since one diastereoisomer cannot be transformed into the other by the operation of a twofold axis. The second alternative can be excluded since a twofold screw axis cannot be a symmetry element in a nonpolymeric molecule.

If the space group is $P2_1/m$, the symmetry of the cell requires that each of the two molecules in the cell lie on a crystallographic center of symmetry. This requires that the molecules have a center of symmetry, which neither the *d* nor *l* isomer has. Thus the *dl* form cannot crystallize in space group $P2_1/m$.

Since the *dl* isomer cannot be accommodated either in $P2_1$ or $P2_1/m$, with two molecules in the cell, it follows that the isomer with the lower melting point, from crystals of which the diffraction patterns were obtained, must be the meso isomer.

Since the meso isomer itself has a center of symmetry, it is probable that its space group will be $P2_1/m$ with the molecular center of symmetry coinciding with the crystallographic center of symmetry. The space group $P2_1$, however, cannot be entirely ruled out. Fortunately, the above argument does not require an unambiguous space group assignment to the meso form.

Experimental Section

All nuclear magnetic resonance spectra were taken on a Varian A-60A instrument, using saturated solutions in chloroform-d_1 and tetramethylsilane as an internal standard. All chemical shifts are reported in τ units (τ = 10.00 for tetramethylsilane). Infrared spectra were taken on a Beckman IR-5 spectrophotometer in KBr. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were uncorrected.

Preparation of 6,12-Diketo-*trans*-isojanusene (1b).—To a solution of 78 mg (0.19 mmol) of 6,12-dihydroxy-*trans*-isojanusene[2b] in 20 ml of acetone at 0° was added slowly 1 ml of Jones reagent (6.75 g of CrO_3, 5.75 ml of H_2SO_4, 100 ml of water).[6] The reaction mixture was stirred for 2.5 hr at 0° and then poured into 100 ml of ether. The ether solution was washed with three 200-ml portions of water and once with 150 ml of saturated NaCl solution. The ether solution was dried ($MgSO_4$) and filtered and the solvent evaporated under reduced pressure giving 65 mg (83%) of **1b**. Crystallization was from acetone–95% EtOH: mp 334–335° dec; ν_{max} 1705, 1595, 1463, 1283, 1097, 997, 764, 720, 687 cm^{-1} (KBr); pmr ($CDCl_3$) τ 4.97 (s, 2), 1.90–3.10 (m, 16, aromatics).

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.80; H, 4.39. Found: C, 87.58; H, 4.39.

Preparation of 6,12-Diketo-*cis*-isojanusene (2b).—To a solution of 330 mg (0.80 mmol) of 6,12-dihydroxy-*cis*-isojanusene[2b] in 20 ml of acetone at 0° was added slowly 4.9 ml of Jones reagent (6.75 g of CrO_3, 5.75 ml of H_2SO_4, 100 ml of H_2O). The reaction mixture was stirred at 0° for 2 hr and then poured into a mixture of 100 ml of methylene chloride and 100 ml of water. The methylene chloride solution was washed twice with 100-ml portions of water, dried ($MgSO_4$), and filtered, and the solvent evaporated under reduced pressure giving 300 mg (91%) of diketone **2b**. Crystallization was from CH_2Cl_2–acetone: mp >360°; ν_{max} 1690, 1590, 1450, 1248, 904, 778, 746, 693 cm^{-1} (KBr); pmr ($CDCl_3$) τ 4.96 (s, 2), 2.25–3.00 (m, 16, aromatics).

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.80; H, 4.39. Found: C, 87.68; H, 4.34.

Registry No.—**1b**, 29339-42-2; **2b**, 29339-43-3.

Acknowledgment.—The authors are indebted to the National Institute of General Medical Sciences (Public Health Service Grant GM 12139) for support in this work.

(6) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. Weedon, *J. Chem. Soc.*, 39 (1946).

Bridged Polycyclic Compounds. LXX. Rearrangements Accompanying Free-Radical Addition of Thiophenol to 3-Methylenenortricyclene[1]

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The free-radical addition of thiophenol to 3-methylenenortricyclene (**1**) gives the 1,2-addition product, 3-nortricyclylmethyl phenyl thioether (**2**), and a variety of unsaturated thioethers (**7**, **10**, **11**, and **12**) which can be formulated as derivable, under reaction conditions, from the 1,5-homoconjugate addition product, 2-norbornen-2-yl phenyl thioether (**3**). Variation in product compositions with reagent concentrations demonstrates the existence of classical radical intermediates, rather than a single nonclassical free radical.

A considerable degree of attention has been focussed on homoallyl–cyclopropylcarbinyl rearrangements both in ionic and free-radical systems.[2] Bridged polycyclic compounds have been particularly fruitful in elucidating the nature of homoallyl–cyclopropylcarbinyl free-radical intermediates.[3-21] In continuing our research in this area, we undertook a study of thiophenol addition to the symmetrical olefin, 3-methylenenortricyclene (**1**).

(1) Paper LXIX: W. M. Macintyre, M. A. Imhoff, and S. J. Cristol, *J. Org. Chem.* **36**, 1865 (1971).

(2) R. Breslow in "Molecular Rearrangements," part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 289–293, and references therein.

(3) D. I. Davies and S. J. Cristol in "Advances in Free Radical Chemistry," Vol. I, G. Williams, Ed., Logos Press, London, 1966.

(4) C. Walling in "Molecular Rearrangements," part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 407–451, and references therein.

(5) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, **80**, 635 (1958).

(6) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).

(7) S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964).

(8) N. O. Brace, *ibid.*, **27**, 3027 (1962).

(9) D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963).

(10) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

(11) D. I. Davies, J. N. Done, and D. H. Hey, *Chem. Commun.*, **20**, 725 (1966).

(12) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

(13) E. S. Huyser and G. Echegaray, *ibid.*, **27**, 429 (1962).

(14) S. J. Cristol, T. W. Russell, and D. I. Davies, *ibid.*, **30**, 207 (1965).

(15) (a) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **88**, 4262 (1966); (b) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968).

(16) S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, **34**, 1762 (1969).

(17) J. A. Berson, C. J. Olson, and J. S. Walia, *J. Amer. Chem. Soc.*, **82**, 5000 (1960).

(18) D. I. Davies, J. A. Claisse, and C. K. Alden, *J. Chem. Soc.*, 1498 (1966).

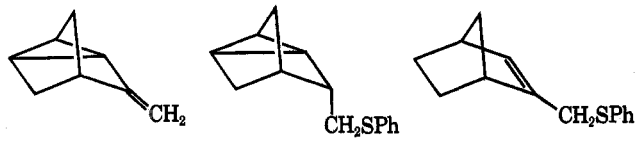
(19) D. I. Davies and C. K. Alden, *ibid.*, 1017 (1967).

(20) J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968).

(21) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969).

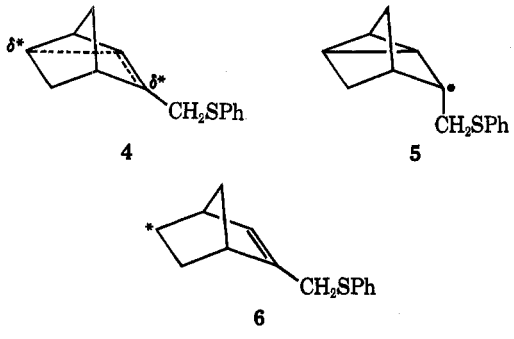
Discussion of Results

Based upon previous work in these laboratories, prediction of both the products and mechanism of thiol addition to **1** seemed straightforward. One would predict the formation of 3-nortricyclylmethyl phenyl



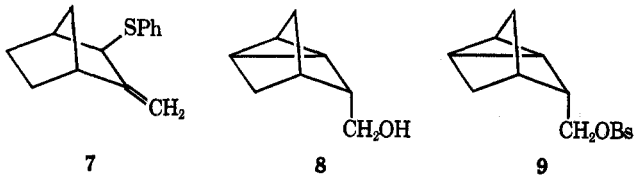
1 **2** **3**

thioether (**2**) *via* 1,2 addition and 2-norbornen-2-yl methyl phenyl thioether (**3**) *via* 1,5-homoconjugate addition. Addition should proceed in an anti-Markovnikov manner with initial phenylthiyl radical attack leading possibly to the delocalized nonclassical radical, **4**, or, more likely,[3,5] to the classical radical **5** which could isomerize to **6**. In either case, chain transfer with the intermediate radicals would lead to the predicted products (**2** and **3**). The distinction between classical and nonclassical intermediates could be made by a study of product distribution with dilution of the reactants.[5]



4 **5** **6**

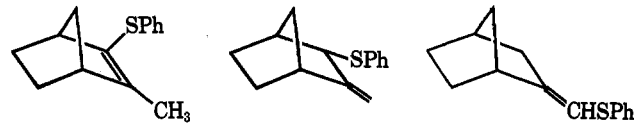
When thiophenol addition to **1**, initiated by ultraviolet irradiation, was actually carried out (at *ca.* 42°) for 30 min, **2** was formed in 80% yield and an unanticipated unsaturated material, *exo*-3-thiophenoxy-2-methylenenorbornane (**7**), was present in 19.5% yield. A third thioether of undetermined structure made up the remaining 0.5% yield of product. Mass spectral analysis showed molecular ions at *m/e* 216



7 **8** **9**

for each of the reaction products, the value expected for a 1:1 adduct. Identification of **2** was established by an independent unequivocal synthesis. Oxidative hydroboration of **1** to give alcohol **8**, conversion to *p*-bromobenzenesulfonate **9**, and direct displacement by thiophenoxide ion to **2** are described in the Experimental Section.

When both **2** and **7** were subjected to the conditions of addition, they were recovered essentially unchanged. However, when the unsaturated thioether **7**, was subjected to prolonged irradiation (*ca.* 2 hr), 2-methyl-3-thiophenoxynorborn-2-ene (**10**) was obtained in 5% yield and a second incompletely characterized product, which appears to be *endo*-3-thiophenoxy-2-methylenenorbornane (**11**), in 7% yield.



10 **11** **12**

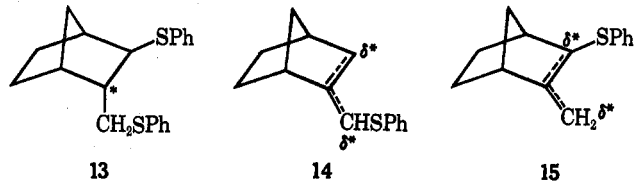
When the addition of thiophenol to 3-methylenenortricyclene was carried out over a 150-W incandescent tungsten lamp at 175°, the product mixture contained 34% **2**, 22% **7**, 27% **10**, 14% 8-thiophenoxy-2-methylenenorbornane (**12**), 2% **11**, and 2% of an unknown thioether.

Control experiments, analogous to those previously described and designed to learn the source of **10** and **12**, were carried out. When subjected to severe conditions of thiol addition, **2** and **12** were recovered unchanged in 98 and 100% yield, respectively, while **7** afforded a mixture of 23% **10** and 71% **12**. Under similar conditions, 90% thioether **10** was recovered unchanged with the balance giving 4% **7** and 6% **12**.

The formation of **7**, **10**, and **12** as well as the absence of **3** must be considered and explained. Work by Kharasch and by Oswald and their coworkers has shown that allylic halides and sulfides undergo "allylic reversal" *via* an addition–elimination process with great facility.[22,23] Walling[4] has pointed out, in systems subject to allylic reversal, that isolated products may not be kinetically controlled ones.

For our case, the allylic reversal process fits the available data. The presumed kinetic product **3** suffers attack by phenylthiyl radical at C-3 to give the bis(thioether) radical **13** which subsequently loses phenylthiyl radical from either C-3 or C-8 to give **3** or **7**, respectively. The failure to observe any of the first-formed thioether suggests that equilibration *via* allylic reversal is faster than addition and that equilibration is in favor of the exocyclic thioether **7**.[24]

The appearance of **10** and **12** as major reaction products during thiophenol addition must be the result of reversible allylic hydrogen abstraction. That the rate of hydrogen abstraction competes with those of other free-radical reactions as the temperature is increased is well documented.[4,27] Thus abstraction of the C-8 allylic hydrogen atom from **3** gives radical **14**. Subsequent hydrogen transfer at C-3 affords **12**.



13 **14** **15**

(22) M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, **1**, 393 (1936).

(23) D. N. Hall, A. A. Oswald, and K. Griesbaum, *ibid.*, **30**, 3829 (1965).

(24) That the exocyclic olefinic thioether is more stable than its endocyclic isomer is in agreement with the results of studies in similar systems reported in the recent literature.[25,26]

(25) C. K. Alden and D. I. Davies, *J. Chem. Soc. C*, 709 (1968).

(26) (a) P. v. R. Schleyer, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1956, p 290; (b) N. A. Belihova, A. F. Platé, G. M. Tabrina, Kh. E. Sterin, V. M. Lukashina, V. P. Pakhomov, and V. A. Berezkin, *Zh. Org. Khim.*, 498 (1965).

(27) L. H. Gale, *J. Amer. Chem. Soc.*, **88**, 4661 (1966).

TABLE I

ADDITION OF THIOPHENOL TO 3-METHYLENENORTRICYCLENE (1)

Run	Solvent	[Olefin]$_i$, M	Thiol equivalents	Temp, °C	% reaction[b]	% yield of thioethers[c] 2	7	11	10	12	Ratio of tricyclic/olefinic thioethers
1[a]	Neat	4.6	0.96	42	70	80	19.5	0	0	0	4.1
2[a]	$C_6H_3Cl_3$	3.2	0.86	42	64	71	25	2.7	0	0	2.6
3[a]	C_6H_5Cl	1.5	0.99	42	29	59	35	3.1	0	0	1.5
4[d]	Neat	4.8	0.85	175	92	34	22	2.0	27	14	0.54

[a] Reactions were carried out using a GE H100-4A/T 100-W ultraviolet lamp. [b] Per cent reaction was calculated from the amount of converted olefin with respect to the theoretical conversion of olefin. [c] Per cent yields were based on the amount of olefin converted to thioether. In each case the reaction was quantitative. [d] Reactions were carried out using a 150-W unfrosted Westinghouse tungsten lamp, with benzoyl peroxide as initiator.

Likewise hydrogen abstraction from C-3 in **7** gives **15** and hydrogen transfer at C-8 leads to thioether **10**.

Fortunate for the original purpose of this investigation is the fact that there is no crossover between tricyclic and olefinic thioethers under any of the conditions employed. Thus, a comparison of the total of the olefinic thioethers with the amount of tricyclic thioether gives an accurate measure of 1,5-homoconjugate addition *vs.* 1,2 addition, respectively.

To determine the nature of the product-determining radical intermediate(s) involved in the addition of thiophenol, a series of dilution experiments, based on the method used originally by Seubold[28] and used extensively in our laboratory,[5,14,16] was carried out. Dilution of the addition reaction medium causes a decreased rate of chain transfer and hence provides a longer lifetime for the intermediate radicals. If a nonclassical delocalized species (**4**) is the product-determining intermediate, then dilution will effect no change in product distribution. Alternatively, if the product-determining intermediates are the discrete cyclopropylcarbinyl (**5**) and homoallyl (**6**) radicals and if isomerization and hydrogen transfer rates are comparable, significant changes in product distribution toward the olefinic thioether products will be observed. Both chlorobenzene and 1,2,4-trichlorobenzene were used as diluents for the reactants. The results of these experiments are listed in Table I. Although the reactions were not allowed to proceed to completion, the yields were quantitative, based on the per cent of converted olefin. The ratio of tricyclic/olefinic thioether was computed from the yield of **2** and the total yield of unsaturated thioethers. Examination of the experimental results (Table I, runs 1–3) shows that the second possibility obtains. That is, the observed tricyclic/olefinic product ratio decreasing with increasing dilution is incompatible with a single radical intermediate.

Furthermore, comparison of the results of expt. 1 and 4 points up a pronounced temperature effect on the distribution of products. This increase toward the olefinic thioether at elevated temperatures suggests that the energy of activation for cyclopropylcarbinyl–homoallyl radical interconversion, with **4** serving as a transition state, is greater than that for chain transfer.

Thus these experiments, like others that we have reported,[5-7,14-16,21] do not permit the intervention of nonclassical radicals, except as transition states, as important reaction paths. Put another way, the search for π-bridged radicals as product-determining reaction intermediates remains unrewarded.

(28) F. H. Seubold, *J. Amer. Chem. Soc.*, **75**, 2532 (1953).

Nmr and Mass Spectral Studies.—The pmr spectrum of **2** showed no olefinic hydrogen absorptions, indicating that this product was a saturated thioether. A two-proton doublet of doublets (J = 7.2 and 1.5 Hz) at τ 7.28 was assigned to the C-8 methylene protons. A triplet (J = 7.2 Hz), centered at τ 8.26, was attributed to the C-3 methinyl hydrogen. Double irradiation experiments confirmed that the larger coupling constant was a result of the spin–spin interaction between the methinyl and methylene hydrogens. The hydrogen at the C-4 bridgehead position gave a broad unresolved band at τ 8.14. The remaining aliphatic absorptions integrating for eight protons appeared at τ 8.95, 8.76, and 8.64. The aromatic protons displayed a complex multiplet centered at τ 2.80.

The two olefinic hydrogens of the exocyclic unsaturated thioether **7** appeared as a broad band at τ 5.01. This absorption is characteristic of terminal methylene protons and is in particularly good agreement with the chemical shifts of known methylenenorbornane derivatives.[14] Broad apparent "singlets" with chemical shifts at τ 7.68 and 7.28 were assigned to the bridgehead protons at C-4 and C-1, respectively. The endo proton α to the exo thiophenoxy group at C-3 appeared as a poorly resolved doublet (J = 2.0 Hz) at τ 6.36. This small coupling constant is consistent with the long-range splitting commonly observed between the anti C-7 and endo protons of the norbornane system.[29] An exo C-3 proton would be expected to exhibit a coupling constant of *ca.* 3.4–3.8 Hz with the C-4 bridgehead proton.[29] The observed coupling constant of 0 Hz is the expected value for endo C-3 and C-4 bridgehead coupling.

The pmr spectrum of **10** did not show any resonance signals with chemical shifts corresponding to protons α to a thiophenoxy group or to olefinic protons. A broad unresolved band at τ 7.23 was assigned to the two bridgehead protons and a sharp singlet at τ 8.20 integrating for three equivalent hydrogens to the allylic C-8 methyl protons.[30]

The mass spectrum of **10** exhibited a rather intense molecular ion at m/e 216 (35% of base peak). The base peak occurred at m/e 188. The appearance of this fragment was attributed to a retro-Diels–Alder

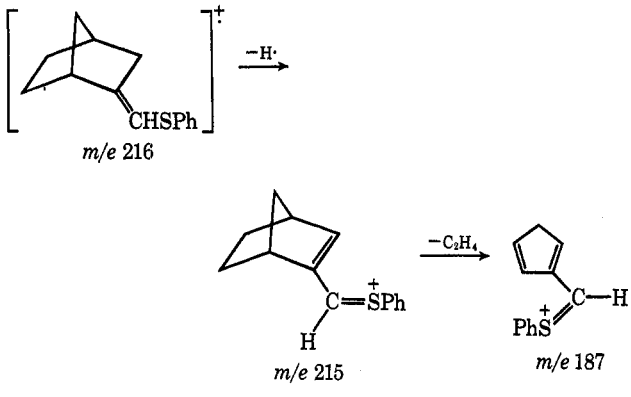
(29) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(30) The C-8 allylic methyl group of the corresponding sulfone gave a singlet at τ 7.77. The magnitude of this downfield shift (*ca.* 0.4 ppm) is similar to that for protons located α to a benzenesulfonyl group. Apparently, the deshielding effect of the sulfone group is transmitted through the double bond. This is analogous with the results reported for the methyl protons of acetaldehyde (τ 7.80) *vs.* the methyl protons of *trans*-crotonaldehyde (τ 7.97).[31]

(31) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Varian Associates, Lithographed by National Press, 1962.

process.[32] This was confirmed by the detection of a metastable ion at *m/e* 164.

The pmr spectrum of **12** had a signal at τ 4.06 attributable to the single C-8 olefinic proton, which is deshielded by the electronegative thiophenoxy function located at the C-8 position.[33] The exo and endo allylic protons at C-3 gave a complex multiplet at τ 7.95. Broad "singlets" at τ 7.18 and 7.60 were assigned to the bridgehead protons. The normal five-proton aromatic pattern was observed at τ 2.85. The mass spectral fragmentation pattern showed an extremely intense molecular ion as the base peak of the spectrum. The intensity of a molecular ion is dependent on its stability and tendency to fragment.[32] 8-Thiophenoxy-2-methylenenorbornane (**12**) has a conjugated π-electron system. Loss of an electron through electron impact would lead to a stable delocalized molecular



ion. Further, thioethers suffer predominant α- and β-cleavage fragmentations.[34] These pathways are energetically unfavorable in this case because they would require rupture of an sp^2-hybridized σ bond. However, loss of a hydrogen atom from the C-3 position (*i.e.*, β cleavage with respect to the double bond function) affords an allylic cation which finds additional stabilization through resonance involving the unshared electron pairs on the sulfur atom. This allylic cation (*m/e* 215) can now undergo a retro-Diels–Alder reaction as a secondary fragmentation process to give *m/e* 187 (77% of base peak). The fragmentation pathway was confirmed by detection of a metastable ion at *m/e* 163.

Experimental Section

General.—Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points and boiling points are uncorrected. All solvents and reagents utilized were reagent grade unless specified otherwise.

Spectra.—Pmr data were measured on Varian Associates A-60 and A-60A spectrometers and are reported in τ units, with τ 10.00 for tetramethylsilane as internal standard. Infrared spectra were measured on Perkin-Elmer 21 and Beckman IR-5 spectrophotometers. Mass spectra were taken on a CEC 21-103C mass spectrometer.

Gas Chromatography.—Preparative and analytical gas chromatography were carried out on Varian Aerograph Model A-700 and Model A-90-P3 instruments, respectively, using helium as carrier gas. A 20% fluorosilicon QF-1-0065 (Analabs, Inc.) on Anakrom ABS or Anakrom SD, 70–80 mesh (Analabs, Inc.) column packing was used for both the preparative and analytical gas chromatography. Gas chromatographic analyses were determined on a 7 m × 0.25 in. stainless steel column operated at 185 ± 2° with a carrier gas flow of 130 ml/min. Inert internal standards, 1,2,4-trichlorobenzene (Eastman Organic Chemicals) and 1-bromo-3-chlorobenzene (Matheson Coleman and Bell, Inc.) were used for analytical gas chromatography. The analyses were made by the method of triangulation using an area to weight of compound relationship. Retention times for the thioethers eluted follow: **10**, 31 min; **7**, 39 min; **11**, 41 min; **2**, 53 min, and **12**, 56 min. Preparative gas chromatographic separation and collection were carried out on a 6 m × 0.375-in. copper tubing column at conditions suitable to the separation desired.

Preparation of 3-Methylenenortricyclene (1).—To a solution of Wittig reagent,[35] prepared from 71.0 g (0.199 mol) of methyl triphenylphosphonium bromide and 12.1 g (0.189 mol) of *n*-butyllithium in ether, was added 15.0 g (0.142 mol) of nortricyclanone dissolved in 225 ml of anhydrous ether. The mixture was allowed to stir at room temperature overnight. Cold water was added dropwise until the milky white triphenylphosphine oxide precipitate dissolved. The ethereal solution was separated and the aqueous layer was extracted three times with 200-ml portions of *n*-pentane. The pentane extracts combined with the original ethereal solution were washed three times with 250-ml portions of cold water and with three 100-ml portions of saturated sodium chloride solution. The pentane–ether solution was dried ($MgSO_4$), concentrated, and distilled, bp 45–50° (24 mm), to give 9.5 g (65%) of 3-methylenenortricyclene (**1**) with properties similar to those reported[36] for **1** prepared in a different fashion.

Addition of Thiophenol to 3-Methylenenortricyclene (1). A. Ultraviolet Irradiation.—This entire reaction series was carried out in Pyrex glass tubes (6 mm × 5 cm) which were equipped with rubber serum stoppers. In each case, the tube was placed at a distance of 5 cm from a GE H100-4 A/T 100-W ultraviolet lamp used for free-radical initiation. Each sample was irradiated for a period of 30 min. It was observed that the temperature rose to a maximum of 42° during the irradiation period. Immediately after irradiation, the crude reaction mixture was subjected to gas chromatographic analysis, the results of which are listed in Table I.

First Experiment.—A solution of 151 mg (1.42 mmol) of **1** and 150 mg (1.36 mmol) of thiophenol was irradiated as described above. Immediately after irradiation 62 mg (0.34 mmol) of 1,2,4-trichlorobenzene as internal standard was added to the solution, and gas chromatographic analysis was undertaken.

Second Experiment.—A solution of 79.1 mg (0.746 mmol) of **1**, 70.6 mg (0.642 mmol) of thiophenol, and 106.4 mg (0.588 mmol) of 1,2,4-trichlorobenzene (internal standard) as dilutent was similarly irradiated and analyzed.

Third Experiment.—A solution of 60.9 mg (0.574 mmol) of **1**, 63.0 mg (0.573 mmol) of thiophenol, and 69.8 mg (0.386 mmol) of 1,2,4-trichlorobenzene (internal standard) in chlorobenzene was prepared. This solution, 1.5 *M* in both **1** and thiophenol, was irradiated and analyzed as previously described.

B. Tungsten Lamp Irradiation.—A solution of 35.2 mg (0.332 mmol) of **1**, 31.0 mg (0.282 mmol) of thiophenol, and 1.4 mg (0.006 mmol) of benzoyl peroxide was sealed in a 3 mm × 5 cm Pyrex glass tube. The tube was irradiated at 175 ± 5° over a 150-W tungsten lamp for 2.5 hr. The tube was cooled and opened and the crude reaction mixture was subjected to gas chromatographic analysis. These results are listed in Table I.

This reaction was repeated on a preparative scale and the results obtained were in substantial agreement with those described above. A solution of 3.58 g (33.8 mmol) of **1**, 3.96 g (36. mmol) of thiophenol, 30 mg (0.12 mmol) of benzoyl peroxide, and 2.92 g (16.1 mmol) of 1,2,4-trichlorobenzene as internal standard was sealed in a 1.5 cm × 12 in. thick-walled Pyrex glass tube. The tube was placed over a 150-W tungsten lamp and heated at 170 ± 5° for 2.5 hr. Gas chromatographic analysis indicated yields of 957 mg (16%) of **10**, 2.27 g (38%) of **7**, 1.81 g (30%) of **2**, 643 mg (11%) of **12**, and 353 mg (6%) of two unknown thioethers. These per cent yields are based on an 82% conversion of **1**. The product mixtures from both reactions were combined, separated, and collected by preparative gas chromatography. Separation was effected at a column temperature of 190°. The infrared, pmr, and mass spectra of each com-

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(33) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, pp 60–62.

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ponent were taken. Each of the collected materials was placed in an ordinary sublimation apparatus and was allowed to evaporate (with the use of a hot-water bath) and recondense on the cold finger at *ca.* 1-mm pressure. The droplets were drawn up into a (1/8-in. o.d.) glass tube *via* capillary action, sealed, and used for elemental analysis.

Anal. Calcd for $C_{14}H_{16}S$: C, 77.71; H, 7.47. Found for **10**: C, 77.42; H, 7.30. Found for **7**: C, 77.55; H, 7.54. Found for **2**: C, 77.77; H, 7.82. Found for 48% **12**–52% **2** mixture: C, 77.77; H, 7.30.

Preparation of 3-Nortricyclomethyl Alcohol (8).—Into a stirred solution of 5.1 g (0.048 mol) of **1** in 40 ml of freshly distilled diglyme was bubbled an excess of diborane gas from a separate reaction flask. The reaction mixture was cooled to 0° and the unreacted diborane gas was destroyed by cautious addition of 20 ml of wet ether and small pieces of ice. When the frothing had stopped, 38 ml of 0.5 *N* sodium hydroxide solution was added; this addition was followed immediately by the careful addition of 19 ml of 30% hydrogen peroxide solution. The reaction mixture was stirred for 30 min and poured into a 150-ml ice–water mixture. The aqueous phase was extracted three times with 100-ml portions of ether. The combined ether extracts were washed ten times with 300-ml portions of cold water and with 100-ml portions of 10% ferrous ammonium sulfate solution until the excess hydrogen peroxide was destroyed. Finally, the ethereal solution was washed with 100-ml portions of saturated brine solution and dried ($MgSO_4$). The ether was removed by distillation through a 12-in. Vigreux column. The oily residues were distilled, bp 105–107° (8 mm), to give a 4.1 g (69%) yield of the desired alcohol (**8**).

Anal. Calcd for $C_8H_{12}O$: C, 77.36; H, 9.76. Found: C, 77.22; H, 9.84.

Preparation of 3-Nortricyclomethyl *p*-Bromobenzenesulfonate (9).—To a solution of 1.18 g (9.6 mmol) of **8** in 6 ml of dry pyridine at −30° was added 2.45 g (9.7 mmol) of *p*-bromobenzenesulfonyl chloride. The mixture was shaken until all of the solids dissolved and was then placed in a freezer at −30° for 15 hr. A yield of 3.19 g (97%) of the desired *p*-bromobenzenesulfonate was obtained. The product was recrystallized from *n*-heptane. A sample, mp 61.5–63.0°, was used for elemental analysis.

Anal. Calcd for $C_{14}H_{15}O_3BrS$: C, 48.99; H, 4.41. Found: C, 48.62; H, 4.46.

Preparation of 3-Nortricyclomethyl Phenyl Thioether (2).—A solution of 5.63 g (16.4 mmol) of **9** in 200 ml of dimethyl sulfoxide was stirred at room temperature. Potassium thiophenoxide (2.43 g, 16.4 mmol) dissolved in 100 ml of dimethyl sulfoxide was added dropwise over a 30-min period. After being stirred for 24 hr the solution was poured into 500 ml of cold water The resulting suspension was extracted three times with 150-ml portions of *n*-pentane. The combined pentane extracts were washed five times with 200-ml portions of cold water and twice with 150-ml portions of saturated sodium chloride solution. The pentane solution was dried ($MgSO_4$) and concentrated by careful distillation through a 12-in. Vigreux column. The oily residues were distilled, bp 135–137° (1.0 mm), to yield 2.38 g (67%) of the desired tricyclic thioether. The gas chromatographic retention time as well as the infrared and pmr spectra were identical with those of **2**, obtained by the free-radical addition of thiophenol to 3-methylenenortricyclene.

Attempted Rearrangement of 3-Nortricyclylmethyl Phenyl Thioether (2).—A solution of 18.9 mg (0.088 mmol) of **2** and 3.6 mg (0.033 mmol) of thiophenol contained in a 3 mm × 5 cm Pyrex glass tube was irradiated with a GE-H100-4A/T 100-W ultraviolet lamp for 1 hr. Immediately after irradiation, the crude reaction mixture was analyzed *via* gas chromatography. This analysis revealed the starting thioether as the only product without any observable rearrangement. Identification was made by retention time comparison with those of thioethers obtained *via* thiophenol addition to 3-methylenenortricyclene.

A solution of 14.6 mg (0.068 mmol) of **2**, 3.0 mg (0.027 mmol) of thiophenol, and 0.5 mg (0.002 mmol) of benzoyl peroxide was sealed in a 1.5 mm × 5 cm Pyrex glass tube. The tube was placed over a 150-W tungsten lamp and irradiated for 2.5 hr at 175 ± 5°. After cooling, the tube was opened and the crude reaction mixture was subjected to gas chromatographic analysis. The results of this analysis indicated a 98% recovery of **2** and 2% an unknown thioether.

Attempted Rearrangement of 8-Thiophenoxy-2-methylenenorbornane (12).—A solution of 10.4 mg (0.048 mmol) of **12** and 1.5 mg (0.014 mmol) of thiophenol was irradiated for 1 hr with a GE-H100-4 A/T 100-W ultraviolet lamp. The temperature was observed to reach 42° maximum throughout the irradiation period. After irradiation, the crude reaction mixture was immediately subjected to gas chromatographic analysis. Again gas chromatographic analysis showed no observable rearrangement, with the starting thioether, **12**, as the sole product.

A solution of 9.8 mg (0.045 mmol) of **12**, 2.2 mg (0.02 mmol) of thiophenol, and *ca.* 0.5 mg (0.002 mmol) of benzoyl peroxide was sealed in a 3 mm × 5 cm Pyrex glass tube. This solution was irradiated over a 150-W incandescent lamp at 175 ± 5° for a 2.5-hr period. The reaction mixture was allowed to cool to room temperature and subjected to gas chromatographic analysis. This analysis showed only **12** with no observable rearrangement.

Rearrangement of *exo*-3-Thiophenoxy-2-methylenenorbornane (7).—A solution of 10 mg (0.046 mmol) of **7** and 2 mg (0.02 mmol) of thiophenol was irradiated for 2 hr with a GE-H100-4A/T 100-W ultraviolet lamp. As before, a 42° temperature maximum was observed during the irradiation period. Gas chromatographic analysis carried out immediately after irradiation indicated the following product distribution: 4.9% **10**, 88% **7**, and 6.9% **11**.

In a sealed 3 mm × 5 cm Pyrex glass tube a solution of 10 mg (0.046 mmol) of **7**, 2.0 mg (0.02 mmol) of thiophenol, and *ca.* 3 mg (0.001 mmol) of benzoyl peroxide was irradiated over a 150-W tungsten lamp for 2 hr at 175 ± 5°. The tube was allowed to cool and the crude reaction mixture was subjected to gas chromatographic analysis, which revealed the following product distribution: 23% **10**, 5.8% **7**, and 71% **12**.

Rearrangement of 2-Methyl-3-thiophenoxynorborn-2-ene (10).—A sealed melting point capillary tube containing a solution of 5.7 mg (0.026 mmol) of **10** and 3.2 mg (0.029 mmol) of thiophenol was irradiated for 2.5 hr with a GE-H 100-4A/T 100-W ultraviolet lamp. Gas chromatographic analysis carried out immediately upon completion of irradiation indicated the complete absence of rearrangement and showed **10** as the sole thioether component.

A solution of 5.5 mg (0.026 mmol) of **10**, 2.0 mg (0.018 mmol) of thiophenol, and *ca.* 0.2 mg (0.001 mmol) of benzoyl peroxide was sealed in a melting point capillary tube. The tube was irradiated over a 150-W tungsten lamp for 2.5 hr at 175 ± 5°. After irradiation, the tube was allowed to cool, opened, and subjected to gas chromatographic analysis, which showed the following product distribution: 90% **10**, 4% **11**, and 5.9% **12**.

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