viously in the absence of both galvinoxyl and sulfide **9**. No evidence is seen for an exchange of the added aryl sulfide with **1** to give a new sulfurane.

A mechanism for this radical chain process has been suggested.[2b] Radical initiation involving a reaction between sulfide and sulfurane may involve electron transfer or S–S bond formation, as suggested earlier.[2b] Electron transfer reactions may also be preferred to direct displacements in the chain transfer reaction between solvent α-ethoxyethyl radicals and sulfurane to give **11**.

When the pyrolysis is carried out in the presence of thioanisole, acetal **11** is not observed but rather $C_6H_5SCH_2OR_F$ (**12**) is formed in 70% yield along with a trace of **10a**. Heating a 0.127 mmol sample of **1** in 0.5 ml of ether at 77° for 55 hr in a sealed nmr tube containing 6.1 mg of galvinoxyl and 0.10 mmol of thioanisole results, however, only in the formation of alkoxylation products **10** in the same product ratio (61:14:25) observed previously in the absence of both galvinoxyl and thioanisole. A radical chain sequence similar to that leading to **11** is diverted, in the presence of the more reactive hydrogen atom donor thioanisole, to give **12**.

The great reactivity of sulfurane **1** toward active hydrogen compounds (O–H, N–H, S–H, etc.), an indefinite shelf life in the absence of moisture, and the unique pattern of reactivity which results from the absence in **1** of the halogen ligands present in other sulfuranes[7,15b,24,34] make this compound very attractive as a reagent for dehydrations,[2c,33] etherifications,[2c,33] oxidations, and certain cleavage and coupling reactions. The development of synthetic applications of this reagent, and related compounds, will be the subject of forthcoming publications.

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Sulfuranes. VI.[1] Reactions Involving the Alkoxy Ligands of Dialkoxydiarylsulfuranes. Formation of Olefins and Ethers

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Abstract: Dehydrations of secondary and tertiary carbinols with **1** [$(C_6H_5)_2S(OR_F)_2$, where $R_F = C_6H_5C(CF_3)_2$] proceed under unusually mild conditions to give generally excellent yields of olefin. The synthetic utility of the reaction is demonstrated by the formation of the hitherto inaccessible unrearranged olefin from the dehydration of tricyclopropylcarbinol (**5**). Tertiary alcohols are dehydrated essentially instantaneously, even at −50° in ether or chloroform. The kinetic isotope effect ($k_H/k_D = 1.54$) for the intramolecular competition in the dehydration of partially deuterated *tert*-butyl alcohol, when considered with evidence for carbonium ion rearrangements in certain cases, favors a mechanism with considerable E1 character. A strong preference for trans coplanar disposition of leaving groups in the dehydration of appropriately chosen secondary carbinols gives evidence for the E2 character in these reactions. Primary alcohols react with **1** to form unsymmetrical ethers (R_FOCH_2R) in the absence of structural features increasing the acidity of β protons. The rate of this reaction with various alcohols ($CH_3OH > (CH_3)_2CHCH_2OH > (CH_3)_3CCH_2OH$) is that expected for an SN2 displacement by R_FO^- on an intermediate, postulated to be the alkoxysulfonium ion ($ROS(C_6H_5)_2^+$), formed by reaction of the alcohol with **1**. A similar intermediate is implicated in the dehydration reactions of tertiary and secondary alcohols. The exchange of alkoxy ligands of **1** with added alcohols is shown by nmr to be fast. Reactions of chloroform solutions of **1** with alcohols, such as neopentyl alcohol, which do not give rapid elimination or ether-forming reactions, lead by a radical-chain process to R_FOCCl_3. In this reaction **1** acts as an oxidizing agent.

The use of stable, crystalline dialkoxydiphenylsulfurane (**1**) as a dehydrating agent for the conversion of alcohols to alkenes was suggested by our preliminary observation[3] that the alkoxy ligands of **1** rapidly exchange with added alcohols, and by our earlier observation[4] of isobutylene in the product mixture from a perester decomposition postulated to give sulfurane **2** as an intermediate. The methallyl chloride seen by Walling and Mintz in the *tert*-butyl hypochlorite oxidation of diphenyl sulfide[5] is most conveniently rationalized to result from chlorination of isobutylene formed by a similar process. We here report results[6] which suggest that **1** is indeed a dehydrating agent with unique properties, potentially of great synthetic utility.

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(1) For paper V of this series see R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997 (1972).

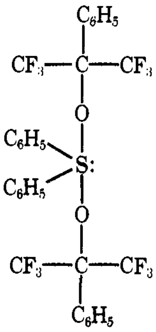
(2) Abstracted from the Ph.D. Thesis of R. J. Arhart, University of Illinois, Urbana, 1971. National Institutes of Health Predoctoral Fellow, 1967–1971.

(3) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2339, 2341 (1971).

(4) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962); D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *ibid.*, **85**, 1938 (1963); R. J. Arhart, Ph.D. Thesis, University of Illinois, Urbana, 1971.

(5) C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967); see also P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N.

(6) Part of this work has appeared in preliminary form: J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 4327 (1971).



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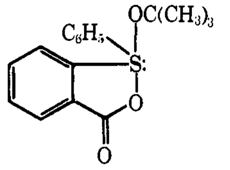

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Experimental Section

Nuclear magnetic resonance spectra were recorded on Varian Associates A-60A, A-56/60A, HA-100, and HR-220 spectrometers. Fluorine chemical shifts are reported as parts per million upfield from fluorotrichloromethane internal standard. Mass spectra were run on Atlas CH-4, CH-7, and Gnom (MAT 111) mass spectrometers. The last two were connected to gas chromatographs and were used to analyze the components of reaction mixtures.

Chloroform-*d* was purified by passage through a short column of Woelm neutral alumina. Ether was dried by distillation from $LiAlH_4$ and stored over sodium wire. Sulfurane **1** was prepared by the reaction of chlorine with R_FOK and diphenyl sulfide in ether as described in the preceding paper.[1]

Alcohols. All used were commercially available except for tricyclopropylcarbinol (**5**) which was prepared by the method of Hart and Sandri,[7] dimethylcyclopropylcarbinol (**9**) which was prepared by methyl Grignard addition to methylcyclopropyl ketone,[8] 2-methyl-2-propanol-*1,1,1,3,3,3*-d_6 which was prepared by the Grignard reaction from acetone-d_6, and 3-nortricyclanol which was prepared by the saponification of the precursor acetate, prepared by addition of acetic acid to norbornadiene.[9]

Dehydration Procedure and Product Analysis. Most of the reactions with sulfurane **1** were carried out in an nmr sample tube. In general, a known amount of **1** dissolved in *ca.* 0.5 ml of dry $CDCl_3$ was added to a known amount of the alcohol at room temperature in an inert atmosphere box. The product yields were determined by using the aromatic proton peak integrals as an internal standard. All nmr peaks outside the aromatic proton region were identified using 220-MHz nmr and authentic samples of products.

Reactions of 1. (a) ***tert*-Butyl Alcohol.** To 0.5 ml of a $CDCl_3$ solution of sulfurane **1** (0.083 mmol) cooled to $< -50°$ was added 1 equiv of *tert*-butyl alcohol in 0.25 ml of $CDCl_3$. (The alcohol was distilled from CaO prior to use.) The ^{19}F nmr spectrum at $-50°$ showed only a singlet for R_FOH at 74.5 ppm. The ^1H spectrum, outside the aromatic proton region, was identical with that of an authentic sample of isobutylene..

(b) Tricyclopropylcarbinol (5). A solution of **5** (0.258 g, 1.70 mmol) in 2 ml of dry $CDCl_3$ was added to excess **1** (1.28 g, 1.91 mmol) in 4 ml of $CDCl_3$ at room temperature in an inert atmosphere box. The nmr shows 68% of 1,1-dicyclopropyl-4-(hexafluoro-2-phenyl-2-propoxy)butene-1 (**7**) (δ 2.59 (q, J = 7 Hz, 2 H, $CH_2C{=}C$), 3.63 (br t, J = 7 Hz, 2 H, CH_2OR_F, width of central peak at half-height is reduced from 3.0 to 1.4 Hz upon irradiation at 94.0910 MHz), 5.18 (t, J = 7.5 Hz, 1 H, $C{=}CH$)) and 32% of (dicyclopropylmethylene)cyclopropane (**6**). All R_FOH was removed from the product mixture by washing twice with 10-ml portions of 10% aqueous NaOH and once with 10 ml of water, drying over Na_2SO_4, and removing solvent *in vacuo*. Flash distillation (10^{-2} mm, pot temperature 60°) of the less volatile material separated **6** (56 mg, 25%) from the even less volatile diphenyl sulfoxide and **7**: nmr ($CDCl_3$) δ 1.42 (br pentet, J = 6.5 Hz, 2 H, methine), 0.97 (t, $J \approx$ 0.9, 4 H, cyclopropylidene CH_2, five-bond coupling with methine protons established by homonuclear spin decoupling), and 0.78–0.50 (m, 8 H, cyclopropyl CH_2); mass spectrum, m/e 134 ($M\cdot^+$).

(c) ***cis*- and *trans*-4-*tert*-Butylcyclohexanol.** Composition of a mixture of epimeric alcohols was shown to be 27% cis and 73% trans from integration of the hydroxymethylene nmr peaks at δ 4.0 and 3.5. Treatment of this mixture (79.4 mg, 0.509 mmol) in dry $CDCl_3$ at room temperature with 0.27 equiv of **1** (89.5 mg, 0.133 mmol) gave 0.13 equiv of 4-*tert*-butylcyclohexene (integrating the olefinic proton multiplet at δ 5.75; presumably 0.14 equiv of **1** was hydrolyzed[10]). In agreement with this, 0.14 equiv or *ca.* 52% of the cis alcohol (equatorial $CHOH$ multiplet at δ 4.0) remained. No loss of the trans alcohol (axial $CHOH$ multiplet at δ 3.5) was detectable by nmr. Addition of excess sulfurane converted the remaining alcohol to 4-*tert*-butylcyclohexene.

(d) ***cis*- and *trans*-2-Methylcyclohexanol.** A procedure similar to that outlined above was used for a mixture of 49% cis and 51% trans alcohol (integration of $CHOH$ protons at δ 3.80 and 3.13). Addition of an amount of **1** sufficient to react with most of the cis alcohol gave a 3:1 mixture of **17** (220-MHz nmr δ 1.63 (s, 3 H, CH_3), 5.45 (m, 1 H, $C{=}CH$)) and **18** (220-MHz nmr δ 0.97 (d, J = 7.0 Hz, 3 H, CH_3, irradiation of methine proton at δ 2.22 collapses doublet to a singlet), 5.63 (four-peak m, 2 H, $C{=}CH$)). No loss of the trans alcohol was detectable by nmr. Addition of excess sulfurane dehydrated the remaining alcohol to give an overall **17**:**18** ratio of 38:62.

(e) ***cis*- and *trans*-3-Methylcyclohexanol.** Addition of excess **1** to a mixture of 68% cis and 32% trans alcohol gave 50% **18** (220-MHz nmr) and 50% 4-methylcyclohexene (220-MHz nmr δ 0.96 (d, J = 6.0 Hz, 3 H, CH_3), 5.69 (br s, 2 H, $C{=}CH$)).

(f) Methanol, purified by refluxing over magnesium turnings for 12 hr and distillation, was added to 1 equiv of **1** in $CDCl_3$ at $< -50°$. Formation of **11a** in 100% yield was complete within seconds at $-50°$: nmr ($CDCl_3$, 25°) ^1H, δ 3.54 (septet, J_{HF} = 1.0 Hz, CH_3, irradiation at 94.0863 MHz gives a sharp singlet), ^{19}F, 70.5 ppm (s, CF_3). R_FOH was removed from the product mixture by washing with 10% aqueous NaOH. Gas chromatography on 5% SE-30 on Chromosorb W (acid washed, DMCS) afforded a peak for **11a**: mass spectrum, m/e 258 ($M\cdot^+$), 189 ($M\cdot^+ - CF_3$).

(g) Benzyl Alcohol. The only product from reaction of 1 equiv of benzyl alcohol with **1** in ether at $-50°$, **11b**, gave nmr ($CDCl_3$) ^1H, δ 4.67 (br s, CH_2, peak width at half-height is decreased from 2.7 to 1.3 Hz upon irradiation at 94.0862 MHz), ^{19}F, 70.4 ppm (s, CF_3).

Reaction of 2 equiv of benzyl alcohol with **1** in $CDCl_3$ at $-50°$ gave **11b** and dibenzyl ether. Recovered benzyl alcohol and dibenzyl ether were identified by glpc on 5% SE-30 on Chromosorb W (acid washed, DMCS). After washing with D_2O the 100-MHz ^1H nmr of the product mixture shows: δ 4.67 (br s, $C_6H_5CH_2OR_F$, irradiation at 94.0862 MHz gives a sharp singlet), 4.63 (s, $C_6H_5CH_2$-OH), and 4.55 (s, $(C_6H_5CH_2)_2O$). Integrals show these three products in the ratio 44:43:13.

(h) Ethanol gave rapid formation of **11c** in 100% yield upon treatment with 1 equiv of **1** in $CDCl_3$ at ambient temperature: nmr, ^1H, δ 1.33 (t, J = 7 Hz, 3 H, CH_3) and 3.70 (br q, J = 7 Hz, 2 H, CH_2, irradiation at 94.0862 MHz decreases peak widths at half-height of quartet component peaks from 2.9 to 1.1 Hz), ^{19}F, 70.7 ppm (s, CF_3).

Solid **1** (*ca.* 250 mg) was added to a frozen solution (liquid N_2) of potassium ethoxide (*ca.* 3 equiv) in 0.5 ml of absolute ethanol in a glove bag. The reaction mixture was warmed slowly to room temperature. Part of the methylene quartet of diethyl ether is visible in the ^1H nmr of the reaction mixture. From ^{19}F integrals the ratio **11c**/R_FOH is 0.034 (by comparison a control sample lacking the ethoxide showed 0.68). The ratio diethyl ether/**11c** [glpc, 20% SE-30 on Chromosorb W (acid washed, DMCS)] is 23 times that for the control sample lacking the ethoxide. The per cent R_FOH observed in the ethoxide-containing sample is considerably in excess of that expected from the observed diethyl ether and **11c** yields. This suggests that some ethylene is formed under these conditions.

(i) Isobutyl alcohol, dried by refluxing over $^1/_{16}$ in. Linde 4A molecucular sieves for 12 hr and distilled, when treated with **1** in $CDCl_3$ at $-50°$, gave evidence for rapid ligand exchange (^{19}F and ^1H nmr) but no **11d**. At 0° the ether is formed slowly and at room temperature rapidly and quantitatively: nmr, ^1H, δ 0.99 (d, J = 6.3 Hz, 6 H, $C(CH_3)_2$), 2.04 (septet, J = 6.5 Hz, 1 H, methine), and 3.42 (br d, J = 6.5 Hz, 2 H, CH_2, irradiation at 94.0862 MHz narrows the peak width at half-height from 3.6 to 2.2 Hz), ^{19}F, 70.3 ppm (s, CF_3).

(j) Neopentyl Alcohol, No Solvent. An equimolar mixture of pure neopentyl alcohol (86.0 mg, 0.977 mmol) and **1** (659.4 mg, 0.980 mmol) was heated periodically for short times up to 65° over a period of 5 days after which time the sample was viscous, but

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(7) H. Hart and J. M. Sandri, *Chem. Ind.* (*London*), 1014 (1956).

(8) R. Van Volkenburg, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 71, 172 (1949).

(9) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 74 (1965).

(10) Some hydrolysis of sulfurane by adventitious water was always observed in these dehydrations.

homogeneous. After heating the sample a total of *ca.* 5 hr at 90° product formation was complete. By comparison to authentic samples of amylenes, nmr integration shows 9% 2-methyl-2-butene, 24% 2-methyl-1-butene, and 67% **11e**: nmr ($CDCl_3$), ^{1}H, δ 1.01 (s, 9 H, $C(CH_3)_3$), and 3.28 (br s, 2 H, CH_2, irradiation at 94.0910 MHz narrows the peak width at half-height from 2.7 to 0.6 Hz), ^{19}F, 70.2 ppm (s, CF_3). In addition, small amounts of recovered neopentyl alcohol (less than 15% of **11e**) and an unknown material[11] showing a singlet at 0.59 (less than 10% of the area of the *tert*-butyl singlet of **11e**) are present.

(k) Neopentyl Alcohol in $CDCl_3$. A solution of neopentyl alcohol was added to excess **1** in $CDCl_3$. Ligand exchange is rapid at room temperature (^{19}F and ^{1}H nmr) but product formation is slow. After >12 hr at room temperature product formation was incomplete. The reaction was complete after heating at 41° for 12 hr. Neopentyl alcohol was recovered in ≥90% yield (nmr). The ^{1}H nmr spectrum of the product mixture shows a peak at δ 1.01 (less than 10% of the area of the *tert*-butyl singlet of neopentyl alcohol at δ 0.90) and in the ^{19}F spectrum a peak at 70.0 ppm (less than 10% of the area of the singlet at 68.5 ppm, R_FOCCl_3) and a trace peak at 70.2 ppm, all due to unknown products.[12]

The product mixture was washed twice with 10% aqueous NaOH to remove R_FOH. The products R_FOCCl_3 (**14**) and diphenyl sulfide were both isolated by preparative glpc on SE-30 on Chromosorb W (acid washed, DMCS). The nmr, ir, and mass spectra of diphenyl sulfide were identical with those of an authentic sample: ether **14**, nmr ($CDCl_3$), 220-MHz ^{1}H, δ 7.71 (m, 2 H, ortho) and 7.50 (m, 3 H, meta and para), ^{19}F, 68.5 ppm (s, CF_3); mass spectrum, *m/e* (rel intensity) 364 (0.21), 362 (0.44), 360 (0.41, $M\cdot^+$), 264 (7.7), 262 (21.2, $C_9H_5F_6Cl$), 227 (100, $C_9H_5F_6$), 207 (41.7, $C_9H_4F_5$), 195 (9.8), 193 (30.5, $C_8H_5F_3Cl$), 123 (0.5), 121 (3.5), 119 (10.4), 117 (10.8, CCl_3), 86 (0.4, intensity high for P + 4 peak for species containing two chlorine atoms), 84 (0.5), 82 (0.7, CCl_2), 65 (1.3), and 63 (4.9, COCl), intense metastable at *m/e* 190 (*m/e* 262 ion is derived from $M\cdot^+$ at *m/e* 360).

(l) Isoborneol in $CDCl_3$. Treatment of isoborneol with excess **1** in $CDCl_3$ at room temperature gave 59% camphene and 41% tricyclene by 220-MHz nmr: camphene, nmr ($CDCl_3$) δ 1.03 and 1.05 (two s, 6 H, $C(CH_3)_2$), 1.89 (m, 1 H, $CHC(CH_3)_2$), 2.67 (m, 1 H, $CHC{=}C$), 4.51 and 4.73 (two s, 2 H, $C{=}CH_2$); tricyclene, nmr ($CDCl_3$) δ 0.83 (s, 6 H, $C(CH_3)_2$) and 1.01 (s, 3 H, bridgehead CH_3).

(m) Isoborneol, Added Base. A solution of isoborneol in ether containing 0.6 *M* 1,4-diazabicyclo[2.2.2]octane (Dabco) was mixed with excess **1** at −78° and brought slowly to room temperature over several hours. Solvent ether was allowed to evaporate from the uncapped sample at room temperature, $CDCl_3$ was added, and the products analyzed by nmr as before; 42% camphene, 58% tricyclene.

(n) Borneol. Reaction of borneol with excess **1** in $CDCl_3$ at room temperature gives rapid ligand exchange (^{19}F and ^{1}H nmr) but further reaction is slow, requiring >12 hr for completion. The 220-MHz nmr integration of the product mixture shows 61% camphene, 17% tricyclene, and 22% bornylene in addition to a comparable amount of R_FOCCl_3 and an unknown product (^{19}F nmr, 70.0 ppm, s, peak area 20% that of R_FOCCl_3). Bornylene was identified by comparison with the nmr of an authentic sample prepared by the dehydration of bornyl bromide in refluxing *n*-pentyl alcohol–alkoxide.[13] Our nmr assignments are in agreement with those of Davies and Powley.[14]

(o) 3-Nortricyclanol and *exo*-2-Norbornen-5-ol. A mixture of 86% 3-nortricyclanol and 14% *exo*-2-norbornen-5-ol was treated with excess **1** in $CDCl_3$ at room temperature. Product formation is rapid at room temperature giving unsymmetrical ethers **22** and **23** in 83.3 and 16.7% yields, respectively. An amount of R_FOCCl_3 (^{19}F nmr 68.5 ppm, s) equal to 7% of the combined yields of **22** and **23** and an unknown (^{19}F nmr, 70.0 ppm, s) showing 40% of the area of the R_FOCCl_3 peak were formed. From the chemical shift this appears to be the same unknown material formed in minor amounts in the reaction of both neopentyl alcohol and borneol with **1** in $CDCl_3$: ether **22**, nmr ($CDCl_3$), ^{19}F, 69.2 (q, J = 10.6 Hz, 3 F, CF_3) and 71.4 ppm (q, J = 10.6 Hz, 3 F, CF_3), ^{1}H, δ 3.82 (br s, 1 H, R_FOCH, irradiation at 94.0862 MHz narrows the peak width at half-height from 4.3 to 3.4 Hz); ether **23**, nmr ($CDCl_3$), ^{19}F, 69.3 (q, J = 10.6 Hz, 3 F, CF_3) and 71.0 ppm (q, J = 10.6 Hz, 3 F, CF_3), ^{1}H, δ 2.80 (m, 1 H, bridgehead $CHCHOR_F$), 2.96 (m, 1 H, bridgehead $CHCH_2$), 3.80 (m, 1 H, R_FOCH, shoulder on δ 3.82 peak), 5.75 (d of d, $J_{2,3}$ = 5.7 Hz, $J_{1,2}$ = 3.0, 1 H, $CH{=}C$ at C_2), and 6.09 (d of d, $J_{2,3}$ = 5.7 Hz, $J_{3,4}$ = 3.0, 1 H, $C{=}CH$ at C_3).[15] The mass spectra of R_FOCCl_3 and diphenyl sulfide obtained by glpc–mass spectrometry on 5% SE-30 on Chromosorb W (acid washed, DMCS) were identical with those of authentic samples. The mass spectrum of a glpc peak containing **22** and/or **23** shows peaks at *m/e* 336 ($M\cdot^+$), 267 ($M\cdot^+ - CF_3$), and 227, 207 (both characteristic of R_FO groups).

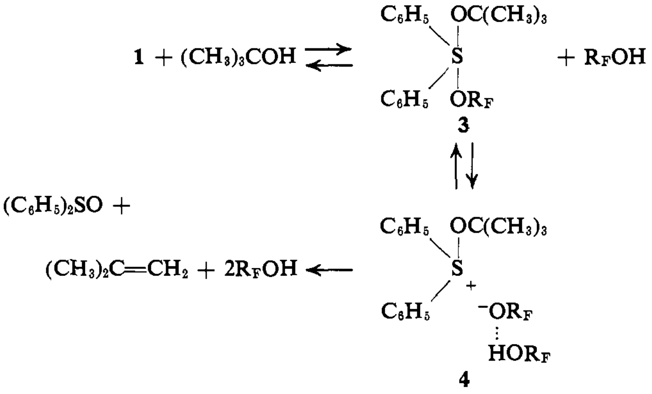
Identical product **22**:**23** ratios were seen for a mixture of carbinols containing 95.5% 3-nortricyclanol and 4.5% *exo*-2-norbornen-5-ol.

Results

The product yields in Table I were determined by nmr using the aromatic proton peak integrals (from a known amount of **1** added to a known amount of alcohol) as an internal standard. All nmr peaks outside the aromatic proton region were identified using 220-MHz nmr and authentic samples of products. In every case the total yields of identified products, determined by careful integrations of completely resolved product peaks, were within ±5 mol % of the amount of alcohol added. The yields quoted assume 100% of identified products. New compounds were identified by nmr (using homonuclear and heteronuclear spin decoupling where appropriate) and glpc–mass spectrometry.

Discussion

All of the alcohols studied appear to exchange rapidly with the alkoxy ligands of **1**. We suggest that this occurs by some variant of the dissociative mechanism outlined in the preceding paper[1] and pictured here for *tert*-butyl alcohol. General acid catalysis for the ionization step by the acidic R_FOH seems very likely.[1] This exchange is followed by an elimination reaction which is so rapid for *tert*-butyl alcohol at −50° that the postulated tetracovalent intermediate **3** was not observed. Evidence for the rapid equilibration of alkoxy ligands in the first step of this mechanism is seen in both ^{19}F and ^{1}H low-temperature nmr spectra of dehydration reaction mixtures of the more slowly eliminating secondary alcohols, however. Other alcohols, for example borneol and neopentyl alcohol, which contain structural features that restrict attainment of the normal transition states for either elimination or unsymmetrical



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[11] 1,1-Dimethylcyclopropane shows a resonance at δ 0.2 in CCl_4 for the methylene protons: W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).

[12] The peak at 70.2 ppm may be a trace of **11e** as shown by addition of an authentic sample.

[13] H. Meerwein and J. Joussen, *Chem. Ber.*, **55**, 2529 (1922).

[14] D. I. Davies and P. J. Rowley, *J. Chem. Soc. C*, 1832 (1968).

[15] The assignments of the exo configuration for **23**, and of the peaks for its two olefinic protons, were made on the basis of comparison with the nmr spectra of the olefinic protons of other 5-norbornenyl derivatives, in particular, *exo*- and *endo*-2-norbornen-5-ol and the unsymmetrical ether derived therefrom by reaction with **1**. See J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965) and A. G. Ludwick and J. C. Martin, *J. Org. Chem.*, **34**, 4108 (1969).

Table I. Reactions of Alcohols with **1** in Chloroform-*d* at Room Temperature

Alcohol	Products	% yield[f]
tert-Butyl alcohol[a]	Isobutylene	100
tert-Amyl alcohol	2-Methyl-2-butene	41
	2-Methyl-1-butene	59
4-Hydroxy-4-methyl-2-pentanone	Mesityl oxide	100
1-Methylcyclohexanol	1-Methylcyclohexene	90
	Methylenecyclohexane	10
Tricyclopropylcarbinol (**5**)	**6**	32
	7	68
Dimethylcyclopropylcarbinol (**9**)	**10**	100
2-Butanol	*cis*- and *trans*-2-butene	44
	1-Butene	56
Cyclohexanol	Cyclohexene	100
27% *cis*- and 73% *trans*-4-*tert*-butylcyclohexanol	4-*tert*-Butylcyclohexene	100
cis-2-Methylcyclohexanol (**16**)	**17**	75
	18	25
trans-2-Methylcyclohexanol (**19**)	**18**	100
68% *cis*- and 32% *trans*-3-methylcyclohexanol	**18**	50
	4-Methylcyclohexene	50
Methanol[a]	**11a**	100
Benzyl alcohol[b]	**11b**	100
Benzyl alcohol[a] (2 equiv)	**11b**	44
	$(C_6H_5CH_2)_2O$	13
	$C_6H_5CH_2OH$ (regenerated)	43
Ethanol	**11c**	100
Isobutyl alcohol	**11d**	100
Neopentyl alcohol[c]	**11e**	67
	2-Methyl-2-butene	9
	2-Methyl-1-butene	24
3-Hydroxypropionitrile	Acrylonitrile	100
Isoborneol	Camphene	59 (42)[d]
	Tricyclene	41 (58)[d]
Borneol	Camphene	61
	Tricyclene	17
	Bornylene	22
exo-2-Norborneol	Nortricyclene	100
3-Nortricyclanol (86%) and	**22**	83 (83)[e]
exo-2-norbornen-5-ol (14%)	**23**	17 (17)[e]

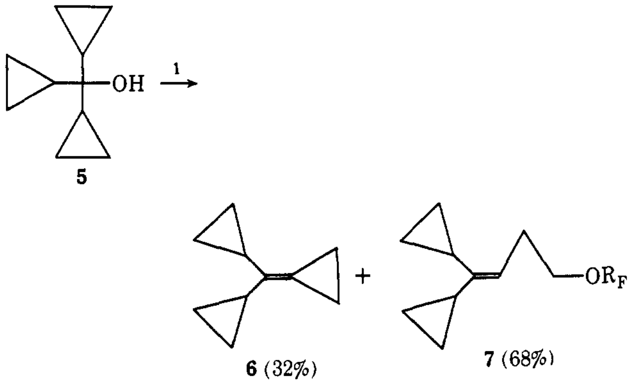
[a] At −50°. [b] In ether at −50°. [c] Neat at 90°. [d] In ether at −78° containing 0.6 *M* Dabco. [e] Starting alcohol mixture 95.5:4.5. [f] Product yields based on nmr (see text). Ratios of products are accurate to ±3%; total yields of products (unisolated) to ±5%.

ether formation, give rapidly equilibrating mixtures of relatively stable sulfuranes at room temperature.

The sulfurane dehydration of *tert*-amyl alcohol gives a slightly greater proportion of internal olefin than is expected from a purely statistical dehydration. Increasing the acidity of the two internal methylene protons by the presence of an adjacent carbonyl group, as in the case of 4-hydroxy-4-methyl-2-pentanone, results in the complete formation of the α,β-unsaturated ketone upon treatment with **1**. Although the dehydrations of 1-methylcyclohexanol either by **1** or by dimethyl sulfoxide[16] (DMSO) give essentially the same product ratios of internal and terminal olefins, the dehydrations of *tert*-amyl alcohol by **1** and by DMSO[17] give quite different product ratios.

The unusually mild conditions for dehydration with **1** compared to other dehydrating agents are illustrated by the marked difference in conditions necessary to dehydrate 1-methylcyclohexanol by **1** (25°, seconds) and by DMSO[16] (180°, 9 hr).

Earlier attempts to dehydrate tricyclopropylcarbinol (**5**) using sulfuric acid or phosphorus pentoxide failed to yield any of olefin **6**.[18] Dehydration with sulfurane **1**, however, gives 32% (by nmr, 25% by isolation) of **6**.



5

6 (32%)

7 (68%)

Attempts to dehydrate **5** using acidic catalysts give only ring-opened products,[18] for example alcohol **8**, derived from the tricyclopropylcarbonium ion. Olefin **6** is probably formed from an alkoxysulfonium ion analogous to **4** by a reaction with some E2 character, with R_FO^- acting as the base and diphenyl sulfoxide as the leaving group. The homoallylic ether **7** may result either from attack of the alkoxide on a cyclopropyl ring of this alkoxysulfonium ion or, more probably, on the tricyclopropylcarbonium ion derived therefrom.[19,20] Carbinol **9**, which would form a less stable carbonium

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(16) V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964).

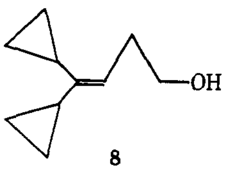
(17) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *ibid.*, **27**, 2377 (1962).

(18) H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, **84**, 2462 (1962).

(19) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959); see ref 18.

(20) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962).

ion, quantitatively yields the unrearranged olefin **10** upon dehydration with **1**.



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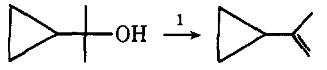

9 **10**

The method used for isolation of **6** is of rather general applicability. The acidic R_FOH is removed by washing with 10% aqueous NaOH. Solvent chloroform is removed *in vacuo* and **6** is removed from the less volatile diphenyl sulfoxide and **7** by flash distillation at 10^{-2} mm, pot temperature 60°. Variations of this procedure using recrystallization or column chromatography to separate nonvolatile olefins from the polar sulfoxide, or using glpc to separate volatile olefins, are also useful.

Most secondary alcohols undergo quantitative and rapid dehydration when treated with **1** at room temperature. At subambient temperatures olefin formation from secondary alcohols is noticeably slower than from tertiary alcohols. No cyclohexene is observed by nmr upon addition of cyclohexanol to **1** at −50°, only an equilibrium mixture of rapidly exchanging sulfuranes. At 0°, however, cyclohexene is seen to appear slowly (within minutes) and at 25°, rapidly (within seconds). In a competitive study using a limited amount of **1** with a mixture of the conformationally fixed *cis*- and *trans*-4-*tert*-butylcyclohexanols, the cis isomer with its axial hydroxyl group was found to react more rapidly to form 4-*tert*-butylcyclohexene than does the trans isomer by a factor of at least 150.[21] No loss of the trans alcohol was detectible by nmr until all of the cis isomer was consumed. In a competitive dehydration of a mixture of *cis*- and *trans*-2-methylcyclohexanols, the cis isomer with its favored axial hydroxyl conformation is completely destroyed by **1** to give a 3:1 mixture of **17** and **18** before detectible loss of the more slowly reacting trans isomer (which gives only **18**, as expected from a favored trans diaxial disposition of leaving groups in the transition state). Upon treatment with **1** a mixture of 68% *cis*- and 32% *trans*-3-methylcyclohexanol gives a 1:1 mixture of 3- and 4-methylcyclohexenes.

The only acyclic secondary alcohol studied, 2-butanol, shows practically no selectivity upon dehydration giving a very nearly statistical mixture of olefins (44% 2-butenes, 56% 1-butene). The acyclic tertiary alcohol, *tert*-amyl, is dehydrated with only a slightly greater selectivity, favoring the internal olefin.

Treatment of primary alcohols with **1** gives unsymmetrical ethers **11** in the absence of structural features increasing the acidity of β protons. (3-Hydroxypropionitrile gives only elimination, no ether.) Unsymmetrical ether formation from primary alcohols and **1** is rapid at room temperature, except for neopentyl alcohol, and even at temperatures as low as −50° in the case of methyl and benzyl alcohols. Carbinols such as ethanol and isobutyl alcohol, which contain a β proton which could be involved in an elimination reaction, give only the corresponding unsymmetrical ethers.[23]

$$RCH_2OH + \mathbf{1} \longrightarrow RCH_2OR_F$$

11a, R = H
b, R = C_6H_5
c, R = CH_3
d, R = $CH(CH_3)_2$
e, R = $C(CH_3)_3$

In no case were oxidation products (aldehydes or ketones) seen in the product mixtures from treatment of primary or secondary alcohols with **1**. Attempts to form aldehydes by increasing the basicity of the medium by adding the potassium alkoxides of the corresponding primary alcohols, for example benzyl and ethyl, all failed. This is, perhaps, not surprising in view of the demonstration by Fenselau and Moffat[25] that the Kornblum oxidation[26] of a primary tosylate or halide with DMSO involves an intramolecular proton abstraction by an intermediate sulfur ylide formed from the alkoxysulfonium ion. The structural features of our alkoxysulfonium ions preclude such a mechanism.

Reaction of 2 mol of benzyl alcohol at −50° results in the formation of dibenzyl ether (13%), in addition to **11b** (44%), and in the recovery of benzyl alcohol (43%). Ethanol and isobutyl alcohol, both of which contain a β proton which could be involved in an elimination reaction, give only the corresponding unsymmetrical ethers **11c** and **d**. Long-range coupling, J_{HF} = 1.0 Hz, visible in the proton spectra of **11** as a resolved multiplet structure (for **11a**) or as line broadening (for **11b–e**), is lost on irradiation at the ^{19}F frequency. This provides excellent evidence for the structures of ether products **11**.

Treatment of separate mixtures of benzyl and ethyl alcohols and of their corresponding potassium alkoxides with **1** fails to yield any of the corresponding aldehydes. The reaction of a *ca.* 0.75 *M* solution of **1** in ethanol containing *ca.* 3 equiv wt of potassium ethoxide results in a 23-fold increase in the diethyl ether–**11c** product ratio from the value observed in the absence of the ethoxide. In the presence of ethoxide a decrease in the total yield of ethers was observed, presumably by diversion of the reaction to the ethylene-forming elimination reaction.

The rate of unsymmetrical ether formation in the case of isobutyl alcohol (0°, slow) is noticeably slower than is seen for methanol (−50°, seconds). Neopentyl alcohol shows a drastically retarded rate (>5 hr at 90°) of product formation in the reaction with 1 equiv of **1** in the absence of solvent. This suggests that the dineopentyloxy sulfurane should be isolable and experiments are underway to attempt this. The order of reactivity is that expected[27] for an SN2 displacement on the alkoxysulfonium ion.

If nucleophilic attack by the bulky and poorly nucleophilic alkoxide anion at the neopentyl methylene

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(21) This value was calculated from the integrated rate expression for competitive reactions,[22] assuming a 2% maximum possible error in nmr analytical results for the *trans*-4-*tert*-butylcyclohexanol.

(22) C. Walling and B. Miller, *J. Amer. Chem. Soc.*, 79, 4181 (1957).

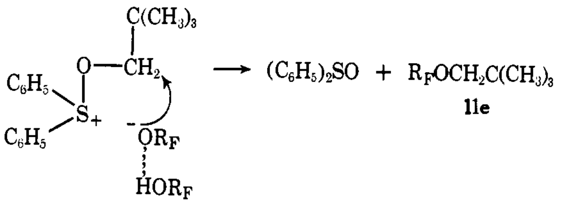
(23) The formation of ethers from primary alcohols is formally, and perhaps mechanistically, analogous to the formation of 1-dimethylaminoalkanes from the reaction of primary alcohols with hexamethylphosphoric triamide,[24] a reaction which could be plausibly proposed to involve a phosphorane intermediate. The analogous dehydration with DMSO has been shown[16,17] to fail for primary alcohols also and even for secondary aliphatic alcohols, though working well for tertiary or benzylic alcohols.

(24) R. S. Monson, *Tetrahedron Lett.*, 567 (1971).

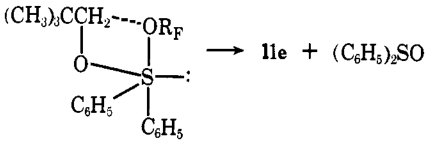
(25) A. H. Fenselau and J. G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 1762 (1966); for a slightly different interpretation, see K. Torssell, *Tetrahedron Lett.*, 4445 (1966).

(26) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, **81**, 4113 (1959).

(27) F. C. Whitmore and G. H. Fleming, *ibid.*, **55**, 4161 (1933); I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157 (1946).



group seems an unlikely[28] route to the large amount of **11e** seen for this alcohol, one can entertain the notion that **11e** is formed by an electrocyclic process. Pseudorotation processes leading to **12**, or an analogous conformer, though probably slow on the nmr time scale,[1] should not be too slow to account for this ether-forming reaction of neopentyl alcohol with **1**. In **12** the proximity of the two alkoxy ligands makes it possible to consider electrocyclic reactions such as that pictured. Further work will be required to establish any possible contribution from this mechanism.



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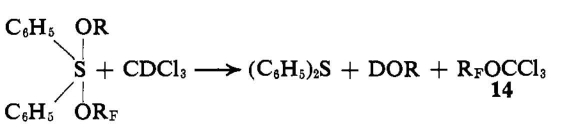
The large amount (67%) of neopentyl ether **11e** formed and the slow rate of its formation are reminiscent of the reaction yielding neopentyl bromide by treatment of neopentyl alcohol with tributylphosphine dibromide. Wiley, Rein, and Hershkowitz[29] have provided support for a mechanism for this reaction which involves a rate-determining displacement by bromide ion on an alkoxyphosphonium ion. A very similar mechanism is proposed for the formation of **11e**. The other identified products, 2-methyl-2-butene (9%) and 2-methyl-1-butene (24%), are typical carbonium ion rearrangement products.

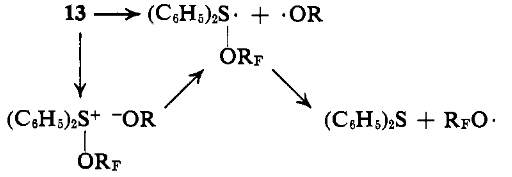
Treatment of **1** in chloroform-*d* at room temperature with neopentyl alcohol, or other unreactive alcohols such as borneol, results in the formation of additional products, R_FOCCl_3 (**14**) and diphenyl sulfide, in a reaction faster than that between neat **1** and neopentyl alcohol but still relatively slow (>12 hr at 25°). The marked reduction in the yield of **14** in the presence of the inhibitor chloranil or the radical scavenger diphenylpicrylhydrazyl suggests a radical-chain process similar to that postulated[1] for the formation of $CH_3CH(OR_F)OCH_2CH_3$ upon heating **1** in ether in the presence of an aryl sulfide. Sulfurane **1** is stable in chloroform-*d* at room temperature in the presence of diphenyl sulfide and at 77° gives only the nuclear alkoxylation products, $C_6H_5SC_6H_4OR_F$, in a ratio (52:48, ortho:meta plus para) similar to that seen in other solvents.[1]



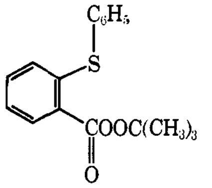
$$(C_6H_5)_2S(OR)(OR_F) + CDCl_3 \longrightarrow (C_6H_5)_2S + DOR + R_FOCCl_3$$

13 **14**

The initiation step is suggested to involve some species such as the unsymmetrical sulfurane **13**. In the absence of an alcohol more basic than R_FOH but unreactive toward dehydration or ether formation, no **14** is formed. It is possible to imagine initiation steps leading to $R_FO\cdot$ (or $RO\cdot$) which would involve electron transfer from the alkoxide anion to the alkoxysulfonium ion. Such radical-forming reactions have analogies in



the reaction postulated[4] to occur in the decomposition of **15**, the perester precursor to **2**, and in the reverse reaction for the rapid reduction of *tert*-butoxy radicals to *tert*-butoxy ions by electron transfer from paraquat cation radical.[30]



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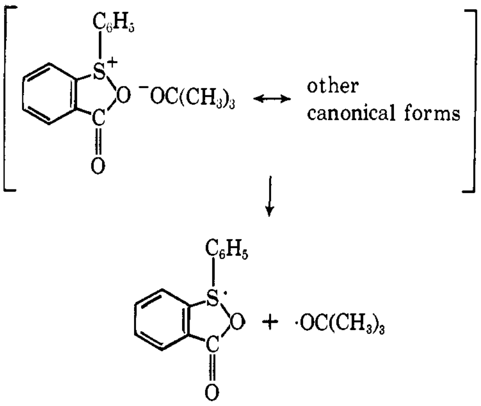

$$(CH_3)_3CO\cdot + PQ\cdot^+ \xrightarrow{\text{fast}} (CH_3)_3CO^- + PQ^{2+}$$

A sensitivity of such electron-transfer initiation to redox potentials of the alkoxysulfonium ion and the alkoxide anion could explain the action of the added neopentyl alcohol in promoting this reaction. A result arguing against this scheme for initiation is the observation that neopentyl alcohol fails to initiate the chain reaction of **1** with diethyl ether. This suggests a possible involvement of chloroform in the initiation step. Attempts to initiate the reaction in chloroform-*d* by addition of low-temperature initiator **15**, by photolysis, or by addition of diphenyl sulfide (a member of a class of compounds found[1] to react with **1** to give radicals in the reaction of **1** with diethyl ether) all failed to increase the yield of **14**.

Clearly the initiation steps for radical formation from **1** are complex and will require further research.

Propagation and termination steps quite conventional for radical-chain induced decompositions involving solvent can be pictured for this reaction.

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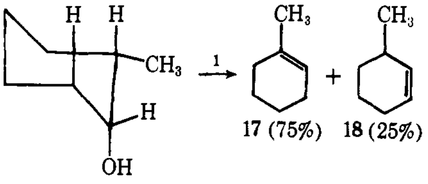
[28] See for example, W. W. Kirmse and K. Horn, *Tetrahedron Lett.* 1827 (1967).

[29] G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *ibid.*, 2509 (1964).

[30] A. S. Hopkins and A. Ledwith, *Chem. Commun.*, 830 (1971).

The evidence quoted earlier for a strongly preferred trans diaxial elimination in substituted cyclohexanols[31] suggests a preferred mechanism for the dehydrations of secondary alcohols near the E2 end of the mechanistic continuum. The dehydration of **16** with **1** gives a product ratio (3:1 favoring **17** over **18**) almost identical with that observed for the dehydration over alumina at 300°.[32] However, the dehydration of trans alcohol **19** over alumina[32] at 300° also gave some **17**, the ratio of **18**:**17** being 4.3. It was suggested[32] that this loss of specificity resulted from the incursion of some E1 process into the dehydration of the less reactive **19**, a process not competitive with the E2 process under our conditions.



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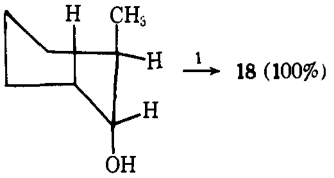

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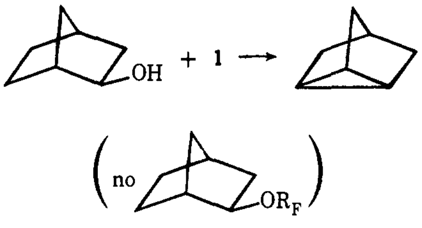
The competing E1 process appears to become important when the resulting carbonium ion is stabilized by structural features and/or the competing E2 or S_N2 processes are sterically hindered. Several systems which were studied provide products most easily rationalized as the result of rearrangements of intermediate carbonium ions. The formation of olefinic products from neopentyl alcohol, for example, or **7** from tricyclopropylcarbinol probably involves carbonium ion rearrangements.

Rearrangement products camphene (59%) and tricyclene (41%) are formed from isoborneol to the exclusion of the unrearranged bornylene.[33,34] The endo epimeric borneol reacts more slowly, as expected for a reaction involving carbonium ion formation,[35] and gives bornylene (22%) in addition to camphene (61%) and tricyclene (17%). The bornylene could arise by a cis coplanar elimination.[36] The difference in the camphene:tricyclene ratios from isoborneol (with and without added tertiary amine) and borneol shows that not all of the reaction leading to these products proceeds through a common intermediate. Whether this difference involves more than a difference in the placement of the anion relative to the cation is a matter for conjecture. Alternative explanations involving simultaneous C–H and C–O bond cleavage, simultaneous with rearrangements of the carbon skeleton, make interesting speculation.

The sole product from *exo*-2-norborneol, nortricyclene, may also involve the intermediacy of carbonium ions. The 4% hydrocarbon portion formed in the acetolysis of *exo*-2-norbornyl brosylate[37] is 98% nortricyclene and 2% norbornene. Under E2 conditions the hydrocarbon products from *exo*-2-norbornyl tosylate[38] and bromide[39] were reported to be predominantly norbornene formed by exo-cis elimination.

The rapid reaction (within seconds) of *exo*-2-norborneol with **1** in chloroform-*d* at room temperature, by a route apparently involving formation of the 2-norbornyl cation, suggests that the leaving group generated by the reaction with **1** (presumably diphenyl sulfoxide) is a very good one.



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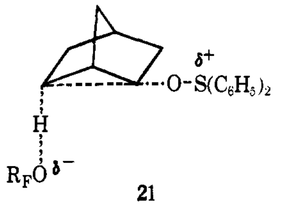
If in fact the norbornyl cation is an intermediate in this reaction, it is surprising that it reacts with the gegenion, R_FO^-, to give nortricyclene by loss of a proton to the complete exclusion of the reaction leading to unsymmetrical ether (**20**) by ion pair collapse. Again one is tempted to speculate on the possibility that some more concerted pathway is being followed, such as that going through transition state **21**.



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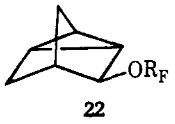
Although the reaction of isomeric mixtures of 3-nortricyclanol and *exo*-2-norbornen-5-ol with **1** in chloroform-*d* is complete within a short while at room temperature, it apparently is slow enough so that a small amount of R_FOCCl_3 (3–7%) is formed. Neither quadricyclene nor norbornadiene[38,39] is formed. The lack of variation in **22**:**23** product ratios (5.0) with composition of mixtures of these two alcohols being dehy-



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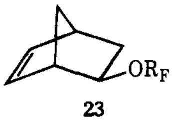

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(31) For related observations of dehydration reactions in this series see G. Vavon and M. Barbier, *Bull. Soc. Chim. Fr.*, **49**, 567 (1931); H. J. Schaeffer and C. J. Collins, *J. Amer. Chem. Soc.*, 78, 124 (1956); H. L. Goering, R. L. Reeves, and H. H. Espy, *ibid.*, 78, 4926 (1956); H. Pines and C. N. Pillai, *ibid.*, **83**, 3270 (1961); K. Kochloefl, M. Kraus, C. Chin-Shen, L. Beránek, and V. Bažant, *Collect. Czech. Chem. Commun.*, **27**, 1199 (1962).

(32) E. J. Blanc and H. Pines, *J. Org. Chem.*, **33**, 2035 (1968).

(33) The gas-phase pyrolysis of isobornyl chloride gives 25% bornylene; A. Maccoll, *Chem. Soc., Spec. Publ.*, No. **16**, 170 (1962); see also W. C. Herndon and J. M. Manion, *Tetrahedron Lett.*, 6327 (1968).

(34) Our result is more closely related to that seen for the high-temperature dehydration over alumina: K. Watanabe, C. N. Pillai, and H. Pines, *J. Amer. Chem. Soc.*, **84**, 3934 (1962).

(35) E. U. Emovon, *J. Chem. Soc. B*, 588 (1966).

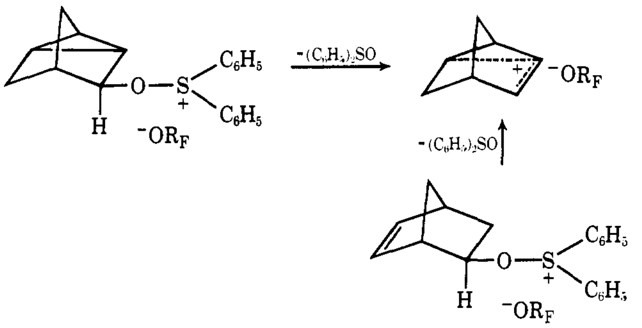
(36) S. J. Cristol and E. F. Hoegger, *J. Amer. Chem. Soc.*, **79**, 3438 (1957); C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

(37) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, 87, 376 (1965).

(38) H. C. Brown and K. T. Liu, *ibid.*, **92**, 200 (1970).

(39) H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).

drated with **1** suggests that there is a common carbonium ion intermediate derived from the two isomers in this case.



The intramolecular kinetic isotope effect (k_H/k_D = 1.54) observed for the dehydration of *tert*-butyl alcohol with **1**, when considered in conjunction with our other evidence for the intermediacy of carbonium ions, supports a mechanism for dehydration of this tertiary carbinol near the E1 end of the mechanistic spectrum. The exothermic loss of a proton from something resembling the carbonium ion presumably proceeds through a transition state with little C–H bond breaking.[40] Other E1 eliminations show a similar kinetic isotope effect.[41]

Acknowledgment. We wish to acknowledge the partial support of this research by a National Institutes of Health Fellowship held by R. J. A. from 1967 to 1971, by National Science Foundation Grant No. GP 13331 and by a departmental equipment grant from the National Science Foundation which provided partial funding for a 220-MHz nmr spectrometer.

[40] F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

[41] V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **75**, 2925 (1953); G. J. Frisone and E. R. Thornton, *ibid.*, **90**, 1211 (1968).

Sulfuranes. VII. The Crystal and Molecular Structure of a Diaryldialkoxysulfurane[1,2]

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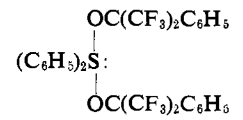
Received November 10, 1971

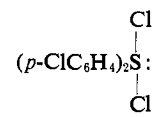
Abstract: The crystal structure for a diphenyldialkoxysulfurane, $(C_6H_5)_2S[OC(CF_3)_2C_6H_5]_2$, reveals an approximate trigonal bipyramidal geometry about sulfur, with a lone pair considered to occupy one equatorial position, the two phenyl ligands occupying the other two equatorial positions (C–S–O angles range from 86.4(2) to 91.2(2)°; the C–S–C angle is 104.4(3)°), and with the electronegative alkoxy ligands occupying apical positions (O–S–O angle is 175.1(2)° with the distortion from linearity in the direction of the equatorial phenyl rings). The S–O bond lengths (1.889(4) and 1.916(4) Å) are approximately 0.2 Å longer than the sum of the covalent radii as would be expected from an S–O bond order less than unity. The crystals are triclinic, the space group is $P\bar{1}$, and there are two molecules in a unit cell of dimensions a = 10.026(3), b = 14.268(3), c = 10.802(3) Å, α = 109° 50′(2′), β = 92° 52′(2′), and γ = 95° 20′(2′). The structure was solved by Patterson-heavy atom methods based on sulfur, and has been refined to a conventional R of 0.070 for 3364 nonzero reflections measured by counter methods. Some comparisons of the bonding scheme with those for tetracovalent sulfur compounds containing halogen ligands are made.

The first example of a stable, crystalline tetracoordinate sulfur(IV) compound lacking halogen atoms, sulfurane **1**, has been recently described.[3] Even more recently[4] Sheppard has reported low-temperature nmr and reactivity data which are interpreted in terms of a postulated tetraarylsulfurane structure. Other sulfuranes which have been studied include derivatives of SF_4,[5,6] molecules with S–Cl bonds,[7,8] and a compound postulated to have the structure of a spirodiacyloxysulfurane.[9] A preliminary X-ray investigation of the latter compound showed that in the crystal it had C_2 molecular symmetry, which would be consistent with a trigonal bipyramidal geometry. A complete crystal structure of $(p\text{-ClC}_6H_4)_2SCl_2$ (**2**) evidenced[7] a trigonal bipyramidal arrangement with the more electronegative chlorine atoms in the apical positions. In general it has been found[10] for trigonal bipyramidal compounds that



$$\begin{array}{c} OC(CF_3)_2C_6H_5 \\ | \\ (C_6H_5)_2S: \\ | \\ OC(CF_3)_2C_6H_5 \end{array}$$

1



$$\begin{array}{c} Cl \\ | \\ (p\text{-ClC}_6H_4)_2S: \\ | \\ Cl \end{array}$$

2

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[1] For Part VI in this series, see R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5003 (1972).

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