Anal. Calcd. for $C_7H_9ClO_4$: C, 43.64; H, 4.68; Cl, 18.44; neut. equiv., 96.3. Found: C, 43.72; H, 4.70; Cl, 18.22; neut. equiv., 96.6.

trans-4-Chloro-*cis*-cyclopentane-1,3-dicarboxylic Acid.—A similar oxidation procedure using *exo*-dehydronorbornyl chloride[10] gave a 30% yield of *trans*-4-chloro-*cis*-cyclopentane-1,3-dicarboxylic acid, m.p. 95.5–97.5° after crystallization.

Anal. Calcd. for $C_7H_9ClO_4$: C, 43.64; H, 4.68; Cl, 18.44; neut. equiv., 96.3. Found: C, 44.29, 44.18; H, 4.90, 5.08; Cl, 18.40; neut. equiv., 95.5.

syn-7-Chloronorbornene.—The following procedure gave the best results of the several which were investigated for conversion of the chlorohydrin to the corresponding chloronorbornene. To 5 g. (0.026 mole) of 2-naphthoyl chloride was added a solution of 4 g. (0.027 mole) of *syn*-7-chloro-*exo*-norborneol in dry pyridine. The reaction mixture became warm and was cooled in an ice-bath. The mixture was allowed to stand overnight and was then poured with stirring into ice-water. The solid ester was collected, washed in cold water, taken up in ether and the ethereal solution washed with dilute acid, dilute sodium carbonate solution, and water and dried over sodium sulfate. *syn*-7-Chloro-*exo*-norbornyl 2-naphthoate was obtained by removal of the ether and recrystallization of the residue from pentane–ether. The yield was 70% of material with m.p. 93–94°.

Anal. Calcd. for $C_{18}H_{17}O_2Cl$: C, 71.87; H, 5.70; Cl, 11.79. Found: C, 71.63; H, 5.89; Cl, 11.75.

The 2-naphthoate ester (10 g., 0.033 mole) was placed in a flask fitted with a 15-cm. Vigreux column and heated at 280° (60–150 mm.) for seven hours in a Woods metal-bath. The distillate was dissolved in pentane and shaken with bicarbonate solution, water and finally dried over sodium sulfate. The ether was evaporated and the residue distilled through a semimicro column.[19] The yield of *syn*-7-chloronorbornene, b.p. 45° (50 mm.), $n^{25}D$ 1.4920, was 1.40 g. (30%).

Anal. Calcd. for C_7H_9Cl: C, 65.37; H, 7.05. Found: C, 65.20; H, 7.19.

The infrared spectrum (Fig. 1) of the material prepared in the above manner indicated the presence of 10–20% of nortricyclyl chloride.

anti-7-Chloronorbornene was prepared from *anti*-7-chloro-*exo*-norbornyl 2-naphthoate, m.p. 92–93° (ether-pentane), as described above.

Anal. Calcd. for $C_{18}H_{17}O_2Cl$: C, 71.87; H, 5.70; Cl, 11.79. Found: C, 72.28; H, 5.78; Cl, 12.05, 11.98.

Pyrolysis of the naphthoate ester gave a 28% yield of *anti*-7-chloronorbornene, $n^{25}D$ 1.4927. The infrared spectrum of the product is given in Fig. 1 and indicates the presence of 10–20% of nortricyclyl chloride.

7-Chloronorbornane.—*syn*-7-Chloronorbornene (0.250 g.) was dissolved in 20 ml. of ether and shaken with hydrogen over platinum oxide at atmospheric pressure for two hours at 10°. Hydrogen uptake ceased after one mole had been absorbed. The catalyst was separated, the ether removed and the residue distilled without fractionation to yield 7-chloronorbornane, $n^{25}D$ 1.4878.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.50; Cl, 27.15. Found: C, 64.94; H, 8.16; Cl, 26.85.

The infrared spectrum of the material obtained above was essentially the same as that of a sample obtained by hydrogenation of *anti*-7-chloronorbornene (see Fig. 1).

Dipole moments were determined by the method described previously.[24] The data are presented in Tables I and II.

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[24] J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, This Journal, **71**, 843 (1949).

Cambridge, Mass.

[Contribution from the Department of Chemistry, University of Colorado]

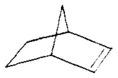
Additions to Bicyclic Olefins. *p*-Thiocresol and Norbornylene

By Stanley J. Cristol and Gordon D. Brindell

Received March 22, 1954

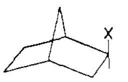
The addition of *p*-thiocresol to norbornylene gave pure *exo*-norbornyl *p*-tolyl thioether, as shown by conversion of the reaction mixture to pure *exo*-norbornyl *p*-tolyl sulfone, in excellent yield, and without contamination with measurable amounts of either the *endo* isomer or of the anticipated rearrangement product, 7-*p*-thiocresoxynorcamphane. The *endo* and *exo* sulfones have been prepared by several straightforward syntheses. The free-radical nature of the addition process has been demonstrated, and the relative reactivity of the *p*-thiocresoxy radical toward norbornylene and cyclohexene has been measured. The question of carbon-bridged mesomeric free radicals in this and analogous systems has been discussed.

The mechanistic details of the addition of mercaptans to olefins *via* free-radical intermediates are well established.[1,2] As part of a program of study of additions to bicyclic olefins, we undertook the present research, the purpose of which was to elaborate the stereochemistry of addition of *p*-thiocresol to (2,2,1)-bicyclo-2-heptene (norbornylene, I)

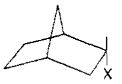


I

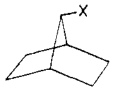
and to determine whether or not rearrangements of the intermediate substituted norbornyl radical occurred. The products of addition without rearrangement might be *exo*-norbornyl *p*-tolyl thioether (IIa) or the *endo* analog (IIIa); the rearrangement product, based upon analogy with ionic rearrangements, would be anticipated to be 7-*p*-thiocresoxynorcamphane (IVa),



II



III



IV

a, X = $SC_6H_4CH_3$-*p*
b, X = $SO_2C_6H_4CH_3$-*p*
c, X = $OSO_2C_6H_4Br$-*p*

This system is of particular interest in consideration of radical-rearrangement processes, as ionic additions to analogous systems are generally accompanied by Wagner–Meerwein rearrangements.[3] Thus, for example, rearrangements have been observed in the addition of strong acids to *endo*-dicyclopentadiene and in the acid-catalyzed solvation of *endo*-

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(1) M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry and Industry*, 752 (1938).

(2) S. O. Jones and E. E. Reid, This Journal, **60**, 2452 (1938).

(3) For a general review of such ionic rearrangements, see P. D. Bartlett in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 55–70.

dicyclopentadiene,[4] the nature of the rearrangement being demonstrated by Bartlett and his coworkers.[5]

Recently Kwart and Kaplan[6] have reported that addition of bromine to norbornylene gives products which arise as a result of Wagner-type rearrangements.

Free-radical additions to norbornylene systems have not received careful scrutiny. Kharasch and Friedlander[7] added bromotrichloromethane to norbornylene and to dicyclopentadiene, but did not carry out a structure proof on their product. Fawcett[8] assigned the structure *trans*-2-bromo-3-trichloromethylnorcamphane to the addition product of norbornylene and bromotrichloromethane on the basis of the difficulty of dehydrobromination with alkali of this material,[7] but the basis for this assumption no longer appears valid.[9] Discussion of other pertinent work is given below.

When norbornylene was treated with an equimolar amount of *p*-thiocresol, a strongly exothermic reaction occurred. The resulting mixture was submitted to vacuum distillation to give an 85% yield of *exo*-norbornyl *p*-tolyl thioether (IIa). The structure of this product was demonstrated to be *exo* by oxidation of the thioether to the pure *exo*-sulfone in 94% yield. This sample of *exo*-norbornyl *p*-tolyl sulfone (IIb), as isolated without purification, had a melting point as high as we have observed with any purified sample and therefore did not contain significant amounts of either IIIb or IVb.

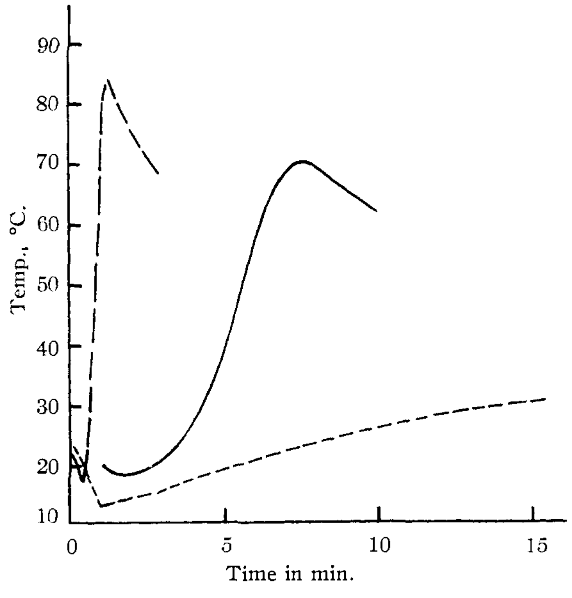

Fig. 1.—Temperatures reached in the reaction of *p*-thiocresol with norbornylene: ——, no addendum; – –, with benzoyl peroxide; ------, with trinitrobenzene.

When the reaction was carried out in chlorobenzene solution, the results were substantially unchanged.

Thus it is clear that free-radical addition of *p*-thiocresol to norbornylene did not lead to rearrangement of a type analogous to the Wagner–Meerwein rearrangement.

The free-radical chain nature of the reaction was confirmed by a study of the effect of peroxide catalysts and of inhibitors upon the rate of the reaction. The addition reaction is vigorously exothermic, and, when a mixture of 4 millimoles of *p*-thiocresol and 4 millimoles of norbornylene (each distilled, but not kept under nitrogen) was placed in a test-tube containing a thermometer, the temperature first fell, due presumably to heat of mixing, then rose slowly to about 70°, requiring 7 to 8 minutes to reach the maximum temperature (see the solid curve, Fig. 1). When 5 mg. (0.02 mmole) of benzoyl peroxide was added, the reaction proceeded much more rapidly, reaching the maximum temperature of 84° in less than 2 minutes (see the dashed curve, Fig. 1). On the other hand, when 67 mg. (0.3 mmole) of trinitrobenzene was added, the reaction was strikingly moderated (Fig. 1, dotted curve). These results appear sufficient to establish the radical course of the reaction.[1]

As none of the possible product thioethers or sulfones, II, III or IV, was known, it was necessary to prepare certain of these of definite configuration to establish the course of the reaction under study. We have prepared IIb and IIIb and have established the configurations by two independent preparations and have thereby established the nature of the mercaptan–norbornylene product as *exo* (IIa).

The best evidence for the configurations involves the formation of the thioethers IIa and IIIa by displacement reactions with lithium *p*-thiocresoxide on the norbornyl *p*-bromobenzenesulfonates IIIc and IIc, respectively.

When *endo*-norbornyl *p*-bromobenzenesulfonate[10] was treated with lithium *p*-thiocresoxide in acetone, and the resulting thioether oxidized with hydrogen peroxide in acetic acid a 48% yield of *exo*-norbornyl *p*-tolyl sulfone was obtained. This material was identical with the sulfone obtained from the norbornylene addition product. The *exo* structure is assigned to this product on the assumption that a Walden inversion occurred in the displacement reaction.[11] This conclusion is strengthened by the fact that treatment of the *exo*-norbornyl *p*-bromobenzenesulfonate[10] led, after oxidation, to a 20% yield of an isomeric sulfone, which may thus be assigned the *endo* configuration.

To the best of our knowledge, no analogous direct displacement reactions of ring substituents in norcamphane and camphane systems appear to be described in the literature, but we were encouraged to attempt these experiments by Dr. Saul Winstein, who kindly informed us of several such displacement reactions conducted by one of his students.

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[4] H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723, 1178 (1945); **68**, 8 (1946).

[5] P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); P. D. Bartlett and I. S. Goldstein, *ibid.*, **69**, 2553 (1947).

[6] H. Kwart and L. A. Kaplan, Abstract of Papers presented at the 124th Meeting of the American Chemical Society, 1953, p. 88–90.

[7] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[8] F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

[9] S. J. Cristol and N. L. Hause, THIS JOURNAL, **74**, 2193 (1952).

[10] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

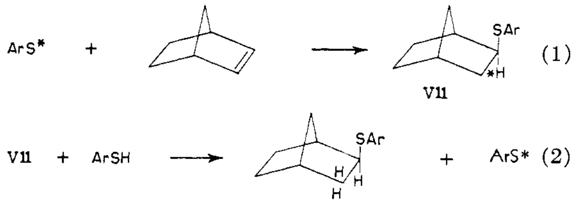
[11] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 181.

The second evidence stems from application of the Alder rule of predominant *endo* addition product in the diene synthesis with cyclopentadiene,[12] as modified by the effect of severity of reaction conditions.[12d,13] Craig,[13] for example, found that although the *endo* isomer was formed exclusively when cyclopentadiene and maleic anhydride react at room temperature,[12b] the *endo* isomer rearranges in part to the *exo* compound upon heating at 190° (this rearrangement was observed to be reversible). Thus a diene synthesis conducted at high temperatures would be expected to have an *endo–exo* ratio of products which would decrease with time.

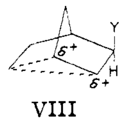
We have used the rule derivable from the above as an additional proof of the *exo-endo* relationship of the norbornyl *p*-tolyl sulfones. When cyclopentadiene was heated with vinyl *p*-tolyl sulfone for one hour at 160°, two isomers of dehydronorbornyl *p*-tolyl sulfone were separable by chromatographic analysis on alumina. The ratio of higher melting product V to lower melting product VI resulting under these conditions was 2.0 to 1.0. When the time of reaction was increased to 18 hours, the ratio was cut to 1.1 to 1.0. This may be offered as evidence that the lower melting form is the *exo* isomer. Hydrogenation of VI led to IIb, identical with the oxidized product of the addition reaction of mercaptan and norbornylene or of the product derived from the *endo*-sulfonate reaction. Hydrogenation of the *endo* isomer V led to IIIb, which depressed the m.p. of the addition compound, and which was identical with the sulfone derived from the *exo* sulfonate.

When cyclopentadiene was added to vinyl *p*-tolyl thioether,[14] and the resulting product was submitted to oxidation, the *exo*-sulfone VI and the *endo*-sulfone V were obtained in yields of 10 and 18%, respectively. Relative yields in this reaction are in accord with the assumed configuration.

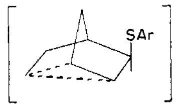
The mechanism for the radical chain portion of the addition reaction may therefore be formulated as



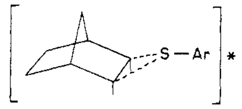
Although ionic additions to bicyclic olefins or rearrangements of the primary addition products appear to require the formulation of mesomeric cations of type VIII as intermediates to account for stereochemical and other results,[15] our data do not require the analogous mesomeric radical IX as an intermediate in this addition reaction. The presently available results may be explained on the basis of reaction at only one position of the bridged radical IX, but seem more logically considered upon the basis of the classical radical VII. The possibility of a sulfur-bridged radical of type X[16] must be considered, but cannot be adequately discussed now in view of lack of knowledge regarding the stereochemistry of addition of the hydrogen atom in step 2 of the chain process.



VIII



IX



X

Our results are consistent with the observed lack of rearrangement in the reactions of camphene[17] with carbon tetrachloride, chloroform and ethyl bromoacetate or in the decarbonmonoxylation of (2,2,2)-bicycloöctane-2-carboxaldehyde,[18] and they are not inconsistent with the rearrangements (ring opening) involved in the reaction of β-pinene with carbon tetrachloride,[19,20] chloroform[20] and ethyl bromoacetate,[20] in view of the recent work of Seubold[21] demonstrating the time lag involved in the rearrangement of the neophyl free radical to the β-phenyl-*t*-butyl radical.

On the other hand, Berson and Swidler[22] have suggested a mesomeric radical analogous to IX to explain the formation of some *exo-cis* dibromide by the free-radical bromination of *exo-cis*-3,6-endoxo-1,2,3,6-tetrahydrophthalic anhydride, a result opposite in nature to the exclusive *trans* addition observed in the free-radical addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene.[16] In this connection, proof of the structure of the addition product of bromotrichloromethane and norbornylene[7] or of similar addition products where both fragments of the addendum are identifiable is essential. We intend to undertake such a study.

The fact that cations of the norbornyl type appear to be mesomeric whereas radicals of equivalent structure apparently are not, may be rationalized

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(12) (a) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937); (b) K. Alder, G. Stein, F. v. Buddenbrock, W. Eckardt, W. Frercks and S. Schneider, *Ann.*, **514**, 1 (1934); (c) K. Alder, G. Stein, M. Leibmann and E. Rolland, *ibid.*, **514**, 197 (1934); (d) K. Alder and R. Rühmann, *ibid.*, **566**, 1 (1950).

(13) D. Craig, THIS JOURNAL, **73**, 4889 (1951).

(14) K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938), have previously reported this addition.

(15) See, for example, references 6, 10, as well as T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939), and H. Kwart, THIS JOURNAL, **75**, 5942 (1953).

(16) This formulation is equivalent to that proposed for an intermediate involved in addition of hydrogen bromide to olefins by H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

(17) G. Dupont, R. Dulou and G. Clement, *Bull. soc. chim.*, 1002 (1951).

(18) W. v. E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, THIS JOURNAL, **74**, 3000 (1952).

(19) D. M. Oldroyd, G. S. Fisher and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950).

(20) G. Dupont, R. Dulou and G. Clement, *Compt rend.*, **230**, 2027 (1950); *Bull. soc. chim.*, 1115 (1950); *ibid.*, 257 (1951).

(21) F. H. Seubold, THIS JOURNAL, **75**, 2532 (1953).

(22) J. A. Berson and R. Swidler, *ibid.*, **75**, 4366 (1953).

in terms of the much greater unsaturation of the cationic center (compared with the radical center) providing the impetus for the bond delocalization. Thus, the resonance energy for the mesomeric cation VIII may be favorable because the energy gained in making the second "half-bond" is greater than that lost in the conversion of the normal bond in a classical non-mesomeric cation to a "half-bond." The equivalent radical, with an additional electron compared with the cation, does not have so serious an electron deficiency and stabilization by carbon-bridging mesomerism would therefore appear to be less likely. This argument cannot be extended to reject structure X, in view of the possibilities of expansion of the valence shell of sulfur.[23]

Dr. J. de Heer of this Department has informed us that his approximate calculations indicate that the lowest lying molecular orbital in systems of this type is bonding, whereas higher molecular orbitals are antibonding. Such calculations are therefore consistent with the concepts of the mesomeric cation VIII and the non-mesomeric radical VII.

The fact that the *p*-thiocresoxy radical adds exclusively *exo* to norbornylene is consistent with the previous examples in non-chain processes.[24,25,26]

Kharasch and Friedlander[7] found that norbornylene was five times as reactive as cyclohexene toward the trichloromethyl radical. When equimolar amounts of these two olefins were allowed to compete for an amount of *p*-tolyl mercaptan slightly in excess of the amount necessary to react with one-half of the olefin present, the resulting product was a mixture of 94% of cyclohexene and 6% norbornylene. Calculations indicate that norbornylene is therefore about 45 times as reactive toward the *p*-thiocresoxy radical as is cyclohexene. Whether this enhancement in reactivity is due to stabilization in the transition state for the norbornylene case because of contributions of resonance structures analogous to IX or to relative destabilization owing to the strained norbornylene molecule cannot now be decided, but the latter explanation is favored in view of the discussion regarding IX above.

Acknowledgments.—The authors are indebted to Julius Hyman and Company and to the Shell Development Company for support of this work and for a fellowship for one of us. It is also their pleasure to acknowledge helpful discussions with Dr. Rex E. Lidov and Dr. Saul Winstein. Analyses were performed by Galbraith Laboratories.

Experimental

exo-Norbornyl *p*-Tolyl Thioether (IIa).—To 25 g. (0.266 mole) of norbornylene[27] in a flask equipped with a magnetic stirrer, thermometer and a reflux condenser, 32.9 g. (0.266 mole) of *p*-thiocresol was added in small portions. The temperature rose to 53° about ten minutes after the first addition. The remainder of mercaptan was added at such a rate that the temperature remained between 60 and 70°. Magnetic stirring was employed after the reaction had started and the solid mixture had liquefied. When the addition of mercaptan was complete the mixture was heated at 75° for 30 minutes with stirring. The mixture was then subjected to vacuum distillation. A small quantity of *p*-thiocresol, b.p. 110–113° (32 mm.), solidified in the condenser. The product distilled at 175–176° (11 mm.) and weighed 49.3 g. (85.5%). The product was colorless and had a refractive index, n^{20}_{D} 1.5758.

Anal. Calcd. for $C_{14}H_{18}S$: C, 77.01; H, 8.31. Found: C, 76.86; H, 8.40.

exo-Norbornyl *p*-Tolyl Sulfone (IIb).—To a solution of 527 mg. of the thioether (2.42 mmoles) in 2 ml. of glacial acetic acid was added 0.8 ml. of 30% hydrogen peroxide. The mixture was heated for 30 minutes on a steam-bath and was then allowed to stand at room temperature for two days. Addition of water to the reaction mixture and seeding with known *exo*-norbornyl 2-*p*-tolyl sulfone produced a white crystalline powder which when dry weighed 565 mg. (93.5%), m.p. 81–82°. When mixed with a sample of *exo*-norbornyl 2-*p*-tolyl sulfone (m.p. 78–79°) described below, it had m.p. 79–80°, whereas a mixture with the *endo* isomer showed a m.p. depression.

A preparation carried out as described above except that the addition of mercaptan to norbornylene was conducted in chlorobenzene gave a similar product. The sulfone melted at 81–82° without purification.

Proof of Free-radical Nature of Addition Reaction.—A mixture of 500 mg. (4 mmoles) of *p*-tolyl mercaptan and 379 mg. (4 mmoles) of norbornylene (both freshly distilled, but not kept under nitrogen) was prepared in a small insulated test-tube containing a thermometer. The temperature of the mixture fell at first, then increased to a maximum of 70° at 7.5 minutes.

A similar experiment was conducted, except that 5 mg. of benzoyl peroxide was added. The maximum temperature (84°) was reached in 1.25 minutes.

When a similar experiment was conducted (no peroxide added) in the presence of 67 mg. of trinitrobenzene, the temperature had not reached a maximum at the end of 18 minutes.

Details of the time–temperature curves in these reactions are given in Fig. 1.

Conversion of *endo*-Norbornyl *p*-Bromobenzenesulfonate (IIIc) to *exo*-Norbornyl *p*-Tolyl Sulfone (IIb).—Lithium *p*-thiocresoxide was prepared by evaporating to dryness a solution obtained by neutralizing *p*-tolyl mercaptan with aqueous lithium hydroxide to the bromophthalein end-point. The salt had to be protected from air to prevent formation of the disulfide.

A mixture of 894 mg. (2.70 mmoles) of *endo*-norbornyl *p*-bromobenzenesulfonate,[10] m.p. 60.5–62.0°, 354 mg. (2.72 mmoles) of lithium *p*-thiocresoxide and 25 ml. of dry acetone was sealed in a glass tube and heated on a steam-bath for several hours. The reaction mixture was decolorized by treatment on an alumina column. The solvent was then removed, and the residue was taken up in glacial acetic acid and treated with 30% hydrogen peroxide. The product was worked up as described above to give 324 mg. (48%) of slightly impure *exo*-norbornyl *p*-tolyl sulfone, m.p. 75.5–77°. One recrystallization from petroleum ether raised the m.p. to 78.5–79.3°. The melting point of this product was not depressed when mixed with the product derived from norbornylene and *p*-tolyl mercaptan, but was depressed by addition of the *endo* isomer.

Conversion of *exo*-Norbornyl *p*-Bromobenzenesulfonate (IIc) to *endo*-Norbornyl *p*-Tolyl Sulfone (IIIb).—The procedure described in the section above was substantially followed starting with 331 mg. (1.0 mmole) of *exo*-norbornyl *p*-bromobenzenesulfonate,[10] m.p. 56.5–57.3°, 130 mg. of lithium *p*-thiocresoxide and 10 ml. of dry acetone. The product was 47 mg. (20%) of slightly impure *endo*-norbornyl *p*-tolyl sulfone, m.p. 76–80°. One recrystallization from petroleum ether raised the m.p. to 78–81°. A mixed m.p. with a sample, m.p. 85–85.3°, prepared *via* the Diels–Alder synthesis (see below) was 81–83°.

Formation of Sulfones IIb and IIIb *via* Addition of Cyclopentadiene and *p*-Tolyl Vinyl Thioether.—Dehydronorbornyl *p*-tolyl thioether was prepared[14] from cyclopentadiene and *p*-tolyl vinyl thioether. One gram of this product was subjected to oxidation with 2.5 ml. of 30% hydrogen peroxide in 2.5 ml. of glacial acetic acid, and the reaction mixture was evaporated to dryness in an open beaker on a steam-bath. The glassy solid which remained was subjected

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(23) In this regard, compare C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950).

(24) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); **515**, 185 (1935).

(25) R. B. Woodward and H. Baer, THIS JOURNAL, **70**, 1161 (1948).

(26) G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstabler, *ibid.*, **75**, 384 (1953).

(27) L. M. Joshel and L. W. Butz, *ibid.*, **63**, 3350 (1941).

to chromatographic analysis on activated alumina and was eluted with 2–4 volume % of ethyl acetate in benzene. The *exo* sulfone was eluted first, although the separation was not clean. The recoveries were not good, giving 108 mg. (9.5%) of ***exo*-dehydronorbornyl *p*-tolyl sulfone**, m.p. 70–71° after recrystallization from petroleum ether, and 202 mg. (17.5%) of ***endo*-dehydronorbornyl *p*-tolyl sulfone**, m.p. 80–80.5° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.50. Found: (*exo*) C, 67.62; H, 6.42; (*endo*) C, 67.44; H, 6.50.

When the *exo*-dehydronorbornyl *p*-tolyl sulfone was subjected to catalytic hydrogenation in ethanol over palladium-on-charcoal catalyst at one atmosphere pressure, one mole of hydrogen was absorbed per mole of olefin to give *exo*-norbornyl *p*-tolyl sulfone (IIb), m.p. 81–82° after three recrystallizations from petroleum ether.

Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.24. Found: C, 67.00; H, 7.34.

A similar experiment with the *endo* unsaturated sulfone gave the *endo* compound IIIb, m.p. 85.3–85.5° after three recrystallizations from petroleum ether.

Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.24. Found: C, 67.00; H, 7.31.

_p_-Tolyl Vinyl Sulfone.—This sulfone was prepared according to the procedure described by Ford-Moore, Peters and Wakelin[28] for the phenyl analog.

To a solution of 98.6 g. (0.471 mole) of *p*-tolyl β-chloroethyl sulfone[29] in 900 ml. of benzene, 50.6 g. (0.5 mole) of triethylamine was added. The mixture was allowed to stand overnight. It was filtered and 53.9 g. (83%) of triethylammonium chloride was obtained. The filtrate was steam distilled to remove benzene. The residue was crystallized from 95% ethanol and gave a first crop of crystals weighing 33 g., m.p. 66° (reported[30] 65°). Partial evaporation of the mother liquors produced an additional 4.7 g. of crystals. The yield was 44% on the basis of isolated sulfone.

Dehydronorbornyl *p*-Tolyl Sulfones from Cyclopentadiene and *p*-Tolyl Vinyl Sulfone.—Solutions of freshly distilled cyclopentadiene (375 mg., 5.7 mmoles) and *p*-tolyl vinyl sulfone (863 mg., 4.7 mmoles) in 10 ml. of benzene containing a few mg. of 4-*t*-butylcatechol were heated in a furnace at 160 ± 3° for one hour and for 18 hours. At the end of the appropriate time, the tubes were removed, cooled and opened. The solutions were poured onto activated alumina columns and the *endo* and *exo* sulfones were separated fairly well by elution with 2–4% ethyl acetate in benzene. The middle fractions of the eluant often were mixtures of the two isomers and the compositions of these fractions were established with reference to a melting point–composition diagram. The one-hour sample gave 604 mg. (51%) of *endo*-dehydronorbornyl sulfone and 302 mg. (26%) of the *exo* sulfone, while the 18-hour sample gave 36% of the *endo* compound and 33% of the *exo* isomer. Intermediate times of reaction gave intermediate *endo-exo* ratios.

Competition of Norbornylene and Cyclohexene for a Limited Amount of *p*-Thiocresol.—Into a reaction flask cooled in a Dry Ice-bath was added 1.81 g. (19.2 mmole) of norbornylene and 2.00 ml. (1.62 g., 19.2 mmoles) of freshly distilled cyclohexene (n^{20}D 1.4460). When this mixture was cold, 2.45 g. (19.7 mmoles) of *p*-thiocresol was added. The cold-bath was removed and the reaction began as the mixture warmed to room temperature. The flask was shaken several times to aid mixing. The temperature in the reaction flask rose slowly to a maximum of 56°. When the reaction was complete, as evidenced by a decrease in the temperature in the reaction flask, the flask was heated to recover the unreacted olefin; the temperature of the heating-bath was raised finally to 150°. The distillate, which was collected in a receiver immersed in a Dry Ice-bath, weighed 1.202 g. and had a refractive index n^{20}D 1.4471. A plot of refractive index at 20° against mole per cent. norbornylene in cyclohexene from mixtures of known composition indicated the distillate to be approximately 6 mole per cent. in norbornylene. This was substantiated by the preparation of the triazole derivative of norbornylene. The refractive index plot which was linear over the range studied (0–50% norbornylene) gave an extrapolated value of n^{20}D 1.4634 for norbornylene.

Reaction of Phenyl Azide with the Norbornylene–Cyclohexene Distillate.—To the cyclohexene-norbornylene distillate obtained above, n^{20}D 1.4471, was added 508 mg. (4.28 mmoles) of phenyl azide.[31] The mixture was allowed to stand at room temperature overnight. Evaporation to dryness gave 63 mg. (0.53 mmole) of crude 3a,4,5,6,7,7a-hexahydro-1-phenyl-4,7-methanobenzotriazole, which melted at 96–97.5° after one recrystallization from methanol. A mixed m.p. with an authentic sample of the norbornylene phenylazide adduct[32] (m.p. 100–101°) was 97–99.5°.

Another experiment showed that the triazole derivative was formed in 62% yield based on norbornylene under the above conditions. Assuming a 60% yield in the present experiment, about 0.9 mmole of norbornylene was present in the original distillate. The amount of cyclohexene present was therefore 1.1 g. (14 mmoles). The composition of the distillate was thus 6 mole per cent. norbornylene. This result checks the quantitative refractive index experiment.

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[28] A. H. Ford-Moore, R. A. Peters and R. W. Wakelin, *J. Chem. Soc.*, 1754 (1949).

[29] H. Gilman and N. J. Beaber, THIS JOURNAL, **47**, 1449 (1925).

[30] French Patent 789,947 (1935); *Chem. Z.*, **107**, I, 1504 (1936).

[31] R. O. Lindsay and C. F. H. Allen, *Org. Syntheses*, **22**, 96 (1942).

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

[CONTRIBUTION FROM DEFENCE RESEARCH CHEMICAL LABORATORIES]

Some Derivatives of Bicyclo[2,2,1]heptane-1-thionium Bromide[1]

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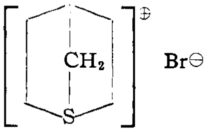
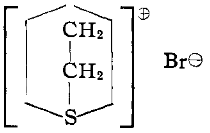
7-Hydroxymethylbicyclo(2,2,1)heptane-1-thionium bromide, and 7-ethylbicyclo(2,2,1)heptane-1-thionium chloride, bromide and nitrate were synthesized and tested for biological activity.

As part of a study of the synthesis of bicyclic ring systems, Prelog has described two such molecules in which one of the bridgehead atoms is sulfur[2,3] (I and II). In view of the unusual nature of these compounds, it was of interest to attempt to introduce substituents into this type of molecule, preferably close to the sulfur atom. Such an alteration in structure might be expected to affect the biological properties.


I


II

Tetrahydrothiapyran-4-carboxylic acid (III)[2,4]

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[1] Issued as DRCL Report No. 147.

[1a] Monsanto Canada Limited, Ville La Salle, Quebec.

[2] V. Prelog and E. Cerkovnikov, *Ann.*, **537**, 214 (1939).

[3] V. Prelog and D. Kohlbach, *Ber.*, **72B**, 672 (1939).

[4] V. Hanousek and V. Prelog, *Coll. Czech. Chem. Communs.*, **4**, 259 (1932).