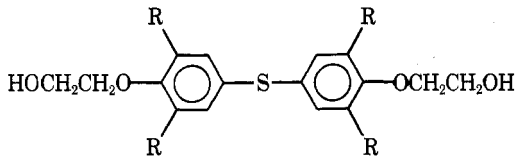

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The reaction of phenol and monosubstituted phenols with sulfur under these conditions takes a different course and will be the subject of a future publication.

Experimental Section

4,4'-Thiobis(2,6-diphenylphenol). To a 3-l., round-bottom, three-necked flask equipped with stirrer, thermometer, Dean-Stark trap, and condenser and maintained under a nitrogen atmosphere were placed 246 g (1.0 mol) of 2,6-diphenylphenol and 1230 ml of xylene. A solution of 40 g (1.0 mol) of sodium hydroxide in 80 ml of water was then added. The mixture was heated to reflux with stirring and the water removed. When removal of the water was complete, the reaction mixture was cooled to about 70–80 °C and 32 g (1.0 mol) of sulfur was added. The reaction mixture was again heated to reflux and the xylene was removed via the Dean-Stark trap until the temperature reached 169 °C. The reaction mixture was not homogeneous and vigorous stirring was needed. After 2 h, the reaction mixture was cooled and water was added. The solidified product was separated by filtration, washed well with more water and finally with pentane, and then dried in the vacuum oven overnight. The crude product was then triturated with 2 l. of hot heptane and the heptane-insoluble material was recrystallized from acetic acid. There was obtained 83.7 g (0.16 mol, 32.0% yield) of material melting at 151 °C. Recrystallization raised the melting point to 162–163 °C. Anal. Calcd for $C_{36}H_{26}O_2S$: C, 82.73; H, 5.01; S, 6.13. Found: C, 82.4; H, 4.98; S, 5.9.

General Procedure for the Reaction of 2,6-Dimethylphenol and Sulfur in the Presence of Acrylonitrile or Alkylene Oxides. A. Acrylonitrile. To a 500-ml round-bottom flask equipped with a Vibromixer stirrer, condenser, and thermometer with temperature controller attached, there was added 122.2 g (1.0 mol) of 2,6-xylenol and 2.3 g (0.1 g-atom) of sodium metal. The reaction mixture was heated under N_2 until the sodium dissolved, then cooled. There was added 48.0 g (1.5 g-atoms) of sulfur and the reaction mixture was heated and maintained at 80 °C. Over a period of 4.25 h there was added 53.0 g. (1.0 mol) of acrylonitrile. During this period the sulfur slowly went into solution. The reaction mixture was cooled and after diluting with ether it was washed with 10% hydrochloric acid and then with water until neutral. The ether was then removed by distillation to yield 201.6 g of crude product. The unreacted 2,6-xylenol (24.0 g) was removed by distillation at 0.2 mm, leaving a residue of 177.6 g. The residue was dissolved in ether and washed with 10% sodium hydroxide solution, leaving 12.1 g of base-insoluble material, principally β,β'-dithiodipropionitrile. After acidification with dilute hydrochloric acid the base-soluble fraction weighed 139.7 g. Recrystallization from heptane yielded 90.7 g (66.2% yield) of thiobis(2,6-dimethylphenol), mp 124 °C.

B. Propylene Oxide. 1. 2 Equiv. The reaction was performed in the same manner as the preceding example using 122.2 g (1.0 mol) of 2,6-xylenol, 1.2 g (0.05 g-atom) of sodium, 4.8 g (1.5 g-atoms) of sulfur, and 58.1 g (1.0 mol) of propylene oxide. The reaction was performed at 100 °C and the propylene oxide was added over a 4-h period. There was obtained 17.7 g (0.15 mol) of unreacted 2,6-xylenol (conversion 85%), 20.9 g (0.12 mol) of 2,6-dimethylphenoxy-2-propanol, 100.0 g (0.73 mol, 85.8% yield) of thiobisxylenol, and 3.4 g of the mono-O-alkylated thiobisxylenol.

When this reaction was performed at 50 °C, the only significant product was 2,6-dimethylphenoxy-2-propanol.

2. 4 Equiv. The reaction was performed as above except that an additional 2 mol of propylene oxide was added in the same time period. After the addition was complete, there was added 50 ml of 20% sodium hydroxide solution and the reaction was maintained at temperature for 30 min. The reaction mixture was then cooled, washed with water, and distilled. There was obtained a 76% yield of 4,4'-thiobis[1-(2,6-dimethylphenoxy)-2-propanol], mp 90–92 °C. Anal. Calcd for $C_{22}H_{30}O_4S$: C, 67.67; H, 7.74; S, 8.20. Found: C, 67.40; H, 7.98; S, 8.3.

C. Ethylene Oxide. Reactions with ethylene oxide were performed as above except that introduction of the ethylene oxide from a cylinder was continued until completion of the reaction was indicated by gas chromatography.

4,4'-Thiobis[2-(2,6-dimethylphenoxy)ethanol]. Yield 67%; mp 99 °C. Anal. Calcd for $C_{20}H_{26}O_4S$: C, 66.28; H, 7.23; S, 8.83. Found: C, 66.4; H, 7.2; S, 8.9.

Registry No.—**4** (R = Ph), 58426-07-6; **6**, 576-26-1; **7**, 18525-99-0; **21** (R = CH_3), 58426-08-7; sulfur, 7704-34-9; acrylonitrile, 107-13-1; propylene oxide, 75-56-9; 4,4'-thiobis[1-(2,6-dimethylphenoxy)]-2-propanol, 58426-09-8; 2,6-diphenylphenol, 2432-11-3; ethylene oxide, 75-21-8.

References and Notes

(1) Presented in part at the VIth Symposium on Organic Sulphur Chemistry, Bangor, U.K., July 1974.
(2) For leading references, see C. Ellis, "The Chemistry of Synthetic Resins", Reinhold, New York, N.Y., 1935.
(3) A. J. Neale, P. J. S. Bain, and T. J. Rawlings, *Tetrahedron*, **25**, 4583, 4593 (1969).
(4) E. J. Geering, U.S. Patent 3 717 682 (Feb 20, 1973).
(5) T. Fujisawa, K. Hata, and T. Kojima, *Synthesis*, **5**, 38 (1973).
(6) T. Fujisawa and T. Kojima, *J. Org. Chem.*, **38**, 687 (1973).

Stereochemistry of Nucleophilic Addition Reactions. Addition of Thiophenol to Ethyl 4-*tert*-Butylcyclohexene-1-carboxylate

Rudolph A. Abramovitch* and Sandra S. Singer

Department of Chemistry, University of Alabama, University, Alabama 35486

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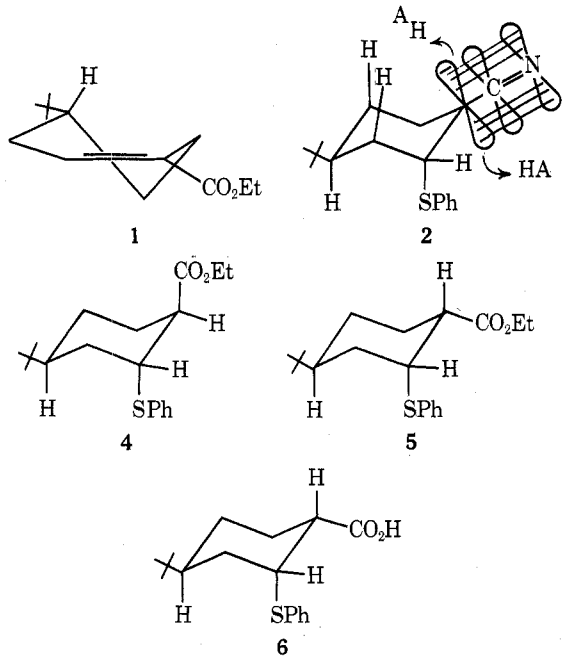
The addition of thiophenoxide ion to ethyl 4-*tert*-butylcyclohexene-1-carboxylate gives the two products **4** and **5** containing an axial thiophenoxy group. The stereochemistries of the products were established by a combination of NMR spectroscopy and chemical transformations into compounds of known stereochemistry. Under conditions of kinetic control the ratio of **4** to **5** was 5.5:94.5. Under conditions of thermodynamic control it was 14:86. The results are discussed. A number of sulfones in this series were also prepared and their NMR spectra discussed.

In previous papers in this series we have described the nucleophilic addition of malonate anion to two activated olefins of biased conformation, namely 4-*tert*-butyl-1-cyanocyclohexene[1] and ethyl 4-*tert*-butylcyclohexene-1-carboxylate (1),[2] and the addition of thiophenoxide ion and of hydrogen chloride to the above unsaturated nitrile.[3] In the additions of the malonate anion, the main product formed in protic solvents under conditions of kinetic control is the equatorial malonate, with an axial nitrile or ethoxycarbonyl compound. Under conditions of thermodynamic control the diequatorial product predominates. In the addition of thiophenoxide to the unsaturated nitrile, kinetic and thermodynamic control of the addition gave the axial thiophenoxy, equatorial nitrile isomer as the main product, but the pro-

portion of diaxial isomer was much greater under thermodynamic than under kinetic control conditions. These results were explained as follows: the preferred equatorial approach of the bulky malonate was attributed[1] to large diaxial nonbonded interactions in the transition state for axial addition, which transition state was assumed to resemble the intermediate. With smaller nucleophiles such as PhS^- and Cl^- such 1,3-diaxial repulsions would be less important, and axial approach of the nucleophile would be favored because of almost continuous overlap between the developing σ bond and the conjugated system in the formation of the transition state leading to axial product.[3] Kinetically controlled protonation of the intermediate anion from the least hindered side would account nicely for the observed stereoselectivities. Thus, in the case of the intermediate anion (**2**) from the axial addition of thiophenoxide to 4-*tert*-butyl-1-cyanocyclohexene protonation would involve approach from the side remote from the hindering thiophenoxy group.



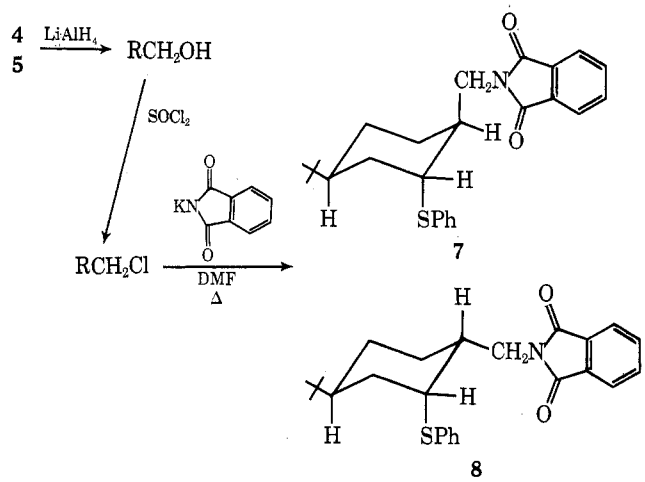
It was of interest to determine the preferred stereochemistry of kinetically controlled addition and protonation in the case where the linear nitrile group in **2** would be replaced by the bulkier carbethoxy group which could give rise to $A^{(1,3)}$ strain with an equatorial 2 substituent,[4] but in which relief of such a strain by chair–chair interconversion is not possible owing to the presence of the 4-*tert*-butyl group. To this end the addition of thiophenoxide ion to **1** under various conditions was studied.

In contrast to the addition of thiophenoxide ion (**3**) to 4-*tert*-butyl-1-cyanocyclohexene, which, under suitable conditions, gave three isomeric adducts, the addition of **3** to **1** gave only two adducts under all the experimental conditions examined. These proved to be *r*-1-*tert*-butyl-*c*-4-carbethoxy-*t*-3-thiophenoxycyclohexane (**4**) and *r*-1-*tert*-butyl-*t*-4-carbethoxy-*t*-3-thiophenoxycyclohexane (**5**). Under kinetic control conditions[3] (ethanolic sodium ethoxide, 25 °C, 42 days) **5** was the main product, **4**:**5** = 5.5:94.5. Under thermodynamic control conditions (NaOEt–EtOH, 80 °C)[3] **4**:**5** = 14:86, corresponding to $\Delta G°_{COOEt} = -1.2$ kcal/mol, in excellent agreement with the literature value of −1.1 to −1.2 kcal/mol.[5]

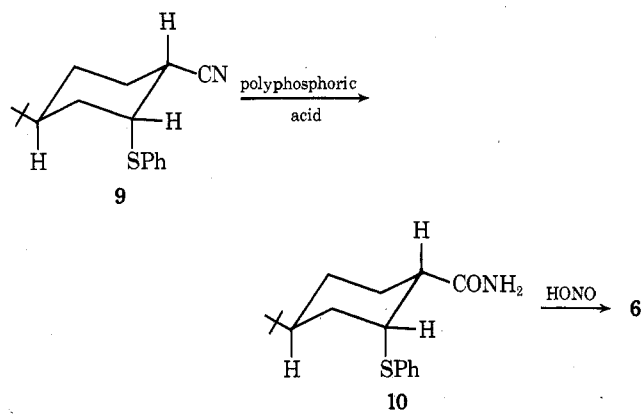
The assignment of the configurations to **4** and **5** was based initially mainly on the proton magnetic resonance spectra of the isomers. While the proton geminal to the ethoxycarbonyl group was clearly visible, that α to the thiophenoxyl group was obscured by the ethoxycarbonyl methylene group. In **4** the C-4 proton appears as an unresolved broad singlet at δ 2.67, thus suggesting an axial $-CO_2Et$ group. In **5** this proton gives rise to a doublet of doublet of doublets at δ 2.50 ($J_{4a,5a} = 11$, $J_{3e,4a} = J_{4a,5e} = 5$ Hz), indicating an equatorial CO_2Et group and possibly an axial PhS residue (giving rise to the low $J_{3e,4a}$ value). Since **4** and **5** are in equilibrium with each other,[6] this suggests that the thiophenoxy group is axial in **4** as well.

Hydrolysis of **5** with 3 N HCl gave the acid **6** whose configuration could be established unambiguously by ^1H NMR. The C-4 proton gave rise to a broad multiplet at δ 2.60 ($J_{4a,5a} = 12$, $J_{3e,4a} = J_{4a,5e} = 3.5$ Hz, axial H), while the C-3 proton gave rise to a broad doublet at δ 3.90 ($J_{3e,4a} = 3.5$ Hz, equatorial H).

The assigned stereochemistries could be confirmed chemically by the conversion of each of the stereoisomers **4** and **5** to the known[3] phthalimides **7** and **8**, respectively, via the corresponding alcohols and chlorides:



Alternatively, **5** could be correlated with *r*-1-*tert*-butyl-*t*-3-thiophenoxy-*t*-4-cyanocyclohexane (**9**) by conversion of the latter to **6** via the amide **10**.



Some important ^1H NMR data for the compounds described above are summarized in Table I. As has already been pointed out,[3] all equatorial side-chain methylene groups in this series give rise to an eight-line AB multiplet of an ABX system owing to the nonequivalence induced by the anisotropy of the vicinal axial thiophenoxy group. Axial methylenes give rise to broad doublets (A_2X).

The addition of thiophenoxide to **1** is thus analogous to the addition to the corresponding cyano olefin in that axial addition of thiophenoxide is followed by protonation from the least hindered side, i.e., that remote from the axial thiophenoxyl group, to give the product of trans-diaxial addition **5** as the kinetically controlled product. Since this is also the thermodynamically more stable isomer it is also the main product of addition under conditions of thermodynamic

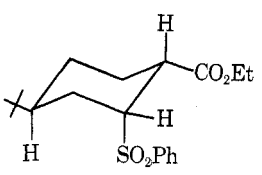
Table I. Selected ^{1}H NMR Chemical Shifts for *r*-1-*tert*-Butyl-*t*-3-thiophenoxyl-4-X-cyclohexanes

Registry no.	X (*c* or *t*)	C-4 H δ	CH_2Y δ	C-3 H δ
58463-31-3	*c*-4-CO_2Et	2.67 s		
58463-32-4	*t*-4-CO_2Et	2.50 d of t		
58463-33-5	*t*-4-CO_2H	2.60 d of t		3.90
58463-34-6	*t*-4-CH_2OH		3.60 **ABX**	3.72 s
58463-35-7	*c*-4-CH_2OH		3.50 br d	3.66 s
58463-36-8	*t*-4-CH_2Cl		3.60 **ABX**	3.70 s
58463-37-9	*c*-4-CH_2Cl		3.52 br d	3.70 s
35905-89-6	*t*-4-CH_2NR_2[a]		3.60 **ABX**	3.60 s
35905-93-2	*c*-4-CH_2NR_2[a]		3.68 br d	3.38 s

[a] R = phthalimido.

control. $A^{(1,3)}$ strain between the bulkier (than nitrile) ethoxycarbonyl group and an equatorial substituent does not come into play since only axial addition is observed. The results thus support the generalization proposed to rationalize the protonation of 2-substituted cyclohexyl anions.[6] The only difference between the additions reported here and those to the unsaturated nitrile is that, in the latter case, some equatorial thiophenoxy derivative was formed in THF and in DMF. This was not the case in the additions of thiophenoxide to **1**. That this is not due solely to the greater $A^{(1,3)}$ interactions possible in the transition state by the CO_2Et group than by the linear nitrile is clear since in the case of the addition of the bulkier diethyl malonate anion equatorial addition does occur.

Some very interesting and unusual relative stabilities of *tert*-butyl-3-phenylsulfonyl-4-phthalimidomethylcyclohexanes were reported and discussed earlier.[3] It was of interest, therefore, to prepare the sulfones corresponding to the phenylthio derivatives described above. Oxidation of **5** with peracetic acid gave the sulfone ester **11**. Similar oxidation of **4** led to a mixture of epimers, **12** and **13** on one occasion, but this result was not reproducible: in other similar oxidations, no **13** was formed. No explanation of this discrepancy is available. Authentic **13** was synthesized from *r*-1-*tert*-butyl-*c*-4-cyano-*c*-3-thiophenoxycyclohexane[3] by oxidation to the sulfone, hydrolysis to the amide with polyphosphoric acid, treatment with nitrous acid to give the sulfone acid, and then esterification. The ^{1}H NMR of **11** was interesting. The C-4 proton gave rise to a doublet of triplets at δ 2.70 (J_{aa} = 11, J_{ae} = 4.5 Hz) while the C-3 proton signal could be discerned at δ 3.84, buried under the methylene absorption. The ester



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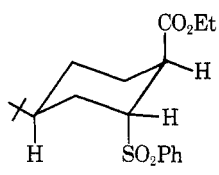

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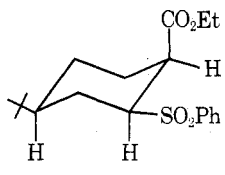

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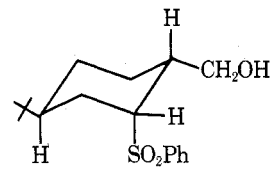

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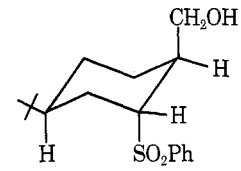

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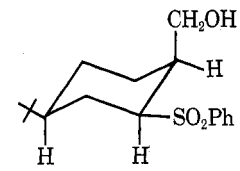

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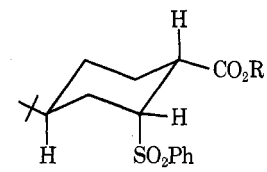


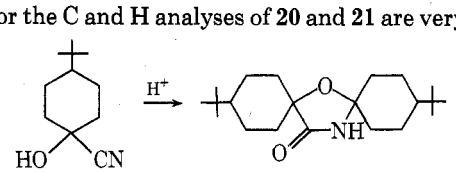
17, R = H

18, R = Me

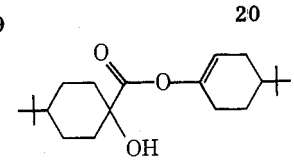
methylene gave rise to a complex 16-line multiplet, as is predicted for an ABX_3 system.[8] This suggests that free rotation of the ethoxyl group is greatly restricted, either sterically or by electronic repulsions between the $PhSO_2$ and ester oxygens, so that the methylene protons constitute an AB system. Other recent examples of magnetic nonequivalence of ethyl ester methylene protons have been reported.[1,9,10] In the ester sulfone **12** this situation cannot obtain and the ester methylene protons gave rise to a quartet at δ 4.08. As expected, the ester methylene group in **13** gave rise to a complex multiplet which simplified to an AB multiplet on irradiation of the ester methyl group.

Other sulfones synthesized at this time are the alcohols **14, 15,** and **16,** the acid **17,** and the ester **18** (see Experimental Section). No unusual features appeared in their NMR spectra except that the carboxyl proton in **17** resonated at δ 9.26, which is higher than the normal range reported (δ 11.5–12.5)[11] for such protons. This could be due to shielding of the carboxyl proton by the π cloud of the phenyl group.

During preliminary studies on the synthesis of **1**, ethanolysis of cyanohydrin **19** was studied. This gave rise to a troublesome by-product with little of the desired hydroxy ester formed. The by-product's spectral and analytical data corresponded to those expected for dispiro[bis(4-*tert*-butylcyclohexane-1,2′,5′,1″-oxazolid-4′-one)] (**20**), $C_{21}H_{37}NO_2$. This compound is identical with the one prepared earlier[12] and also with the one prepared by treatment of **19** with polyphosphoric acid,[13] to which had been attributed[12] structure **21**. The calculated values for the C and H analyses of **20** and **21** are very similar.



19 **20**



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Experimental Section

Addition of Thiophenol to Ethyl 4-*tert*-Butylcyclohexane-1-carboxylate. A. Kinetic Control Conditions. Sodium (4.38 g, 0.19 mol) was dissolved in absolute ethanol (200 ml). Thiophenol (31.4 g, 0.286 mol) and ethyl 4-*tert*-butylcyclohexane-1-carboxylate (20 g, 0.095 mol) were added. The flask was flushed with dry, oxygen-free nitrogen, and allowed to stand at room temperature for 42 days. The solution was acidified with glacial acetic acid, basified with 5% aqueous NaOH, and extracted with ether (4 × 200 ml). The combined extracts were washed with 5% NaOH (2 × 200 ml) and brine (2 × 200 ml), dried ($MgSO_4$), and evaporated. Unreacted olefin was removed by vacuum distillation. The residue (8.5 g) was dissolved in light petroleum (bp 30–60 °C). GLC analysis (20% SE-30 on 60–100 mesh Chromosorb

W, 6 ft × 3/16 in., 245 °C, 60 ml/min flow rate of helium carrier gas) indicated the presence of two compounds which were subsequently shown to be the isomeric ester sulfides **4** and **5** in the molar ratio of 5.5:94.5. The major product, ethyl *r*-1-*tert*-butyl-*t*-3-thiophenoxycyclohexane-*t*-4-carboxylate (**5**), crystallized from light petroleum: mp 58–59 °C (from light petroleum); ir (KBr) 3060 (aromatic C–H), 1720 cm^{-1} (ester C=O); NMR (CCl_4) δ 7.35 (m, 5, ArH), 3.88 (m, 3, $COOCH_2CH_3$ and C_3 H), 2.50 (d of t, J_{aa} = 11, J_{ae} = 5 Hz, 1, C_4 H), 0.87 (s, 9, *tert*-butyl); mass spectrum (70 eV) *m/e* (rel intensity) 320 (16) ($M^{\cdot+}$), 155 (17), 154 (20), 137 (55), 121 (15), 110 (42), 109 (34), 108 (16), 57 (100).

Anal. Calcd for $C_{19}H_{28}O_2S$: C, 71.20; H, 8.81. Found: C, 71.28; H, 8.46.

The minor product was resolved by column chromatography of the mother liquor (vide supra) on silica gel (benzene–light petroleum, 4:6 v/v, as eluent) to give ethyl *r*-1-*tert*-butyl-*t*-3-thiophenoxycyclohexane-*c*-4-carboxylate (**4**): bp 144–148 °C (0.25 mm); ir (neat) 3060, 3050 (aromatic C–H), 1725 cm^{-1} (ester C=O); NMR (CCl_4) δ 7.10 (m, 5, ArH), 4.04 (m, 3, $COOCH_2CH_3$ and C_3 H), 2.67 (br s, 1, C_4 H), 1.18 (t, 3, $COOCH_2CH_3$), 0.87 (s, 9, *tert*-butyl); mass spectrum (70 eV) *m/e* (rel intensity) 320 (11) ($M^{\cdot+}$), 154 (15), 137 (33), 110 (32), 109 (27), 57 (100).

Anal. Calcd for $C_{19}H_{28}O_2S$: C, 71.20; H, 8.81. Found: C, 70.77; H, 8.76.

Thermodynamic Control Conditions. Sodium (19.8 g, 0.86 mol) was dissolved in absolute ethanol (860 ml). Thiophenol (150 g, 1.29 mol) and ethyl 4-*tert*-butylcyclohexane-1-carboxylate (90 g, 0.43 mol) were added. The solution was boiled under reflux for 75 h. It was then worked up as described in the previous experiment. The product mixture (121 g, 90%) was dissolved in light petroleum. GLC of the mixture (conditions as given in the preceding experiment) indicated the presence of the two isomeric ester sulfides **4** and **5** in the molar ratio of 14:86. A white solid crystallized (56 g) from the solution of the product mixture. It was identified as **5**, its melting point, ir, and NMR spectra being identical with those of the material previously obtained. The mother liquor was chromatographed on silica gel to obtain the other isomer (4 g), which was shown to be the *r*-1, *t*-3, *c*-4 ester sulfide (**4**), identical with material previously obtained.

Addition in Dimethylformamide. Lithium thiophenolate (0.53 g, 5 mmol), ethyl 4-*tert*-butylcyclohexene-1-carboxylate (1.05 g, 5 mmol), and thiophenol (1.6 g, 15 mmol) were dissolved in dimethylformamide (10 ml). The solution was boiled under reflux for 6 h, cooled, poured into water (40 ml), and extracted with ether (3 × 20 ml). The combined ether extracts were washed with 5% NaOH (3 × 20 ml) and brine (2 × 20 ml), dried ($MgSO_4$), and evaporated. GLC analysis of the residual oil (conditions given previously) indicated the presence of unreacted olefin and the two isomeric ester sulfides (**4** and **5**) in the ratio of 1.2:1. The two products were separated by column chromatography (total yield 100 mg, 6.3%) and were identical in every respect with the compounds obtained with ethanol as solvent.

Equilibration of the *r*-1, *t*-3, *t*-4 Ester Sulfide (5). *r*-1-*tert*-Butyl-*t*-4-carbethoxy-*t*-3-thiophenoxycyclohexane (**5**, 640 mg, 2 mmol) was added to a solution of sodium (92 mg, 4 mmol) and thiophenol (0.66 ml, 6 mmol) in absolute ethanol (4 ml). The solution was boiled under reflux for 5 days, and worked up as described previously. GLC analysis of the residual oil (0.513 g) indicated the presence of the isomeric ester sulfides **4:5**, 9:91. The isomers were separated by column chromatography on silica gel (50 g) using benzene–light petroleum (1:1 v/v) as eluent and had infrared spectra identical with those of material obtained previously.

Attempted Equilibration of the *r*-1, *t*-3, *c*-4 Ester Sulfide (4). *r*-1-*tert*-Butyl-*c*-4-carbethoxy-*t*-3-thiophenoxycyclohexane (**4**, 0.320 g, 1 mmol) was dissolved in a solution of sodium (46 mg, 2 mmol) and thiophenol (0.33 ml, 3 mmol) in absolute ethanol (2 ml). The solution was boiled under reflux for 5 days. It was then worked up as described previously. GLC analysis of the residual oil (0.224 g) indicated that very little equilibration had occurred. The oil was dissolved in a solution of sodium ethoxide and thiophenol and the solution was boiled under reflux for 2 weeks. The reaction was worked up as described previously. GLC analysis of the residual oil (0.118 g) indicated the presence of the isomeric ester sulfides **4:5**, 55:45. The isomers were separated by column chromatography and had ir spectra identical with those of material obtained previously.

The equilibration was repeated in a sealed tube heated at 120° for 1 week. GLC analysis of the oil obtained on workup indicated the presence of the isomeric ester sulfides in the ratio **4:5**, 67:33.

***r*-1-*tert*-Butyl-*t*-4-hydroxymethyl-*t*-3-thiophenoxycyclohexane.** The *r*-1, *t*-3, *t*-4 ester sulfide (**5**, 3.2 g, 10 mmol) in dry ether (10 ml) was added dropwise to a solution of lithium aluminum hydride (0.53 g, 15 mmol) in dry ether (6 ml) at such a rate as to maintain gentle reflux. The solution was stirred at room temperature for 1 h after the addition was completed. The excess lithium aluminum hydride was decomposed with ethanol, the mixture poured into 1 N HCl (100 ml), the ether layer removed, and the aqueous layer extracted with ether (4 × 25 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated to give an oil (2.58 g, 96%). This solidified on standing and was recrystallized from *n*-hexane to give white crystals of the alcohol: mp 58.5–60 °C; ir (KBr) 3350 cm^{-1} (OH); NMR (CCl_4) δ 7.26 (m, 5, ArH), 3.72 (br s, 1, C_3 H), 3.60 (m, 2, **ABX**, CH_2OH), 2.63 (s, 1, OH, exchangeable with D_2O), 0.88 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{17}H_{26}OS$: C, 73.34; H, 9.41. Found: C, 73.60; H, 9.36.

***r*-1-*tert*-Butyl-*c*-4-hydroxymethyl-*t*-3-thiophenoxycyclohexane.** The diaxial alcohol was prepared from the corresponding ester in the same manner as was the alcohol from **5** (0.53 g, 66%): bp 120–124 °C (0.007 mm); ir (neat) 3350 cm^{-1} (OH); NMR (CCl_4) δ 7.20 (m, 5, ArH), 3.66 (br s, 1, C_3 H), 3.50 (br d, 2, CH_2OH), 3.30 (s, 1, OH, exchangeable with D_2O), 0.90 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{17}H_{26}OS$: C, 73.34; H, 9.41. Found: C, 73.67; H, 9.44.

***r*-1-*tert*-Butyl-*t*-4-chloromethyl-*t*-3-thiophenoxycyclohexane.** The *r*-1, *t*-3, *t*-4 alcohol (1.65 g, 6 mmol) and thionyl chloride (2.14 g, 18 mmol) were boiled under reflux for 6.5 h. Excess thionyl chloride was removed in vacuo and the residue was dissolved in ether (30 ml). The ethereal solution was washed with water (2 × 30 ml), 5% aqueous NaOH (2 × 30 ml), and brine (2 × 30 ml), dried ($MgSO_4$), and evaporated. The yellow residual oil (1.3 g, 73%) had bp 140–144 °C (0.025 mm); ir (neat) no OH; NMR (CCl_4) δ 7.30 (m, 5, ArH), 3.70 (s, 1, C_3 H), 3.60 (m, 2, **ABX**, CH_2Cl), 0.90 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{17}H_{25}ClS$: C, 68.74; H, 8.49. Found: C, 68.42; H, 8.45.

***r*-1-*tert*-Butyl-*c*-4-chloromethyl-*t*-3-thiophenoxycyclophexane.** This was prepared from the corresponding alcohol as described for the *r*-1, *t*-3, *t*-4 isomer. The chloride (0.212 g, 73%) had bp 106–110 °C (0.005 mm); ir (neat) no OH; NMR (CCl_4) δ 7.20 (m, 5, ArH), 3.70 (br s, 1, C_3 H), 3.52 (br d, 2, CH_2Cl), 0.90 (s, 9, *tert*-butyl); mass spectrum *m/e* 298, 296 ($M^{\cdot+}$). The crude material was used directly in the conversion to the corresponding phthalimide.

***r*-1-*tert*-Butyl-*c*-4-phthalimidomethyl-*t*-3-thiophenoxycyclohexane.** The above *r*-1, *t*-3, *c*-4 chloride (0.20 g, 0.172 mmol) and potassium phthalimide (0.463 g, 2.5 mmol) were dissolved in dimethylformamide (2 ml). The reaction was carried out as described below for the *r*-1, *t*-3, *t*-4-isomer. The *r*-1, *t*-3, *c*-4 phthalimide (**7**, 81 mg, 29%) was recrystallized from ethanol–water and had mp 85–89 °C (lit.[3] 90–92.5 °C), identical in all respects with the compound previously obtained.

***r*-1-*tert*-Butyl-*t*-4-phthalimidomethyl-*t*-3-thiophenoxycyclohexane (8).** The *r*-1, *t*-3, *t*-4 chloride (0.297 g, 1 mmol) and potassium phthalimide (0.740 g, 4 mmol) were dissolved in dimethylformamide (4 ml). The solution was boiled under reflux for 24 h, diluted with water (5 ml), and extracted with ether (3 × 15 ml). The desired phthalimide was separated from starting material by column chromatography on silica gel (starting with light petroleum as eluent and gradually adding benzene). The phthalimide (177 mg, 44%) was eluted with benzene–light petroleum (4:1 v/v) and was recrystallized from ethanol–water to give white crystals: mp 144–146 °C (lit.[3] 144–145 °C); ir (KBr) 1770, 1710 cm^{-1} (C=O); NMR (CCl_4) δ 7.50 (m, 9, ArH), 3.60 (m, 3, **ABX**, CH_2NR_2 and C_3 H), 0.94 (s, 9, *tert*-butyl), identical with an authentic sample.

***r*-1-*tert*-Butyl-*t*-3-thiophenoxycyclohexane-*t*-4-carboxylic Acid (6).** The *r*-1, *t*-3, *t*-4 ester (**5**, 2.72 g, 8.5 mmol) and 3 N HCl were boiled under reflux for 132 h. The mixture was cooled, diluted with water (50 ml), and extracted with ether. The combined ether extracts were washed with 5% NaOH (4 × 30 ml). Three layers were formed, a small brown layer being present between the ethereal and aqueous layer. The middle layer was the sodium salt of the desired acid and was taken with the aqueous layer. The aqueous mixture was acidified to pH 1, and the white precipitate was filtered to give the *r*-1, *t*-3, *t*-4 acid (**6**, 0.60 g, 24%): mp 164.5–166 °C (acetone–water); ir (KBr) 3200–2500, 1705 cm^{-1} (C=O); NMR (CCl_4) δ 7.25 (m, 5, ArH), 3.90 (d, J_{ae} = 3.5 Hz, 1, C_3 H), 2.60 (d of t, J_{ae} = 12, J_{ae} = 3.5 Hz, 1 H, C_4 H), 0.82 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.50; H, 8.33.

The same acid could be obtained (88%) by diazotization of the *r*-1, *t*-3, *t*-4 sulfide amide.[3]

***r*-1-*tert*-Butyl-*t*-3-thiophenoxycyclohexyl-*t*-4-carboxamide (10).** The *r*-1, *t*-3, *t*-4 nitrile sulfide (**9**, 2 g, 7 mmol) and polyphosphoric acid (20 g) were warmed on a steam bath for 5 h. The mixture

was poured into water (100 ml) and extracted with ether (2 × 100 ml). The extracts were evaporated and the residue resolved by column chromatography on silica gel (50 g). Elution with ether gave the *r*-1, *t*-3, *t*-4 amide sulfide (**10**, 1.7 g, 80%): mp 160.5–161.5 °C (aqueous ethanol); ir (KBr) 3390, 3220, 1645, 1615 cm^{-1}; NMR ($CDCl_3$) δ 7.30 (m, 5 H, ArH), 5.98 (br s, 2 H, $CONH_2$), 3.87 (d, J_{ae} = 5 Hz, 1 H, C_3 H), 2.55 (d to t, J_{aa} = 12, J_{ae} = 5 Hz, 1 H, C_4 H), 0.81 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{25}NOS$: C, 70.07; H, 8.65. Found: C, 69.73; H, 8.76.

***r*-1-*tert*-Butyl-*t*-3-thiophenoxycyclohexyl-*c*-4-carboxamide.** The *r*-1, *t*-3, *c*-4 nitrile (1.53 g, 0.57 mol) was heated at 80 °C with polyphosphoric acid (20 g) for 9 h. The mixture was poured into water (100 ml) and extracted with $CHCl_3$ (4 × 100 ml). The extracts were washed with 5% NaOH (200 ml) and brine (3 × 200 ml), dried ($MgSO_4$), and evaporated to give a yellow oil (1.19 g, 68%) which solidified. Recrystallization from aqueous ethanol gave the amide: mp 117.5–118.5 °C; ir (KBr) 3310, 3180, 1660, 1605 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 5 H, ArH), 4.08 (br s, 1 H, C_3 H), 2.58 (br s, 1 H, C_4 H), 0.78 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{25}NOS$: C, 70.07; H, 8.65. Found: C, 69.99; H, 8.79.

***r*-1-*tert*-Butyl-*t*-3-thiophenoxycyclohexane-*t*-4-carboxylic Acid (6) from the Amide.** The amide **10** (0.11 g, 0.38 mmol) in glacial acetic acid (3 ml) containing sulfuric acid (2.12 ml) and water (1.64 ml) at 0 °C was treated with sodium nitrite (0.10 g) slowly. After being stirred at 0 °C for 1 h the mixture was kept at room temperature overnight. It was diluted with water (20 ml) and extracted with ether and the ether evaporated. The residue (0.097 g, 88%) was identical (ir) with an authentic sample of the acid.

A similar reaction using the *r*-1, *t*-3, *c*-4 amide was unsuccessful, starting material being recovered. Repeated diazotizations led to a mixture of at least five products which were not examined further.

Ethyl *r*-1-*tert*-Butyl-*t*-3-phenylsulfonylcyclohexane-*t*-4-carboxylate (11). The *r*-1, *t*-3, *t*-4 ester sulfide (**5**, 1.5 g) was dissolved in a mixture of glacial acetic acid (25 ml), 30% hydrogen peroxide (1.5 ml), and concentrated sulfuric acid (2 drops). The solution was stirred at room temperature for 9 h, the solvent was evaporated, and the residue (1.28 g, 78%) was recrystallized from aqueous ethanol to give the sulfone **11**: mp 148–148.5 °C; ir (KBr) 1715 (C=O), 1330, 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.80, 7.50 (m, 5 H, ArH), 4.00 (m, **ABX**$_3$, 2 H, $CO_2CH_2CH_3$), 3.84 (br s, 1 H, C_3 H), 2.70 (d of t, J_{aa} = 11, J_{ae} = 4.5 Hz, 1 H, C_4 H), 1.28 (t, 3 H, $CO_2CH_2CH_3$), 0.90 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01. Found: C, 64.61; H, 8.13.

Oxidation of the *r*-1, *t*-3, *c*-4 Ester Sulfide (4). The sulfide (0.15 g) was dissolved in peracetic acid solution (7 ml) [from glacial acetic acid (50 ml), 30% hydrogen peroxide (3.0 ml), and concentrated sulfuric acid (4 drops)] and stirred at room temperature for 7.75 h. The solvent was evaporated and the residue was resolved by column chromatography on silica gel (40 g). Elution with chloroform–benzene (1:1 v/v) gave the *r*-1, *t*-3, *c*-4 ester sulfone (**12**, 93 mg, 55%): bp 160 °C (0.007 mm) (with some decomposition); ir (film) 1725 (C=O), 1310, 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.85, 7.55 (m, 5 H, ArH), 4.08 (q, J = 7 Hz, 2 H, $CO_2CH_2CH_3$), 3.56 (br s, 1 H, C_3 H), 3.23 (br s, 1 H, C_4 H), 1.24 (t, J = 7 Hz, 3 H, $CO_2CH_2CH_3$), 0.84 (s, 9, H, *tert*-butyl).

Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01. Found: C, 64.83; H, 8.08.

Further elution gave the *r*-1, *c*-3, *c*-4 ester sulfone (**13**, 47 mg, 28%): mp 114.5–115 °C (aqueous ethanol), identical with the sample prepared as described below from the *r*-1, *c*-3, *c*-4 sulfone acid; ir (film) 1725 (C=O), 1305, 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.85, 7.55 (m, 5 H, ArH), 4.00 (m, **ABX**$_3$, 2 H, $CO_2CH_2CH_3$), 2.80 (m, 2 H, C_3 H and C_4 H), 1.20 (t, 3 H, $CO_2CH_2CH_3$), 0.90 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01. Found: C, 65.00; H, 8.22.

When this oxidation was repeated using **4** (0.60 g), glacial acetic acid (15 ml), 30% hydrogen peroxide (0.9 ml), and concentrated sulfuric acid (1 drop) at room temperature, only **12** could be detected after 2 h and after 20.5 h. No explanation of the discrepancy is available at this time.

Ethyl *r*-1-*tert*-Butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxamide. The *r*-1, *c*-3, *c*-4 sulfone nitrile[3] (1.17 g) and polyphosphoric acid (30 g) were heated at 80 °C for 3 h. The solution was poured into water (50 ml) and extracted with $CHCl_3$ (3 × 100 ml). The organic layer was dried ($MgSO_4$), concentrated (after decolorizing with charcoal), and triturated with light petroleum to give the amide sulfone (0.434 g, 38%): mp 192–193.5 °C (sublimation) (aqueous ethanol); ir (KBr) 3460, 3360 (NH_2), 1685 (C=O), 1605, 1280, 1150 cm^{-1}; NMR ($CDCl_3$) δ 7.90, 7.60 (m, 5 H, ArH), 4.10 (m, 2 H, C_4 H, C_3 H), 0.80 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.12; H, 8.44. Found: C, 63.22; H, 7.99.

***r*-1-*tert*-Butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxylic Acid.** The above amide (0.123 g) in glacial acetic acid (3 ml), concentrated sulfuric acid (2.12 ml), and water (1.64 ml) at 3 °C was treated with sodium nitrite (0.10 g) with stirring. The white precipitate was stirred at 0 °C for 1 h and at room temperature for 12 h and water (20 ml) was then added. The mixture was extracted with ether (4 × 20 ml) and the dried ($MgSO_4$) combined extracts were evaporated to give the sulfone acid (0.102 g, 84%): mp 183–184 °C (from ether–light petroleum); ir (KBr) 3300–2400 (CO_2H), 1695 (C=O), 1305, 1140 cm^{-1} (SO_2).

Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46. Found: C, 62.77; H, 7.64.

Ethyl *r*-1-*tert*-Butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxylate (13). The acid was esterified with ethanol and sulfuric acid to give the ester (29%), identical with the one obtained above in the oxidation and epimerization.

***r*-1-*tert*-Butyl-*c*-4-hydroxymethyl-*c*-3-phenylsulfonylcyclohexane (16).** The above *r*-1, *c*-3, *c*-4 sulfone acid (1.154 g) in dry ether (10 ml) was boiled under reflux for 6 h with a solution of $LiAlH_4$ (116 mg) in dry ether (10 ml). Careful addition of water followed by pouring the solution into 1 N HCl and extraction with ether gave the alcohol (**16**) as a yellow oil (0.56 g, 50%) which was purified by chromatography on a column of silica gel (50 g) and elution with benzene–$CHCl_3$ (1:1 v/v): ir (film) 3450 (OH), 1305, 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.95, 7.65 (m, 5 H, ArH), 3.80 (m, 3 H, **ABC**, $CHCH_2OH$), 3.10 (d of t, J_{aa} = 14, J_{ae} = 5 Hz, 1 H, C_3 H), 2.92 (s, 1 H, OH, exchange with D_2O), 0.88 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{26}O_3S$: C, 65.77; H, 8.44. Found: C, 65.63, H, 8.59.

***r*-1-*tert*-Butyl-*t*-4-hydroxymethyl-*t*-3-phenylsulfonylcyclohexane (14).** The ester **11** (1.85 g) in dry ether (30 ml) was treated with a solution of lithium aluminum hydride in ether (2 M, 3 ml) dropwise at such a rate as to maintain reflux. The solution was then stirred at room temperature for 2 h and excess hydride was decomposed with EtOH. Workup as above gave the alcohol **14** (1.63 g, 74%): mp 103–105 °C (from *n*-hexane); ir (CCl_4) 3530, 1308, 1145 cm^{-1}; NMR ($CDCl_3$) δ 7.90, 7.60 (m, 5 H, ArH), 4.20 (m, 3 H, CH_2OH and C_3 H), 3.07 (s, 1 H, OH, exchanges with D_2O), 0.69 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{26}O_3S$: C, 65.77; H, 8.44. Found: C, 65.61; H, 8.49.

***r*-1-*tert*-Butyl-*c*-4-hydroxymethyl-*t*-3-phenylsulfonylcyclohexane (15). A.** This was prepared from **12** by $LiAlH_4$ reduction as described above for **14**. The alcohol (68%) had bp 160 °C (0.007 mm) (dec); ir (CCl_4) 3450, 1310, 1150 cm^{-1}; NMR ($CDCl_3$) δ 7.90, 7.50 (m, 5 H, ArH), 4.20 (s, 1 H, OH exchangeable), 3.60 (m, 3 H, CH_2OH and C_3 H), 2.60 (s, 1 H, OH, exchangeable), 0.80 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{26}O_3S$: C, 65.77; H, 8.44. Found: C, 65.58; H, 8.49.

B. Oxidation of the *r*-1, *t*-3, *c*-4 alcohol sulfide[3] with peracetic acid solution initially gave the corresponding sulfone acetate [δ 1.92 (s, 3 H, CH_3CO_2)] which, following repeated attempts at recrystallization, gave the above alcohol.

Methyl *r*-1-*tert*-Butyl-*t*-3-thiophenoxycyclohexane-*t*-4-carboxylate. The acid **6** (1 g) was esterified with methanol (30 ml) and sulfuric acid (4 drops) to give the ester (0.96 g, 90%): mp 69–69.5 °C; ir (KBr) 1740 cm^{-1}; NMR (CCl_4) δ 7.30 (m, 5 H, ArH), 3.84 (q, J_{ae} = 4 Hz, 1 H, C_3 H), 3.42 (s, 3 H, CO_2CH_3), 2.60 (d of t, J_{aa} = 10, J_{ae} = 4 Hz, 1 H, C_4 H), 0.84 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.75; H, 8.55. Found: C, 70.51; H, 8.68.

Methyl *r*-1-*tert*-Butyl-*t*-3-phenylsulfonylcyclohexane-*t*-4-carboxylate (18). The above ester (0.618 g) in glacial acetic acid (25 ml) containing 30% hydrogen peroxide (1.5 ml) and concentrated H_2SO_4 (2 drops) was stirred at room temperature for 3 h. The solvent was evaporated and the sulfone **18** (0.68 g, 100%) was recrystallized from aqueous ethanol: mp 143–143.5 °C; ir (KBr) 1740, 1305, 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.85, 7.55 (m, 5 H, ArH), 3.82 (br s, 1 H, C_3 H), 3.54 (s, 3 H, CO_2CH_3), 2.50 (d of t, 1 H, C_4 H), 0.80 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{18}H_{26}O_4S$: C, 63.87; H, 7.74. Found: C, 64.01; H, 7.83.

***r*-1-*tert*-Butyl-*t*-3-phenylsulfonylcyclohexane-*t*-4-carboxylic Acid (17).** Sulfide **6** was oxidized in the same manner as was ester **18** to give the sulfone **17** (100%): mp 160 °C (sublimation); ir (KBr) 3300–2500 (br), 1720, 1300, 1140 cm^{-1}; NMR ($CDCl_3$) δ 9.26 (br s, 1 H, CO_2H, exchangeable), 7.90, 7.60 (m, 5 H, ArH), 3.95 (br s, 1 H, C_3

H), 2.60 (d of t, J_{aa} = 11, J_{ae} = 4 Hz, 1 H, C_4 H), 0.80 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46. Found: C, 62.83; H, 7.66.

Dispiro[bis(4-*tert*-butylcyclohexane-1,2',5',1''-oxazolid-4'-one)] (20). 4-*tert*-Butylcyclohexanone cyanohydrin (**19**, 2 g) was dissolved in a mixture of 95% EtOH (5 ml) and concentrated HCl (5 ml). The solution was boiled under reflux for 13 h. The precipitated oxazolidone (0.20 g, 9%) was filtered and had mp 330 °C; ir 3400, 3290, 1685 (C=O), 1090 cm^{-1}; the NMR spectrum could not be determined owing to the insolubility of this compound in the usual solvents; mass spectrum (70 eV) *m/e* (rel intensity) 336 (0.8), 335 ($M\cdot^+$, 2.4), 320 (2.6) 236 (100), 182 (3.4), 180 (4.6), 164 (70), 154 (9.2), 138 (9.2).

Anal. Calcd for $C_{21}H_{37}NO_2$: C, 75.17; H, 11.12; N, 4.18. Found: C, 75.55; H, 11.14; N, 4.23.

The same compound (identical ir spectra) could be obtained, albeit in even lower yield (3.5%), by keeping a mixture of the cyanohydrin and polyphosphoric acid at room temperature.[13]

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Registry No.—**1**, 23022-33-5; **9**, 35905-86-3; **10**, 58463-38-0; **10** 4-*c* isomer, 58463-39-1; **11**, 58463-32-4; **12**, 58463-40-4; **13**, 58463-41-5; **14**, 58463-42-6; **15**, 58463-43-7; **16**, 58463-44-8; **17**, 58463-45-9; **18**, 58463-46-0; **19**, 941-44-6; **20**, 58463-47-1; ethyl *r*-1-*tert*-butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxamide, 58463-48-2; *r*-1-*tert*-butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carbonitrile, 35905-99-8; *r*-1-*tert*-butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxylic acid, 58463-49-3; methyl 1-*r*-*tert*-butyl-*t*-3-thiophenoxycyclohexane-*t*-4-carboxylate, 58463-50-6; thiophenol, 108-98-5.

References and Notes

(1) R. A. Abramovitch and D. L. Struble, *Tetrahedron*, **24**, 357 (1968).
(2) R. A. Abramovitch, S. S. Singer, M. M. Rogić, and D. L. Struble, *J. Org. Chem.*, **40**, 34 (1975).
(3) R. A. Abramovitch, M. M. Rogić, S. S. Singer, and N. Venkateswaran, *J. Org. Chem.*, **37**, 3577 (1972).
(4) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5495 (1965); S. K. Malhotra and F. J. Johnson, *ibid.*, **87**, 5493 (1963); F. Johnson, *Chem. Rev.*, **68**, 375 (1968).
(5) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965, p 436.
(6) Equilibration appears to occur, at least partly, via retro-Michael addition followed by readdition.[3] The isolation of olefin **1** from some equilibration experiments supports this suggestion. Since elimination from **4** would be expected to be more difficult than from **5** this could explain slight differences observed between the ratio obtained starting from pure **5** and from the addition under thermodynamic control conditions, and also the different ratio obtained in the dipolar aprotic solvent, DMF, used.[1]
(7) R. A. Abramovitch, M. M. Rogić, S. S. Singer, and N. Venkateswaran, *J. Am. Chem. Soc.*, **91**, 1571 (1969).
(8) V. J. Kowaleski and D. G. de Kowaleski, *J. Chem. Phys.*, **33**, 1794 (1960).
(9) W. L. Meyer, D. L. Davis, L. Foster, A. S. Levinson, V. L. Sawin, D. C. Shaw, and R. F. Weddleton, *J. Am. Chem. Soc.*, **87**, 1573 (1967).
(10) J. W. Pavlik, N. Filipescu, and R. S. Egan, *Tetrahedron Lett.*, 4631 (1969).
(11) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Oxford, 1959, p 71.
(12) L. Munday, *J. Chem. Soc.* 1413 (1964).
(13) H. R. Snyder and C. T. Elston, *J. Am. Chem. Soc.*, **76**, 3039 (1954).

Reaction of Pyridine 1-Oxides and *N*-Iminopyridinium Ylides with Diazonium Salts. *N*-Aryloxypyridinium Salts and Their Base-Catalyzed Rearrangement

Rudolph A. Abramovitch,* Muthiah N. Inbasekaran, Shozo Kato, and George M. Singer

Department of Chemistry, University of Alabama, University, Alabama 35486

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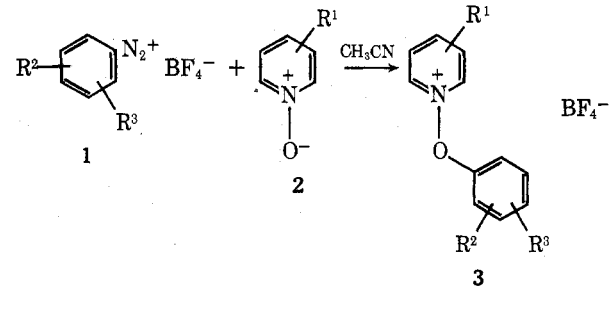
N-Aryloxypyridinium tetrafluoroborates are prepared by the reaction of pyridine 1-oxides with aryldiazonium tetrafluoroborates bearing an electron-withdrawing substituent in the aryl ring. The scope, limitations, and possible mechanism of the reaction are discussed. The salts undergo base-catalyzed rearrangement to give 2-*o*-hydroxyarylpyridines. *N*-Aminopyridinium tetrafluoroborates react with aromatic diazonium salts in acetonitrile to give 1-[(*N*-arylacetimidoyl)amino]pyridinium tetrafluoroborates (**14**) but no *N*-arylaminopyridinium tetrafluoroborates. Related compounds are formed in propionitrile and malononitrile, but not in butyronitrile and benzonitrile. In butyronitrile, for example, 1-(*N*-butyrimidoylamino)iminopyridinium tetrafluoroborate (**16**) is formed. Compounds **14** give the corresponding ylides with base. Treatment of *N*-aryliminopyridinium ylides with base does not lead to their rearrangement to 2-*o*-aminoarylpyridines.

N-Alkoxypyridinium salts are well-known compounds whose preparation[1] and properties[1,2] have recently been reviewed. They are usually readily made from the *N*-oxide and an alkyl halide, dialkyl sulfate, or alkyl sulfonate. In contrast, the *N*-aryloxy compounds were not known when this work was initiated.[3] Attempts to phenylate pyridine 1-oxide with diphenyliodonium bromide or benzenediazonium tetrafluoroborate failed.[4] We now report[3] a convenient synthesis of such compounds and a novel molecular rearrangement which they undergo.

It was expected that, for a direct arylation to occur between a diazonium salt and an *N*-oxide, the salt would have to be more electrophilic than unsubstituted benzenediazonium tetrafluoroborate, rather than going the other way and making the *N*-oxide more nucleophilic. It was felt that if the latter were the case the *N*-oxide might induce a homolytic decomposition via the diazo compound[5] which would defeat the purpose. To this end, the diazonium tetrafluoroborate (**1**) of



an aromatic amine bearing an electron-withdrawing substituent was added to a solution of a pyridine 1-oxide (**2**) in acetonitrile and the solution was either stirred at room temperature or warmed gently to give the desired *N*-aryloxypyridinium tetrafluoroborate (**3**). The salts so prepared are listed in Table I.

The structures of the salts **3** were established by spectro-