Acknowledgment.—We are indebted to Professor Pelham Wilder, Jr., for samples of certain norbornene derivatives as well as for advice on the synthesis of such derivatives. We would also like to thank Professor J. R. Wiseman of the University of Michigan for helpful suggestions concerning the structure proof.

Bromohydrin Formation in Dimethyl Sulfoxide. V.[1] The Reaction of Norbornene

D. R. DALTON,* [2] RONALD K. RODEBAUGH,[2,3] AND CHARLES W. JEFFORD[4]

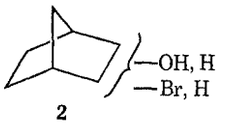
Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, and Université de Genève, Ecole di Chimie, Genève, Switzerland

Received April 13, 1971

The reaction of bicyclo[2.1.1]heptene (norbornene) with *N*-bromosuccinimide (NBS) in moist dimethyl sulfoxide (DMSO) has been examined in detail. The structures of the products have been elucidated and it has been shown (contrary to an earlier report) that no 2,3-bromohydrin products are obtained. In addition, bromohydrins which were not obtained, but which might have been, *a priori*, expected, were synthesized and shown to be stable to the reaction conditions. The products which were obtained, also stable to the reaction conditions, are accounted for on the basis of ionic and free-radical processes.

We have demonstrated[1,5] that a wide variety of olefins react with *N*-bromosuccinimide (NBS) in moist dimethyl sulfoxide (DMSO) to generate, without rearrangement, stereo- and regiospecifically, the corresponding bromohydrins. Unique among all olefins we have examined, in that rearrangement occurs, is bicyclo[2.2.1]heptene (norbornene) (**1**).

In our initial report[5] concerning the results of the reaction of norbornene (**1**) with NBS in moist DMSO we indicated that 3-bromobicyclo[2.2.1]heptan-2-ol (geometry unspecified) (**2**), *syn*-7-bromobicyclo[2.2.1]-



2

heptan-2-*exo*-ol (**3**), and nortricyclene bromide (**4**) were formed in the ratio 3:3:1. This result was based solely upon gas–liquid partition chromatography (glpc) comparison of the products obtained in the NBS–DMSO system with those obtained in *tert*-butyl alcohol–water–sulfuric acid by earlier workers.[6]

Since positive halogen reagents usually do not provide unrearranged material in large amounts when permitted to react with norbornene,[7] and since the geometry of the 2,3 product could potentially provide insight into the reason for the lack of rearrangement, we felt that a thorough investigation of this system merited our attention.

Results and Discussion

When norbornene (**1**) is permitted to react with NBS in moist DMSO six products (99.2%) are, in fact, formed. These products and the relative per cent yields in which they were obtained are shown in Table I

TABLE I

Product	Yield, %
Nortricyclene bromide (**4**)	61.8
syn-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (**3**)	21.7
exo-syn-2,7-Dibromobicyclo[2.2.1]heptane (**11**)	8.3
anti-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (**8**)	4.4
syn-7-Bromobicyclo[2.2.1]heptan-2-one (**7**)	2.2
endo-exo-2,3-Dibromobicyclo[2.2.1]heptene (**10**)	1.6

and can be accounted for by the species shown in Scheme I.

Thus, **1** is converted (perhaps after initial complexation)[8] into a bromocation which can be represented as the α-bromocarbonium ion A, the bromonium ion B, or some other positive species for which these structures (Scheme I) represent idealized constructions.[9] In either ion A or B the bulk of the bromine atom would presumably preclude exo attack by DMSO[7b,10] but not endo attack by this nucleophilic reagent.

Indeed, formation of the ultimate product of endo attack [*i.e.*, *exo*-3-bromobicyclo[2.2.1]heptan-2-*endo*-ol (**5**)] would be expected either from attack on the first ion or a rearrangement product of this ion resulting from 6,1-hydride migration in the nonclassical ion C (Scheme I).[11] Nevertheless, this product, although sought, is not found and we attribute its absence to the bulky nature of the solvated nucleophile and the requirement that it attack the endo face of the system. Thus, the major product (nortricyclene bromide) (**4**) derives simply from loss of a proton, presumably to succinimide anion.

Transformation of the first ion A or B into C, through σ bond delocalization, or D by a Wagner–Meerwein rearrangement, followed by attack of solvent at C_1 (norbornene numbering) in C or at the positive charge in D from the exo direction results in formation of *syn*-7-

(1) For paper IV in this series, see D. R. Dalton and V. P. Dutta, *J. Chem. Soc. B*, 85 (1971).

(2) Department of Chemistry, Temple University, Philadelphia, Pa. 19122.

(3) Taken in part from the doctoral dissertation submitted by R. K. R. to the Graduate School of Temple University, June 1971, in partial fulfillment of the requirements for the Ph.D. degree.

(4) Université de Genève, Ecole de Chimie, Genève, Switzerland.

(5) D. R. Dalton, V. P. Dutta, and D. G. Jones, *J. Amer. Chem. Soc.*, **90**, 5498 (1968).

(6) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **29**, 1625 (1964).

(7) (a) L. Kaplan, H. Kwart, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **82**, 2341 (1960), and references cited therein; (b) D. R. Marshall, P. Reynolds-Warnhoff, and E. W. Warnhoff, *Can. J. Chem.*, **49**, 885 (1971).

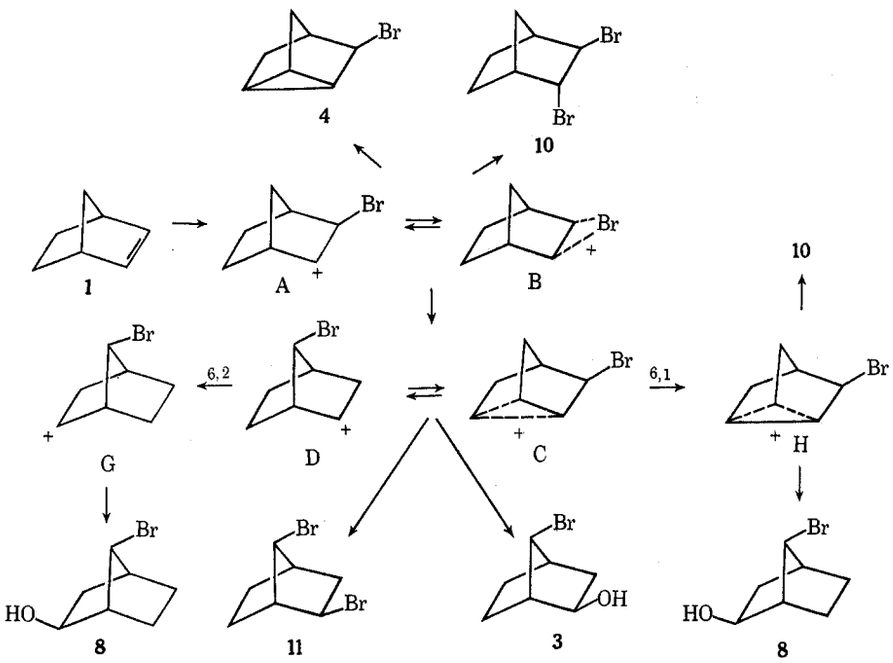
(8) J. E. Dubois and F. Gerner, *Tetrahedron Lett.*, 3961 (1968).

(9) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

(10) J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, **89**, 2573 (1967).

(11) J. A. Berson, "Molecular Rearrangements," Part 1, P. deMayo, Ed., Wiley-Interscience, New York, N. Y., 1963, pp 162, 163.

SCHEME I



bromobicyclo[2.2.1]heptan-2-*exo*-ol (**3**), the second major product. Presumably, endo attack on D is precluded for the same reasons given above (*vide supra*), while the delocalized bond in C shields that face which would also yield *syn*-7-bromobicyclo[2.2.1]heptan-2-*endo*-ol (**6**) as this material, too, is not found.

It is interesting to speculate, nevertheless, that the small amount of *syn*-7-bromobicyclo[2.2.1]heptan-2-one (**7**) isolated in the reaction mixture (Table I) might have come from endo rather than exo addition of DMSO to a species such as D. We suggest this may be a possibility since precedent does exist, in nonbicyclic systems, for the presumed dimethylsulfoxonium intermediate (E or F, Scheme II) to undergo oxidation by the path shown;[12] and proton loss in E (from the exo face) should certainly be more facile than from the endo face in F. Indeed, relief of steric strain in the crowded intermediate E would aid the process and further help to explain this unusual product.[13]

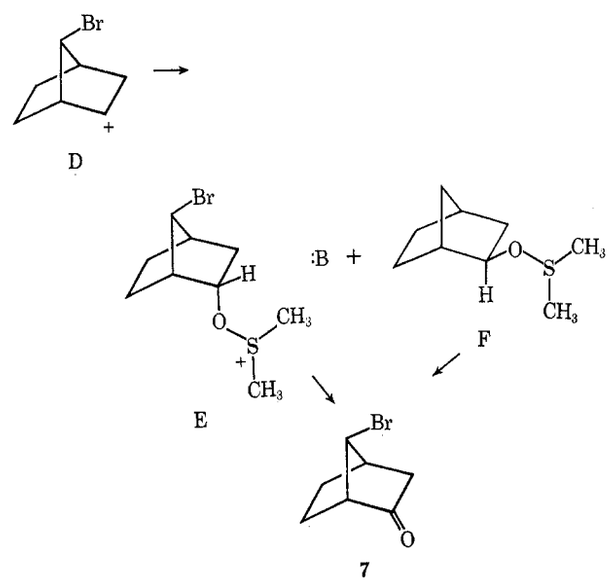
Now, a 6,2-hydride migration in D or a 6,1-hydride migration in C generates new ions G and H, respectively (Scheme I). Ion G, suffering attack from the exo direction by DMSO, would, on hydrolysis, afford *anti*-7-bromobicyclo[2.2.1]heptan-2-*exo*-ol (**8**) as would attack at C_6 (norbornene numbering) in H. Although ion G should certainly be subject to endo attack, product which might arise from this process was not detected. Indeed, product arising from exo attack, which should predominate in any case, was only present to the extent of *ca.* 4% (Table I) so that *anti*-7-bromobicyclo[2.2.1]heptan-2-*endo*-ol (**9**), had it been formed, might have gone undetected.

The final two products observed, *i.e.*, *endo-exo*-2,3-dibromobicyclo[2.2.1]heptane (**10**) and *exo-syn*-2,7-dibromobicyclo[2.2.1]heptane (**11**), are worthy of special comment.

(12) K. Torssell, *Acta Chem. Scand.*, **21**, 1 (1967).

(13) Despite the fact that we have now run this reaction on more than 30 olefins, we have been unable to detect ketonic or aldehydic materials in any other case.

SCHEME II



It is generally true[5] that dibromide products are not observed in reactions of olefins with NBS in DMSO unless the olefin is sterically (*e.g.*, 2,3,3-trimethyl-1-butene) or electronically (*e.g.*, *p*-nitrostyrene) inhibited from rapid reaction with NBS and DMSO, presumably because initial ion formation is difficult and there is time for bromine itself to form and react.[14] In addition, olefins (*e.g.*, 1-phenylpropene) which might form specially stabilized ions and do often[15] appear to react as α-bromocarbonium as well as bromonium ions do not, in the NBS–DMSO system, generate dibromide products, presumably because they react rapidly. In this case, however, we suggest that it is

(14) Small quantities of bromine are generated in this reaction by the oxidation of DMSO by Br^+. See, *e.g.*, (a) S. Iriuchijima and G. Tsuchihashi, *Synthesis*, 588 (1970); (b) v. D. Martin, A. Berger, and R. Peschel, *J. Prakt. Chem.*, **312**, 683 (1970).

(15) (a) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469, 1477, 1483 (1969); (b) R. C. Fahey and H.-J. Schneider, *ibid.*, **90**, 4429 (1968).

the inability of the solvent to rapidly attack the initial ion rather than slow initial ion formation which accounts for the dibromide product.

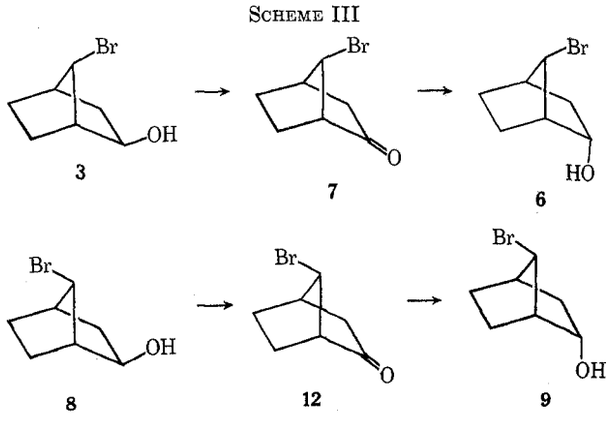
Thus, **10**[16] can arise by attack on the first formed ion from the endo direction by bromide anion or on the rearranged ion H (Scheme I) at C_2 (norbornene numbering) while attack on ions C or D would account for **11**. However, as has been recently pointed out,[7b] **10**, in another system, is also formed *via* radical addition to norbornene. We suggest that the radical pathway to **10** may be important here too, since if bromide anion were attacking the first formed ion (A or B) or the rearranged ion (H) to form this product some competition from DMSO and formation of the corresponding bromohydrin **5** would have been expected.

The complete lack of 2,3-bromohydrins, considered in light of the usual stereo- and regiospecificity of the NBS–DMSO system and the known penchant for rearrangement in the bicyclo[2.2.1]heptane system, led us to question the stability of the products found and the potential, but not obtained, bromohydrins to the reaction conditions.

To answer this question, each of the products (Table I) was resubjected to the reaction conditions (except that norbornene was excluded) and work-up, and reisolated. In addition, the bromohydrins which might have been formed were prepared and subjected to the reaction conditions.

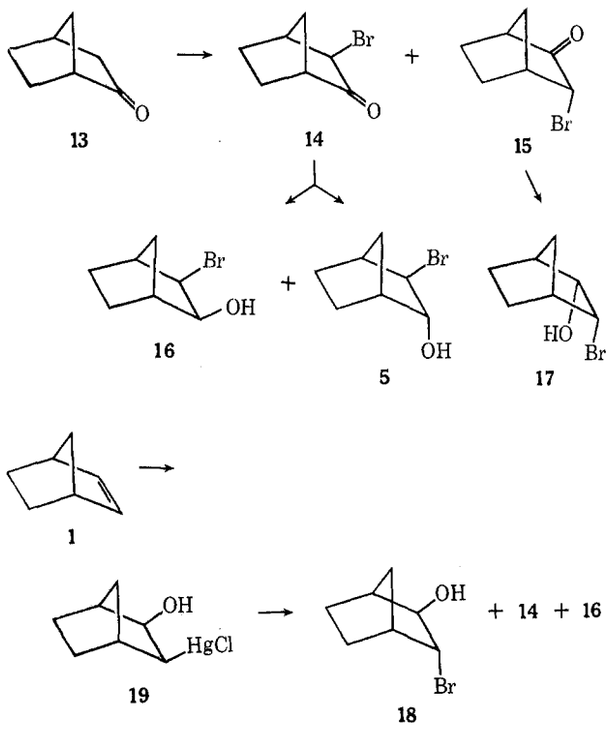
Thus, *syn*-7-bromobicyclo[2.2.1]heptan-2-one (**7**) was prepared in larger quantity by the oxidation of **3** with Jones reagent.[17] Reduction of **7** with diborane[18,19] generated a mixture of **3** and **6** in the ratio 5:3 (pmr integration), from which **6** was separated by distillation followed by column chromatography. Similarly, oxidation of **8** under the same conditions yielded *anti*-7-bromobicyclo[2.2.1]heptan-2-one (**12**) which, on reduction with sodium borohydride generated **9** exclusively (Scheme III).

SCHEME III



The 2,3-bromohydrins were prepared in a similar fashion[20] (Scheme IV). Thus, bicyclo[2.2.1]heptan-2-one (**13**) was brominated with pyridinium bromide perbromide[21] to yield a mixture (95:5 by pmr integration) of *exo*-3-bromobicyclo[2.2.1]heptan-2-one (**14**) and *endo*-3-bromobicyclo[2.2.1]heptan-2-one (**15**). The major isomer was freed from the minor one by several low-temperature crystallizations from ether. The minor isomer (**15**) could be obtained from the mother liquors by preparative gas–liquid partition chromatography (glpc) or, what was more convenient, the crude reaction mixture could be isomerized to a *ca.* 50:50 mixture of isomers with potassium *tert*-butoxide in *tert*-butyl alcohol and the separation effected.

SCHEME IV



Reduction of **14** with diborane[18,19] yielded a mixture of *exo*-3-bromobicyclo[2.2.1]heptan-2-*exo*-ol (**16**) and *exo*-3-bromobicyclo[2.2.1]heptan-2-*endo*-ol (**5**) in a 1:1 ratio from which, through repeated fractional distillation, the known **5** was isolated.

Although **16** could also be isolated from this reaction mixture, we found it more convenient to prepare it by the sodium borohydride reduction of **14**, from which a 78% yield resulted. The preferential addition of hydride to the endo face of the system presumably is accounted for by the steric effect of the bromine at the adjacent carbon.[19]

Thus, *endo*-3-bromobicyclo[2.2.1]heptan-2-one (**15**) on reduction with sodium borohydride generated, exclusively, *endo*-3-bromobicyclo[2.2.1]heptan-2-*endo*-ol (**17**) as would be expected.

The final compound required, *endo*-3-bromobicyclo-[2.2.1]heptan-2-*exo*-ol (**18**), had not previously been reported. We found that it could be prepared conveniently, but in low yield, by the bromination of the known *exo*-3-mercurichloride bicyclo[2.2.1]heptan-2-*exo*-ol (**19**)[22] which also yielded, in somewhat larger quantity, **14** and **16**.

(16) Despite the small amount of dibromide **10** which is formed, we are currently attempting to determine, through the use of radical inhibitors, whether or not this material comes solely from radical sources.

(17) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 255 (1953).

(18) Diborane was obtained, as used as received, as a 1 *M* solution in THF from the Ventron Corp., Beverly, Mass.

(19) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(20) Compounds **5**, **14**, **15**, **16**, and **17** have been reported. The synthetic sequence which we used was similar to that employed by H. Krieger, *Suom. Kemistilehti A*, **31**, 340, 348 (1958); *B*, **31**, 112, 320 (1958).

(21) L. F. Fieser, "Organic Experiments," 3rd ed, D. C. Heath, Boston, Mass., 1964, p 68.

(22) T. G. Taylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

Each of the isolated bromohydrins was characterized and submitted, along with the compounds obtained in the initial reaction, to the conditions of the NBS–DMSO reaction. In no case could evidence for isomerization be found and the material was, in each case, recovered unchanged and in high yield (>90%).

Conclusions

The reaction of norbornene with NBS in moist DMSO leads, contrary to an earlier report, to a complicated mixture of products. It is suggested that the products arise through rearrangements characteristic of the bicyclo[2.2.1]heptane system and that the simple addition product expected is not observed because the initial bromonium or α-bromocarbonium ion experiences difficulty in being attacked by DMSO. Despite these results, however, we remain intrigued by the possibility of a solvent of sufficient nucleophilicity to carry out the desired trapping of the bromo cation before rearrangement is possible.

Experimental Section[23]

Reaction of Bicyclo[2.2.1]heptene (1) with NBS in DMSO.—The olefin 1 (37.0 g, 0.34 mol) was dissolved, with slight warming, in DMSO (300 ml). With stirring, water (14.4 g, 0.80 mol) was added and the solution was placed in an ice bath. The addition of NBS (113.2 g, 0.64 mol) was commenced and regulated so that the heat evolved was sufficient to keep the olefin in solution (5 min was required for complete addition). After the reaction mixture stirred at room temperature for 0.5 hr it was poured, with stirring, into a saturated aqueous solution (900 ml) of sodium carbonate which had been precooled by standing in an ice bath during the course of the reaction. After warming to room temperature, the aqueous solution was extracted with six portions (250 ml each) of ether and the combined ether extracts were washed with water.

The ether extract was dried over anhydrous magnesium sulfate and the solvent was removed at reduced pressure.[27] The pmr spectrum obtained on the crude residue proved to be a composite of the materials subsequently isolated. No evidence, as demonstrated by subsequent synthesis (*vide infra*), could be found for products other than those isolated.

Analysis of the Reaction Mixture. A. Glpc.—The crude ether extract was injected directly onto an XE-60 (10% on firebrick) glass column held at 155° (detector, 200°; collector, 190°; injector port, 170°; He flow rate 102 cc/min) and the products were collected in receivers cooled in Dry Ice–acetone. The analysis of the effluent is shown below (Table II).

TABLE II

Peak no.	Retention time, min	Per cent of reaction mixture	Compd[a]
1	9.69	60.75	4
2	30.47	1.66	10
3	39.90	0.95	...[b]
4	49.50	21.74	3
5	74.42	6.61	7, 8
6	98.03	8.27	11

[a] Each material isolated was reinjected under the conditions of its isolation and reisolated unchanged. In addition, collection of the *total* effluent generated a mixture whose pmr spectrum possessed all of the signals (and lacked none) found in the mixture initially placed on the column although some differences in intensities were observed. [b] Insufficient quantities of this material could be isolated. However, the retention time under the conditions specified was different from that for the bromohydrins subsequently synthesized.

B. Column Chromatography.—The crude reaction mixture, after removal of the solvent[27] (30.135 g), was placed on a column (5 cm i.d., 1000 g) equipped with an automatic fraction collector, and eluted with chloroform; 10 ml fractions were taken.

Fractions 101–137 (5.201 g) consisted of one material (tlc) which was identical with the sample collected as peak 1 from glpc and by comparison to an authentic sample (ir, pmr) was identified as nortricyclene bromide (4),[27,28] n^{20}D 1.5290 (lit.[29] n^{20}D 1.5290).

Fractions 138–189 (1.688 g) were combined and subjected to bulb-to-bulb distillation (82°, 0.3 mm) to yield a material identical with peak 6 collected from glpc. The ir and pmr spectra of this material were superimposable upon that of an authentic sample of 11,[25] n^{20}D 1.5709 (lit.[26] n^{20}D 1.5710). *Anal.* Calcd for $C_7H_{10}Br_2$: C, 33.09; H, 3.97; Br, 62.95. Found: C, 33.01; H, 3.86; Br, 62.99.

Fractions 850–1050 (4.613 g) were combined and found (tlc) to be a mixture of two compounds (**3** and **7**). Oxidation of the mixture with Jones reagent[17] produced a single compound (92% weight recovery) which was identified as **7** (ir, C=O, 5.69): n^{20}D 1.5552; 2,4-DNPH mp 198–199.5° (lit.[6] 201.5–202.5°). *Anal.* Calcd for $C_{13}H_{13}N_4O_4Br$: C, 42.27; H, 3.52; N, 15.13. Found: C, 42.69; H, 3.54; N, 15.13. Examination of the integrated pmr spectrum of collected glpc peak 5 indicated that this ketone constituted 33 ± 2% of that fraction.

Fractions 1051–1150 (4.723 g) were combined and the residue, on removal of the solvent, crystallized. Sublimation of this pale yellow material yielded a white, waxy solid, mp 44.5–46.0°, which proved to be identical with glpc peak 4. This material was identified as **3** by (a) elemental analysis (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 43.82; H, 5.88; Br, 41.93); (b) high yield (93%) conversion to the bromo ketone **7** on treatment with Jones reagent[17] in acetone at 0° for 5 min, and (c) its spectra [ir, –OH, 2.81 (sharp) and 2.90 μ (broad); pmr (100 MHz) δ 3.88 (1 H, $W_{1/2}$ = 3.9 Hz), 3.70 (t of d, $J_{2,3\text{-cis}}$ = 6.0 Hz, $J_{2,3\text{-trans}}$ = 5.5 Hz, $J_{2,7}$ = 1.6 Hz)].

Fractions 1151–1250 (7.086 g) were a mixture (tlc) of two compounds (**3** and **8**). A portion of this mixture (4.0 g) was rechromatographed (2 cm i.d., 250 g) and the column was eluted with 4:1 (v/v) cyclohexane–ether (10-ml fractions were taken). In this chromatography, fractions 151–200 contained material identical with **3**, while fractions 250–499 contained a new material which produced a white waxy solid (0.522 g) on sublimation. This material (mp 53–55°) was identical with the second component of glpc peak 5 by pmr and examination of the integrated pmr spectrum of glpc peak 5 indicated that this material constituted 66 ± 2% of that fraction. This material was identified as **8** by (a) elemental analyses (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 43.98; H, 5.76; Br, 42.04) and (b) high yield (89%) conversion to the corresponding bromo ketone **12** on treatment with Jones reagent as outlined above [The 2,4-DNPH had double mp 119.5–120.5 and 156.5–157.2° (lit.[30] 116.5–117.5 and 151.5–152.5°). *Anal.*

(23) DMSO, Fisher Certified Reagent, was dried over molecular sieve prior to use. NBS was obtained from Arapahoe Chemical Co., Boulder, Colo., and used as received. Bicyclo[2.2.1]heptene (norbornene) was obtained from the Aldrich Chemical Co., Milwaukee, Wis., and distilled from sodium wire prior to use. Gas–liquid partition chromatography (glpc) was carried out on an Aerograph A90-P3 instrument under the conditions specified. Woelm activity grade I columns and thin layer plates of silica gel were used throughout. Infrared spectra were taken as neat oils or KBr pellets on a Beckman IR-5A spectrophotometer.[24] Proton magnetic resonance (pmr) spectra were taken on Varian A-60, A-60A, XL-100-15, and HR-220[25] spectrometers and values are expressed in parts per million (δ) relative to TMS = 0.00.[26] Melting points were obtained on a Thomas–Hoover melting point apparatus in sealed capillaries and are uncorrected. Analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

(24) The spectrophotometer was purchased from funds provided by a grant (CA 08841) from the National Cancer Institute, National Institutes of Health.

(25) These spectra were graciously provided by Professor A. Lewin, Department of Chemistry, Brooklyn Polytechnic Institute, Brooklyn, N. Y. We gratefully acknowledge her interest and constructive comments.

(26) The complete details of the pmr spectra of the compounds reported here will be the subject of a future communication. Copies of the spectra are available from the senior author on request.

(27) Subsequent analysis incidated that significant (30–50%) quantities of nortricyclene bromide as well as smaller amounts of the other products may be lost as the solvent is removed.

(28) These spectra were provided by Professor N. LeBel, Department of Chemistry, Wayne State University, to whom we are grateful.

(29) H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

(30) A. C. Oehlschlager, C. D. Kennedy, and L. H. Zalkow, *J. Org. Chem.*, **31**, 1628 (1966).

Calcd for $C_{13}H_{13}N_4O_4Br$: C, 42.27; H, 3.52. Found: C, 42.18; H, 3.55]; and (c) spectra [ir -OH, 2.74 (sharp) and 3.00 μ (broad); pmr (100 MHz) δ 4.20 (1 H) unresolved multiplet ($W_{1/2}$ = 4.5 Hz), 3.78 (1 H) d of d ($J_{2,3\text{-cis}}$ = 7.2 Hz, $J_{2,3\text{-trans}}$ = 2.6 Hz)].

Compound **10** was not found on column chromatography. Collection of glpc peak 2 and examination of its pmr spectrum (100 MHz) led us to the conclusion (by comparison to the spectrum of an authentic sample)[7b,25] that it was *endo-exo*-2,3-dibromobicyclo[2.2.1]heptane (**10**).

***syn*-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (3) and *syn*-7-Bromobicyclo[2.2.1]heptan-2-*endo*-ol (6).**—The bromo ketone **7** (73.2 g, 0.495 mol) was placed in THF (1 l.) and treated with diborane (550 ml of a 1 *M* solution)[18] added dropwise, with stirring, through an addition funnel. After the addition was complete, the reaction mixture was permitted to stir at room temperature for 3 hr and the resulting solution was extracted with ether (three 300-ml portions). The combined ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent yielded an orange oil (93.9 g, 99%). Analysis (pmr integration) indicated a 5:3 mixture of **3** and what was presumed to be **6**. A portion of the reaction mixture (78.8 g) was fractionated as follows (0.1 mm): fraction 1 (6.0 g), 76–78°; fraction 2, 18.0 g, 80–85°; fraction 3, 29.2 g, 85–88°; fraction 4, 11.9 g, 88–90°. In fraction 4, by pmr integration, the ratio of **3** to presumed **6** was *ca.* 3:5. The earlier fractions were recombined and distilled to yield 37.7 g of material of fraction 4 quality. This material was redistilled to yield a mixture in which the ratio of **3** to presumed **6** was 1:2.5. Chromatography (2.5 cm i.d., 500 g) utilizing 1:1 (v/v) heptane–ether as eluent (250 ml fractions) yielded presumed **6** (fractions 18–30, 3.86 g). This material crystallized from heptane–ether (4:1 v/v) yielding needles, mp 55.5–57.0°, and was characterized as **6** by (a) elemental analysis (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 44.16; H, 5.77; Br, 41.66); (b) high yield (93.5%) conversion under Jones oxidation conditions (*vide supra*) to **7**; and (c) spectra [ir -OH, 2.77 (sharp), 2.98 μ (broad); pmr δ 4.47 (1 H) complex multiplet (d of t), $J_{2,3\text{-cis}}$ = 10.5 Hz, $J_{2,3\text{-trans}}$ = $J_{1,2}$ = 3.0 Hz; 4.12 (1 H), narrow multiplet].

***anti*-7-Bromobicyclo[2.2.1]heptan-2-*endo*-ol (9).**—*anti*-7-Bromobicyclo[2.2.1]heptan-2-one (**12**) (9.481 g, 0.05 mol) was dissolved in absolute methyl alcohol (200 ml) and, with stirring, sodium borohydride (1.805 g, 0.05 mol) was added over several minutes. After the addition was complete, the mixture was stirred for 0.5 hr and poured, with stirring, into water (500 ml). The aqueous solution was neutralized with dilute (6 *N*) HCl and extracted with ether (six 250-ml portions). The combined ether extracts were washed with water and dried over magnesium sulfate, and the solvent was removed to yield essentially pure **9** (8.769 g, 91.5%). Crystallization from heptane–ether (4:1 v/v) followed by several sublimations (0.03 mm) yielded material, mp 67.5–69°, which was identified as **9** by (a) elemental analysis (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 43.82; H, 5.88; Br, 41.93); (b) high yield conversion (96.5%) to **12** under conditions of the Jones oxidation (*vide supra*); and (c) spectra [ir -OH 2.78 (sharp), 2.99 μ (broad); pmr δ 4.25 (1 H) d of t, $J_{2,3\text{-cis}}$ = 10.0 Hz, $J_{2,3\text{-trans}}$ = $J_{1,2}$ = 3.8 Hz].

***exo*-3-Bromobicyclo[2.2.1]heptan-2-one (14).**—Bicyclo[2.2.1]-heptan-2-one (**13**) (50.0 g, 0.453 mol) in glacial acetic acid (500 ml) was treated with pyridinium bromide perbromide[21] and the mixture was warmed on the steam bath until solution was complete (0.5 hr.). The reaction mixture was transferred to a large beaker and aqueous sodium hydroxide (12 *N*) solution was added to neutralize the acetic acid [the final stages of neutralization being completed through addition of sodium carbonate solution (10%)]. The aqueous solution was extracted with ether (five 200-ml portions) and the combined ether extract was washed with water, 10% aqueous sodium carbonate, and water and then dried over magnesium sulfate. Removal of the solvent yielded an orange acrid oil (75.1 g, 89.5%) which was, by pmr integration, predominantly (*ca.* 95%) **14** although about 5% of **15** was clearly present. The oil was dissolved in ether and crystallization was induced by cooling (−78°) and scratching. The crystals of **14** liquefied on warming to room temperature: $n^{20}D$ 1.5295 (lit.[20] $n^{20}D$ 1.5298); ir C=O, 5.80 μ; pmr δ 3.76 (1 H), d, $J_{2,7\text{-anti}}$ = 3.0 Hz; 2,4-DNPH mp 148.5–150°. *Anal.* Calcd for $C_{13}H_{13}N_4O_4Br$: C, 42.27; H, 3.52; N, 15.13. Found C, 42.53; H, 3.76; N, 15.06.

***endo*-3-Bromobicyclo[2.2.1]heptan-2-one (15).**—The concentrate from successive crystallizations of **14** was separated into two components on a 20 ft × 0.375 in. preparative glass glpc column of XE-60 (10% on firebrick) (He flow rate 110 cc/min, column temperature 160°, injector 175°, detector 170°, collector 165°). Component 1 (**14**) had retention time 27.6 min, and component 2 had retention time 35.5 min. The latter was identified as **15**: $n^{20}D$ 1.5319; ir C=O, 5.80 μ; pmr δ 4.30 (1 H), d, $J_{3,4}$ = 4.5 Hz; 2,4-DNPH mp 146.5–147.5°. *Anal.* Calcd for $C_{13}H_{13}N_4O_4Br$: C, 42.27; H, 3.52; N, 15.13. Found: C, 42.48; H, 3.32; N, 14.88. The 2,4-DNPH derivatives of **14** and **15** showed significant (*ca.* 30°) depression on admixture.

Isomerization of 14 to 15.—*exo*-3-Bromobicyclo[2.2.1]heptan-2-one (**14**) (1.58 g, 8 mmol) was dissolved in *tert*-butyl alcohol (50 ml) and treated with potassium *tert*-butoxide (896 mg, 8 mmol). After standing overnight at room temperature, the sample was diluted with water, neutralized, and extracted with ether. The ether extract was dried, the solvent was removed, and the residue was examined by pmr. The spectrum was that of a 1:1 mixture of **14** and **15**.

***exo*-3-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (16) and *exo*-3-Bromobicyclo[2.2.1]heptan-2-*endo*-ol (5).**—*exo*-3-Bromobicyclo-[2.2.1]heptan-2-one (**14**) (9.361 g, 0.049 mol) was dissolved in THF (100 ml) and diborane (58 ml of a 1 *M* solution)[18] was added dropwise with stirring. The reaction mixture was allowed to stir at room temperature for 2 hr after the addition was complete. The resulting mixture was poured, with stirring, into ice–water and worked up as indicated above to yield a colorless oil (9.257 g, 91%) which was a mixture of two compounds (*ca.* 1:1 by pmr integration). A portion of this mixture (4.0 g) was fractionally distilled at 0.02 mm through an 8 in. Vigreux column to yield fraction 1, 35–40° (1.154 g), fraction 2, 40–45° (0.814 g), fraction 3, 50–53° (0.796 g), and fraction 4, 53–55° (1.118 g). In fractions 3 and 4 the ratio of the two compounds was 10:1. Combination and redistillation of fractions 3 and 4 yielded a single compound, identified as **5**: $n^{20}D$ 1.5367 (lit.[20] $n^{20}D$ 1.5375); ir, -OH, 2.78 (sharp) and 2.98 μ (broad); pmr δ 4.49 (1 H), d of d, $J_{2,3\text{-trans}}$ = 2.6 Hz, $J_{1,2}$ = 4.5 Hz, $J_{2,6\text{-exo}}$ = 1.2 Hz; 3.52 (1 H), t, $J_{2,3\text{-trans}}$ = $J_{3,7\text{-anti}}$ = 2.6 Hz. The *p*-nitrobenzoate ester was prepared, mp 129.5–130.5°. *Anal.* Calcd for $C_{14}H_{14}NO_4Br$: C, 49.43; H, 4.15; Br, 23.49; N, 4.12. Found: C, 49.38; H, 3.99; Br, 23.47; N, 4.46. This ester was hydrolyzed with methanolic aqueous sodium hydroxide to the same bromohydrin from which it was formed (84.8%) and the latter was reoxidized, under the usual conditions with Jones reagent (*vide supra*) to yield the bromo ketone **14** in 93% yield. The remainder of the reaction mixture was enriched in the other isomer and was identical with **16** as indicated below.

***exo*-3-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (16). The Sodium Borohydride Reduction of 14.**—*exo*-3-Bromobicyclo[2.2.1]heptan-2-one (**14**) (15.8 g, 0.083 mol) was dissolved in absolute methanol (250 ml) and sodium borohydride (3.403 g, 0.07 mol) was added during 1–2 min. The reaction was permitted to stir at room temperature for 1 hr and was then poured into 500 ml of water, with stirring. The reaction was worked up in the usual fashion to yield a colorless oil (12.1 g, 87.6%). The oil, in heptane–ether (4:1 v/v) crystallized at −10° and the crystals were filtered off at −20°. These crystals reverted to an oil at room temperature and the latter was characterized as **16**, identical with the second component in the diborane reduction of **14** by (a) elemental analysis (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 43.86; H, 5.85; Br, 42.32); (b) $n^{20}D$ 1.5376 (lit.[20] $n^{20}D$ 1.5377); (c) spectra [ir, -OH, 2.83 (sharp) and 2.90 μ (broad); pmr δ 4.06 (1 H) d of d, $J_{2,3\text{-cis}}$ = $J_{3,7\text{-anti}}$ = 2.0 Hz; 3.56 (1 H) d of d, $J_{2,3\text{-cis}}$ = 6.0 Hz, $J_{2,7\text{-anti}}$ = 1.4 Hz].

***endo*-3-Bromobicyclo[2.2.1]heptan-2-*endo*-ol (17).**—*endo*-3-Bromobicyclo[2.2.1]heptan-2-one (**15**) (1.136 g, 6.1 mmol) was dissolved in absolute methanol (25 ml) and sodium borohydride (240.5 mg, 6.4 mmol) was added during about 1 min. The reaction was stirred at room temperature and worked up in the usual fashion (*vide supra*) to yield **17** (970 mg), $n^{20}D$ 1.5426 (lit.[20] $n^{20}D$ 1.5433). *Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.64; Br, 41.88. Found: C, 43.97; H, 5.60; Br, 42.04. Spectra follow: ir -OH, 2.83 (sharp) and 2.91 μ (broad); pmr δ 4.36 (1 H) d of d of d, $J_{2,3\text{-cis}}$ = 9.0 Hz, $J_{3,4}$ = 3.2 Hz, $J_{3,5\text{-exo}}$ = 1.2 Hz; 3.78 (1 H) d of d of d, $J_{2,3\text{-cis}}$ = 9.0 Hz $J_{3,4}$ = 3.2 Hz, $J_{3,5\text{-exo}}$ = 1.2 Hz; 3.78 (1 H) d of d of d, $J_{2,3\text{-cis}}$ = 9.0 Hz, $J_{1,2}$ = 3.3 Hz, $J_{2,6\text{-exo}}$ = 1.0 Hz.

endo-**3-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (18).**—*exo*-3-Mercurichloridebicyclo[2.2.1]heptan-2-*exo*-ol (**19**)[22] (86 g, 0.25 mol) was dissolved in carbon tetrachloride (2 l.) and, with stirring, bromine (40 g, 0.5 mol) in CCl_4 (500 ml) was added through a pressure-equilibrated dropping funnel. The reaction was permitted to stir overnight at room temperature and the precipitate which formed was removed with suction filtration. The CCl_4 filtrate was washed with water and 10% sodium carbonate, and dried over magnesium sulfate. Removal of the solvent at reduced pressure yielded a dark oil (30.7 g) a portion of which (9.50 g) was chromatographed (3.5 cm i.d., 1000 g), 250-ml fractions being taken. Fractions 12–15 (0.965 g) consisted of nearly pure **14** (pmr). Fractions 17–21 (1.524 g) consisted of **16** while fractions 24–35 (1.625 g) were a new compound which crystallized on standing and was identified as **18**, mp 80–81°, by (a) elemental analysis (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 43.88; H, 5.76; Br, 41.26); (b) spectra [ir –OH 2.78 (sharp) and 2.90 μ (broad); pmr δ 3.91 (1 H) complex multiplet ($W_{1/2}$ = 9.0 Hz), 3.76 (1 H), t, $J_{2,3,\text{trans}} = J_{2,7\text{-anti}}$ = 2.1 Hz].

Attempted Isomerization of Products in DMSO in the Presence of NBS.—The product (1.5 g) was dissolved in DMSO (25 ml). Water (0.5 ml) was added and this was followed by NBS (2.0 g). The mixture was heated to 60° and allowed to cool and stir for 0.5 hr. The work-up then paralleled that of the original reaction mixture. The resulting product (1.35–1.45 g) was examined by pmr and tlc. No evidence for rearrangement, within the limits of detectability (*ca.* 2–3%), by comparison to known mixtures, was found.

Registry No.—**1**, 498-66-8; **3**, 32819-60-6; **4**, 695; 02-3; **5**, 32784-96-6; **5** *p*-nitrobenzoate, 32819-61-7-**6**, 32819-62-8; **7**, 7176-91-2; **8**, 32819-64-0; **9**, 7242-94-6; **10**, 2843-52-9; **11**, 32346-69-3; **12**, 7242-95-7; **14**, 1073-25-2; **14** 2,4-DNP, 32784-98-8; **15**, 1073-24-1; **15** 2,4-DNP, 32819-68-4; **16**, 4321-51-1; **17**, 32819-70-8; **18**, 4321-52-2; dimethyl sulfoxide, 67-68-5; NBS, 128-08-5.

A Novel Anodic Synthesis of Sulfonium Salt from Diphenyl Sulfide[1]

KENJI UNEYAMA AND SIGERU TORII*

Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama, Japan

Received July 22, 1971

Diphenyl sulfide (1), dissolved in acetonitrile containing $LiClO_4$, was electrolyzed at 30° to give diphenyl *p*-(phenylthio)phenyl sulfonium perchlorate (**3**), diphenyl sulfoxide (**4**), and 1,4-bisphenylthiobenzene (**5**). Sulfonium salt **3** predominated in the absence of water, while **4** increased as the concentration of water was raised.

The anodic oxidation of organic sulfides examined by Fichter, *et al.*,[2] gave corresponding sulfoxides, sulfones, and sulfonic acids in the mixed media of water and protic solvents such as methanol and acetic acid, but the reaction in aprotic media has received little attention except for some polarographic studies.[3,4] In the previous paper,[1] we reported an anodic oxidation of some phenyl sulfides in acetonitrile in which substrates competitively undergo either sulfoxidation or S–R bond cleavage to thiyl radical PhS· and cation R^+ through electron deficient divalent sulfide of the type $PhS\overset{+}{\cdot}R$ and that the reaction pathways are controlled by the stability of the cation R^+. As an extention of the work, this paper describes a novel anodic synthesis of a sulfonium salt from diphenyl sulfide **1**.

Diphenyl sulfide **1** (465 mg, 2.5×10^{-3} mol) dissolved in 10 ml of acetonitrile containing 500 mg of $LiClO_4$ was electrolyzed at 30° using 3 cm^2 platinum foils as electrodes without separation of the anodic compartment from the cathodic. One equivalent of constant current (200 mA) was applied while terminal voltage range was 6–10 V.

Products were diphenyl *p*-(phenylthio)phenyl sulfonium perchlorate (**3**), diphenyl sulfoxide (**4**), and 1,4-bisphenylthiobenzene (**5**). No diphenyl disulfide was detected by vpc. Sulfonium salt **3** predominated in the absence of water, while sulfoxide **4** increased as the concentration of water was raised (Table I).

TABLE I

PRODUCTS OF ANODIC OXIDATION OF 1 IN ACETONITRILE

$[H_2O]^a$	1[b]	3[c]	4[c]	5[c]
0	19	71	1	4
0.1	25	63	4	3
1.0	27	46	25	2

[a] Milliliters of water in 10 ml of acetonitrile solution. [b] Recovered phenyl sulfide **1**. [c] Per cent on the basis of starting material **1**.

Sulfonium salt **3**, a slightly brown colored amorphous solid, showed a positive Beilstein test and was soluble in chloroform and acetone and insoluble in ether, benzene, and *n*-hexane. Its ir spectrum showed a strong band at 1090 cm^{-1} corresponding to sulfonium perchlorate and the nmr revealed a singlet (10 H) at τ 2.30 in $CDCl_3$ which is consistent with that of triphenyl sulfonium perchlorate.[5]

Oxidation of **3** with hydrogen peroxide in acetic acid afforded sulfone **6** (Scheme I). The sulfone **6** was subjected to nucleophilic substitution with sodium ethoxide in ethanol–tetrahydrofuran at room temperature to afford **1** (50%), *p*-ethoxyphenyl phenyl sulfone (**7**, 62%), and phenyl *p*-(phenylsulfonyl)phenyl sulfide (**8**, 2%) and phenetole **9** (2%). Treatment of **6** with benzenethiol in pyridine provided **1** (62%) and **8** (68%). Thus, sodium ethoxide and benzenethiol preferentially attack the *p*-phenylsulfonylphenyl ring to split out **1**.[6] The structures of **4**, **5**, **7**, and **8** were assigned by comparing their spectrum data with those of authentic samples prepared by the routes as described in the Experimental Section.

It was previously proposed that anodic oxidation of

(1) Electrochemistry of Organic Sulfur Compounds. III. (a) K. Uneyama and S. Torii, *Tetrahedron Lett.*, 329 (1971). (b) K. Uneyama, S. Torii, and S. Oae, *Bull. Chem. Soc. Jap.*, **44**, 815 (1971).

(2) F. Fichter, P. Sjöstedt, W. Wenk, and F. Braun, *Chem. Ber.*, **43**, 3422 (1910); **45**, 1373 (1912); **47**, 1526 (1914).

(3) M. M. Nicholson, *J. Amer. Chem. Soc.*, **76**, 2539 (1954). A. Zweig, G. Metzler, A. H. Maurer, and B. G. Roberts, *ibid.*, **89**, 4091 (1967). D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *ibid.*, **93**, 2258 (1971).

(4) P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, **116**, 1499 (1969).

(5) S. Oae and Y. H. Khim, *Bull. Chem. Soc., Jap.*, **42**, 1622 (1969).

(6) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4803 (1961); H. M. R. Hoffmann, *J. Chem. Soc.*, 823 (1965); S. Oae and Y. H. Khim, *Bull Chem. Soc., Jap.*, **42**, 3528 (1969).