gas chromatograph. The infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer, the ultraviolet spectra on an Applied Physics Corp. Cary 14 recording spectrophotometer, and the n.m.r. spectra on a Varian A-60 n.m.r. spectrometer.

(22) K. Alder and H. F. Rickert, *Ann.*, **543**, 2 (1939).

(23) C. I. Poos, G. I. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 425 (1953).

(24) D. C. Kleinfelter and P. v. R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

(25) D. C. Kleinfelter and P. v. R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

(26) J. D. Roberts, F. R. Trumbell, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(27) The maximum rotation of *exo*-norbornanol is 2.85°: see J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

(28) The maximum rotation of norcamphor is 28.3–29.2°: see J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964); K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962).

(29) The maximum rotation of *endo*-norbornanol is 2.07° if it is assumed that *endo*-norborneol ($[\alpha]^{25}_{\mathrm{D}}$ 1.23°) gives norcamphor ($[\alpha]^{-5}_{\mathrm{D}}$ 17.0°) without racemization [J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961)] and that the maximum rotation of norcamphor is 28.3–29.2°.[28]

(30) C. F. Wilcox, M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

500 ml. of aqueous sodium carbonate which was in turn extracted with a small amount of chloroform. The combined organic phases were washed with water, dried with magnesium sulfate, and fractionated through a Todd column packed with glass helices. The product was (+)-*exo*-norbornyl bromide, b.p. 70–70.8° (15 mm.), $n^{27}\text{D}$ 1.5127, $[\alpha]\text{D}$ 6.52° (*c* 5.62, $CHCl_3$), 15.0 g. (62%). Vapor phase chromatography indicated that the product was homogeneous.

When the above reaction was carried out on racemic product, the bromide isolated was identified by a comparison of its solvolysis rate constant, infrared spectrum, refractive index, and chromatographic retention time with those of an authentic sample and these properties were identical.[26]

On one occasion partial racemization occurred when the hydrogen bromide was not completely removed and the solution was heated above 135° on a vacuum line without rapid collection of the alkyl halide; norbornyl bromide with $[\alpha]\text{D}$ 3.25° (*c* 5.50 $CHCl_3$) was isolated. This product was used subsequently to relate the rotation of the bromide to norcamphor.

(+)-*exo*- and *endo*-**Norbornanecarboxylic Acids.**—The procedure reported recently by Sauers and Kwiatkowski[17] gave a less satisfactory yield of product than the general entrainment method of Pearson.[31] A solution of 4.45 g. [0.0254 mole, $[\alpha]\ ^{5}\text{D}$ 3.25° (*c* 5.50, $CHCl_3$)], of (+)-*exo*-norbornyl bromide, 5.3 g. (0.282 mole) of ethylene bromide, and 30 ml. of ether was added dropwise from a Hershberg addition funnel overnight to a refluxing mixture of 1.65 g. (0.065 mole) of magnesium turnings and 30 ml. of ether. The solution was then diluted with ether and the norbornyl Grignard reagent was carbonated at 0° by passing a stream of dried carbon dioxide through the solution for 6 hr. The solution was decomposed with 6 *N* hydrochloric acid, saturated with sodium chloride, and extracted with several portions of pentane. The combined pentane extracts were washed with water and then extracted with two portions of concentrated aqueous potassium carbonate; the combined basic extracts were then washed with four portions of pentane to remove any neutral material which was present.

The chilled basic solution was carefully acidified with hydrochloric acid and extracted with pentane. The pentane extracts were washed with water until the washings gave a negative silver nitrate test, and the product was then dried with anhydrous magnesium sulfate, filtered, and concentrated. The residual solvent was then removed by evacuation for several hours at 0.5 mm. and the yield of viscous oil obtained was 900 mg. (25%), $[\alpha]^{25}\text{D}$ 3.80 ± 0.10° (*c* 2.48, 95% ethanol). Titrimetric analysis indicated that the product was 98.7% pure norbornanecarboxylic acids but no attempt was made to separate the *exo* and *endo* acids.

Since the maximum rotations observed for the *exo* and *endo* acids are +27.8 and +30.6°, respectively,[16] and since the product contains from 50 to 90% of the *exo* isomer,[32] it was not necessary to separate the two acids to obtain a reliable estimate of the overall stereochemical course of the reaction. From the above data it follows that the optical purity of the acids was 12.5–13.9% which means that the norbornyl bromide must have had at least this optical purity. Therefore, the optical purity of norbornyl bromide with $[\alpha]\text{D}$ +6.53° was 25–28% and, since this is similar to that calculated for the norcamphor (25.6–26.8%) used as the precursor to the alcohol, no racemization accompanied the conversion of *endo*-norbornanol to *exo*-norbornyl bromide.

endo-**Norbornoxytriphenylphosphonium Bromide.**—Triglyme (40 ml.) was added to 13.1 g. (0.05 mole) of triphenylphosphine and 5.5 g. (0.05 mole) of *endo*-norbornanol and the solution was warmed until homogeneous. The reaction was then cooled to 10° and a solution of 7.2 g. (0.045 mole) of bromine and 25 ml. of triglyme was added with the temperature held under 20°. After the addition was complete the suspension was stirred for 1 hr. at 15° and then was added to 500 ml. of anhydrous ether. The oil which formed soon crystallized and was collected by suction filtration under nitrogen. After a brief evacuation at 1–2 mm. the yield of crude product obtained was 21.0 g. (102%). A portion of the product was dissolved in chloroform at room temperature, filtered, and precipitated by the addition of dry ether. The product was filtered under nitrogen, washed with ether, and pressed dry. Reprecipitation was repeated once again and then the last traces of solvent were removed by evacuation at 0.5 mm. for 2 hr. at room temperature. The product melted with decomposition at 82.2–83.1°, but it was not possible to remove all of the hydrogen bromide present without decomposition because of the instability of the compound. The similarity of its chemical and physical properties to those of the 7-norbornyl intermediate described later served to identify it as the *endo*-norbornoxytriphenylphosphonium bromide.

Decomposition of *endo*-**Norbornoxytriphenylphosphonium Bromide.**—A portion of the purified product (2.50 g., 0.055 mole) was pyrolyzed on a vacuum line at 0.1 mm. Decomposition began at the melting point and became vigorous at 115°. After 1 hr. decomposition was complete and the residue (1.50 g., 104%) was isolated and identified as triphenylphosphine oxide, m.p. 156–157° after one recrystallization from triglyme (lit.[33] m.p. 156.5–157°). The distillate (0.95 g., 98.5%) was identified as *exo*-norbornyl bromide by its retention time, refractive index ($n^{25}\text{D}$ 1.5141), infrared spectrum, and by analogy to the decomposition reaction in which triglyme was employed as solvent (*vide supra*).

1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene.—The procedure reported here is similar to the general procedure of Yates and Eaton.[34] Sodium metal (51.5 g., 2.20 g.-atoms) was added in several portions to 1 l. of cold absolute methanol and this solution was then added dropwise to 273 g. (1.00 mole) of hexachlorocyclopentadiene and 800 ml. of methanol. After stirring overnight the mixture was poured into 1100 ml. of ice–water and then extracted with four 200-ml. portions of methylene chloride. The extracts were combined, washed with dilute aqueous hydrochloric acid, water, and then dried over anhydrous magnesium sulfate. Distillation gave 246 g. (93%) of product, b.p. 78–80° (1.5 mm.), lit.[35] b.p. 108–110° (11 mm.). Reaction on twice this scale gave similar results.

7,7-Dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]heptene.—The procedure of Gassman and Pape[36] was used with slight modification. From 119.2 g. (0.45 mole) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and ethylene heated at 165° for 11 hr. was obtained 108.8 g. (83.5%) of product, b.p. 66–73° (0.06 mm.), lit.[36] b.p. 72–81° (0.10 mm.).

7-Norbornenone.—The procedure developed by Gassman and Pape[36] was used with major modifications to permit the reaction to be carried out on a larger scale. 7,7-Dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]heptene (91.0 g., 0.30 mole), 245 g. (3.30 mole) of *t*-butyl alcohol, and 908 g. (9.00 mole) of triethylamine were mixed and 159 g. (6.9 g.-atoms) of sodium metal was added in portions over 1.5 hr. The solution was stirred and heated cautiously for 8 hr. at 60–70° and then stirred overnight at room temperature. Ice–water (300 ml.) was added cautiously to the chilled reaction mixture and the solution was stirred for several hours. After all of the sodium had reacted, the cold solution was acidified with 250 ml. of 20% sulfuric acid and stirred for 24 hr. The liquid was decanted, water was added, and the liquid was again decanted. The residue was extracted with pentane and discarded. The two decanted portions were combined and extracted with 2 l. of pentane, and the extracts were dried with anhydrous magnesium sulfate. Concentration and distillation gave 12.30 g. (38%) of product, b.p. 48–58° (13 mm.), lit.[36] b.p. 70–77° (30 mm.) The product gave a negative silver nitrate test after a sodium fusion.

7-Norbornanol.—7-Norbornenone (5.50 g., 0.051 mole) was catalytically hydrogenated in acetic acid containing a little sodium acetate at room temperature and 3 atm. pressure with Adams catalyst. After work-up the ethereal solution of 7-norbornanone was reduced with lithium aluminum hydride to give 4.0 g. (70.3%) of a white solid which was recrystallized once from hexane to give pure 7-norbornanol, m.p. 147.5–150.5, lit.[37] m.p. 150–151°. No contaminants could be detected by vapor phase chromatography. The *p*-nitrobenzoate was prepared and recrystallized from ligroin, m.p. 110–112°.

7-Norbornoxytriphenylphosphonium Bromide.—The procedure described for the *endo* compound was used and the title compound was isolated in 87% yield: m.p. 161–162°; $\lambda_{\max}^{CHCl_3}$ 244 mμ (log ε 4.10), 269 (3.54); infrared ($CHCl_3$) 1235 cm.$^{-1}$ (P–O–C

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[31] D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

[32] This estimate is based on the assumption that the mixture contains from 50 to 90% of the *exo* isomer instead of 70–90% as suggested by Sauers[17] since the experimental conditions were modified.

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stretch); n.m.r. (deuteriochloroform) aromatic C–H (τ 2.00, 2.12), H–C–O (τ 5.20), aliphatic C–H (τ 7.50–9.10); ratios of band areas, 15:1:10. Volhard analysis for ionic halogen gave an equivalent weight of 472 (calcd. equiv. wt., 454).

Anal. Calcd. for $C_{25}H_{26}BrOP$: C, 66.23; H, 5.78; Br, 17.63. Found: C, 65.78; H, 5.92; Br, 17.52.

Decomposition of 7-Norbornoxytriphenylphosphonium Bromide.—The intermediate (1.0 g., 0.00221 mole) was heated on a vacuum line at 170° for 1 hr. at 0.1 mm. pressure. The distillate had a retention time on vapor phase chromatography which was the same as that of *exo*-norbornyl bromide. Solvolysis of the bromide in a sealed tube at 100° in the presence of aqueous silver nitrate was complete after 48 hr. and the alcohol formed was converted to its *p*-nitrobenzoate, m.p. 110.5–111.5°, which was identical with that of an authentic sample of 7-norbornyl *p*-nitrobenzoate (lit.[38] m.p. 106–107°).

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Bimolecular Displacement Reactions. II. Reaction of *exo*-Norbornanol with Triphenylphosphine and Bromine

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The reaction of optically active *exo*-norbornanol with triphenylphosphine and bromide is solvent dependent and gives 79.1% racemic *exo*-norbornyl bromide, 11.9% of optically active *endo*-norbornyl bromide, and 8.7% of nortricyclene in triglyme; in dimethylformamide these values change to 83.5, 1, and 15.5%, respectively. These data are interpreted in terms of the intervention of the nonclassical norbornyl cation which precipitates a departure in the mechanism of reaction from that which is normally observed.

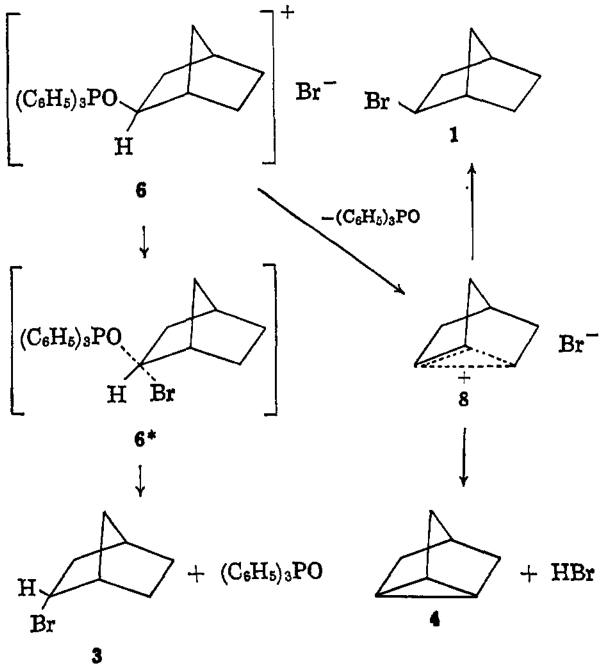
Displacement of the *endo*-triphenylphosphine oxide moiety by bromide from the norbornyl skeleton provides a practical route to *exo*-norbornyl bromide (**1**) and constitutes one of the few well-documented bimolecular displacement reactions in this system.[3] To determine whether an analogous reaction of *exo*-norbornanol (**2**) with triphenylphosphine and bromine would produce *endo*-norbornyl bromide (**3**), we turned our attention to a further study of this reaction.

When **2** was subjected to experiments parallel to those previously described,[3] the reaction products consisted of 11.9 ± 2% of **3**, 79.1 ± 2% of **1**, and 8.7 ± 0.5% of nortricyclene (**4**) if triglyme was used as the solvent; in N,N-dimethylformamide (DMF) these values changed to 1.0 ± 2, 83.5 ± 2, and 15.5 ± 0.5%, respectively. When optically active alcohol was used, the *exo* halide which was produced was racemic but the *endo* halide was optically active. The marked departure of these results from those observed in the *endo* series requires that a change in mechanism has occurred; since the major products are those reasonably expected from the norbornyl cation,[4] it is evident that a competing path which proceeds through the formation of a carbonium ion has become dominant.

These results, coupled with those obtained with *endo*-norbornanol (**5**), are remarkably similar in many respects to those reported earlier by Winstein and Trifan[5] on the tosylate solvolysis reaction, even though these two reactions would normally be classified at opposite extremes of the spectrum of solvolysis–displacement reactions. Although precise kinetic data have not yet been obtained, the above observations are conveniently accommodated in the mechanistic framework outlined in Scheme I.

Scheme I

Decomposition of *exo*-Norbornoxytriphenylphosphonium Bromide



In view of the product structure and the results obtained using optically active **2**, the decomposition of **6** into **3** and triphenylphosphine oxide is obviously the result of a bimolecular displacement process accompanied by a Walden inversion. Alternatively, **1** and **4** must result from a carbonium ion precursor which we have formulated as ion pair **8**. As the dielectric constant of the solvent is increased by changing the reaction medium from triglyme ($\epsilon \sim 2$) to DMF ($\epsilon \sim 37$), decomposition of **6** *via* the ion-pair route becomes more favorable as evidenced by the change

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(2) National Science Foundation Cooperative Fellow, 1960–1962; Phillips Petroleum Fellow, 1962–1963.

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