by preparing and chromatographing samples of the dinitrophenylhydrazones. Fractional crystallization of the crude mixture of 2,4-dinitrophenylhydrazones from ethanol gave a sample (mp 131–132°) which did not depress the melting point of a known sample of cyclopropylacetaldehyde 2,4-dinitrophenylhydrazone.

Cyclopropyloxirane (3). Cyclopropanecarboxaldehyde, 7.0 g (0.10 mol), was stirred under nitrogen with 28.6 g (0.14 mol) of trimethylsulfonium iodide in 60 ml of dimethyl sulfoxide. A solution of 14.0 g of potassium *tert*-butoxide in 150 ml of dimethyl sulfoxide was added dropwise with stirring during 30 min while cooling. After stirring for an additional 15 min, 300 ml of water was added slowly while cooling with ice. The solution was extracted with ether (3 × 500 ml) and the extract was washed with water and dried over molecular sieves. Distillation on a Teflon spinning band column gave, after removal of ether and *tert*-butyl alcohol, 2.6 g of **3**: bp 85–90° (lit.[12b] bp 100°); NMR (neat) δ 0.1–0.4 (m, 4 H, cyclopropyl CH_2), 0.5–0.8 (m, 1 H, cyclopropyl CH), 2.4–2.7 (m, 2 H, oxirane CH_2), 2.1–2.3 (m, 1 H, oxirane CH).[18] Anal.[19] Calcd for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.12; H, 9.75.

Cyclopropyloxirane (**3**) was first prepared from vinylcyclopropane but the amount was not sufficient for complete identification. A solution of 35 g (0.20 mol) of *m*-chloroperoxybenzoic acid in 60 ml of dry ether was added dropwise during 1 hr to a stirred solution of 10.5 g (0.15 mol) of vinylcyclopropane[20] maintained at 20°. After stirring for 2 hr, the mixture was extracted with 10% sodium hydroxide solution, washed with water, and dried. After removal of the ether, VPC using column B[17] indicated one volatile product in addition to ether and a small amount of vinylcyclopropane.

Reaction of Nitrous Acid with 3. A solution of 1.66 g (0.024 mol) of sodium nitrite in 8.0 ml of water was added dropwise to a stirred solution of 2.0 g (0.024 mol) of **3**, 1.9 ml of 12 *M* hydrochloric acid, and 23.5 ml of water. The conditions of the reaction of **1** with nitrous acid were duplicated. The mixture was extracted with two 4-ml portions of ether and the extracts were dried over molecular sieves. Gas chromatography of the ether solution on column B[17] showed only one major component besides ether. This component had a retention time identical with that of **3** and different from those of cyclopropylacetaldehyde, cyclopropanecarboxaldehyde, and cyclopropyl methyl ketone. Treatment of the product with 2,4-dinitrophenylhydrazine yielded no precipitate.

Reaction of Nitrous Acid with 1-Amino-3-methyl-2-butanol. 1-Amino-3-methyl-2-butanol, bp 88–90° (40 mm) [lit.[21] bp 174° (734 mm)], was prepared in 42% overall yield from 2-methylpropanal by the same route used for 2-amino-1-cyclopropylethanol. Dropwise addition of 32 g (0.45 mol) of sodium nitrite in 100 ml of water to a stirred solution of 45 g (0.45 mol) of 1-amino-3-methyl-2-butanol in 500 ml of water containing 35 ml of 12 *M* hydrochloric acid, maintained below 5°, was followed by stirring (30 min), warming, and refluxing (10 min). The reaction mixture was extracted with two 75-ml portions of ether, and the dried ether solution was concentrated. Vapor chromatography on columns A and B[17] showed the presence of only 3-methyl-1,2-epoxybutane and 3-methyl-2-butanone, in a ratio of 1:3 (in approximate 40% yield), identified by comparison of retention times with those of authentic samples. 3-Methylbutanal, with a different retention time, was not present. The 2,4-dinitrophenylhydrazone, mp 123–124°, was prepared and did not depress the melting point of an authentic sample of 3-methyl-2-butanone 2,4-dinitrophenylhydrazone.

Reaction of 3-Methyl-1,2-epoxybutane with Nitrous Acid. The epoxide was prepared in 63% yield from 3-methyl-1-butene by reaction with *m*-chloroperoxybenzoic acid.[22] A solution containing 2.0 g (0.023 mol) of 3-methyl-1,2-epoxybutane, 1.75 ml of 12 *M* HCl, and 25 ml of water was stirred and the temperature maintained below 5° while a solution of 1.60 g (0.023 mol) of sodium nitrite in 5 ml of water was added dropwise. After 30 min, the stirred solution was warmed to 20° and then refluxed for 10 min. It was then extracted with two 4-ml portions of ether, and the ether extract was dried over molecular sieves. Gas chromatography on column B[17] indicated the presence only of ether and 3-methyl-1,2-epoxybutane. Treatment with 2,4-dinitrophenylhydrazine gave no solid.

Registry No.—**1**, 54120-02-4; **2**, 17687-58-0; **3**, 21994-19-4; 1-cyclopropyl-2-nitroethanol, 54120-03-5; cyclopropanecarboxaldehyde, 1489-69-6; nitromethane, 75-52-5; nitrous acid, 7782-77-6; cyclopropanecarboxaldehyde 2,4-dinitrophenylhydrazone, 36873-36-6; cyclopropylacetaldehyde 2,4-dinitrophenylhydrazone, 54120-04-6; potassium *tert*-butoxide, 865-47-4; 2-methylpropanal, 78-84-2; 3-methyl-1,2-epoxybutane, 1438-14-8; 3-methyl-2-butanone, 563-80-4; 3-methyl-2-butanone 2,4-dinitrophenylhydrazone, 3077-97-2.

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(16) Analysis by Dr. F. B. Strauss Microanalytical Laboratory, Oxford, England OX2 7SA.
(17) A, 20% di-2-ethylhexyl sebacate on Chromosorb W; B, 20% Carbowax 4000 on Chromosorb P; C, 10% diethylene glycol adipate on Chromosorb W.
(18) A report of the preparation of **3** (ref 12b) appeared subsequently; our physical constants (boiling point, NMR spectrum) are somewhat at variance, but the spectral data are obtained under different conditions.
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A New Reaction of Trithioorthoacetates. Reaction with Acylating Reagents

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Reactions of trithioorthocarboxylates are relatively unknown.[1] In our earlier work[2] it was found that when aryl trithioorthoacetates $(ArS)_3CCH_3$ were dissolved in trifluoroacetic acid-*d*, rapid and complete isotopic exchange occurred at room temperature and on evaporation of the solvent deuterated compounds $(ArS)_3C-CD_3$ were obtained quantitatively. As an extension of this work trifluoroacetylation of $(ArS)_3C-CH_3$ was tried and we now wish to report the results.

As anticipated, the reaction did proceed quite easily at room temperature, but the products, obtained in high yields, were $(ArS)_2C{=}CHCOCF_3$ instead of $(ArS)_3C-CH_2COCF_3$ (Ar, yield, %: *p*-$CH_3OC_6H_4$, 58; *p*-$CH_3C_6H_4$,

$$(ArS)_3C{-}CH_3 \xrightarrow[rT]{(CF_3CO)_2O} (ArS)_2C{=}CHCOCF_3$$

98; C_6H_5, 100; *p*-ClC_6H_4, 75). Physical properties together with analytical data for the acylation products are listed in Table I.

Similarly, reactions of $(ArS)_3C-CH_3$ with $(CCl_3CO)_2O$ (refluxing for 1 day in $CHCl_3$) gave $(ArS)_2C{=}CHCOCCl_3$ (Ar, yield, %: Ph, 76; *p*-$CH_3C_6H_4$, 28). The acid chloride CCl_3COCl can also be used, the yields being improved in

Table I: Products of the Reaction with Acylating Reagents

Registry no.	Products	Mp,[a] °C	NMR, τ (CDCl3)[b]	Ir, [c] ν_{CO}	Empirical formula	C[e]	H	S	F	Cl
54083-59-9	$(p\text{-}CH_3OC_6H_4S)_2C{=}CHCOCF_3$	101	2.73 (q, 8 H), 4.02 (s, 1 H), 6.15 (s, 6 H)	1660	$C_{18}H_{15}O_3S_2F_3$	53.99	3.78		14.23	
						53.99	3.66		14.24	
54083-60-2	$(p\text{-}CH_3C_6H_4S)_2C{=}CHCOCF_3$	160	2.38–2.75 (m, 8 H), 4.12 (s, 1 H), 7.61 (d, 6 H)	1662	$C_{18}H_{15}OS_2F_3$	58.68	4.10		15.47	
						58.86	4.38		15.39	
54083-61-3	$(C_6H_5S)_2C{=}CHCOCF_3$	88	2.20–2.76 (m, 10 H), 4.00 (s, 1 H)	1670	$C_{16}H_{11}OS_2F_3$	56.46	3.26		16.74	
						56.93	3.36		16.73	
54083-62-4	$(p\text{-}ClC_6H_4S)_2{=}CHCOCF_3$	119	2.28–2.72 (m, 8 H), 4.08 (s, 1 H)	1670	$C_{16}H_9OS_2F_3Cl_2$	46.96	2.22		13.93	17.32
						47.03	2.12		13.87	17.38
54083-63-5	$(p\text{-}CH_3C_6H_4S)_2C{=}CHCOCCl_3$	182	2.69 (m, 8 H), 3.80 (s, 1 H), 7.56 (d, 6 H)	1673	$C_{18}H_{15}OS_2Cl_3$	51.73	3.62	15.34		25.45
						51.68	3.58	15.11		25.44
54083-64-6	$(C_6H_5S)_2C{=}CHCOCCl_3$	145	2.50 (m, 10 H), 3.85 (s, 1 H)	1670	$C_{16}H_{11}OS_2Cl_3$	49.32	2.84	16.45		27.29
						49.14	2.79	16.25		27.32
54083-65-7	$(p\text{-}CH_3C_6H_4S)_2C{=}CHCOCHCl_2$	142	2.36–2.82 (s, 8 H), 4.02 (s, 1 H), 4.30 (s, 1 H), 7.60 (d, 6 H)	1650	$C_{18}H_{16}OS_2Cl_2$	56.39	4.21	16.73		18.49
						56.38	4.26	16.43		18.29
54083-66-8	$(C_6H_5S)_2C{=}CHCOCHCl_2$	120	2.62 (m, 10 H), 3.98 (s, 1 H), 4.30 (s, 1 H)	1660						
54083-67-9	$(p\text{-}CH_3C_6H_4S)_2C{=}CHCOCH_2Cl$	152	2.35–2.77 (m, 8 H), 4.07 (s, 1 H), 6.11 (s, 2 H), 7.62 (d, 6 H)	1630	$C_{18}H_{17}OS_2Cl$	61.96	4.91	18.38		10.16
						62.06	4.90	18.12		10.21
54083-68-0	$(p\text{-}CH_3C_6H_4S)PhC{=}CHCOCF_3$[d]	104.5	2.70–3.02 (s, 8 H), 3.30 (s, 1 H), 7.78 (s, 3 H)	1680	$C_{17}H_{13}OSF_3$	63.34	4.07		17.68	
						63.14	4.20		17.67	

[a] Melting points are uncorrected. [b] The NMR spectra were recorded on a 60-MHz Hitachi R-24 spectrometer and satisfactory integrations were obtained for all compounds. [c] cm^{-1} (KBr). Recorded on a Hitachi ir spectrometer, Model EP1-G3. [d] Probably the acyl group is cis to the sulfide group. [e] Analysis, % (calcd over found).

this case up to 100 and 76% for the phenyl and *p*-tolyl compounds, respectively.

Acylation of $(ArS)_3C{-}CH_3$ with $CHCl_2COCl$ was performed by refluxing in $CHCl_3$ for 15–72 hr, affording $(ArS)_2C{=}CHCOCHCl_2$ (Ar, yield, %: Ph, 54; *p*-$CH_3C_6H_4$, 33).

Monochloroacetylation is also possible. For example, $(p\text{-}CH_3C_6H_4S)_3C{-}CH_3$ gave after refluxing with $CH_2ClCOCl$ in chlorobenzene for 18 hr $(p\text{-}CH_3C_6H_4S)_2C{=}CHCOCH_2Cl$ in 37% yield, with recovery of some starting material. Neither $(CH_3CO)_2O$ nor CH_3COCl[3] reacted with $(ArS)_3C{-}CH_3$.

This reaction can also be applicable to dithioketals; $(p\text{-}CH_3C_6H_4S)_2PhC{-}CH_3$ reacted with $(CF_3CO)_2O$ at room temperature to give a 33% yield of $(p\text{-}CH_3C_6H_4S)PhC{=}CHCOCF_3$.

It seems probable that the products $(ArS)_2C{=}CHCOCF_3$ result from electrophilic attack by the acid anhydride on $(ArS)_2C{=}CH_2$, formed by acid-catalyzed elimination of ArSH from the trithioorthoacetates. In favor of this view, ketene dithioacetals react with the acid anhydride to give the same products.[4] Furthermore, although the reaction of trithioorthoacetates is inhibited by adding small amounts of pyridine, if we start with ketene dithioacetals, the reaction proceeds quite favorably in the presence of pyridine, and formation of resinous materials is avoided. However, we have facts indicating that the two reactions are mechanistically different in some respects.

Experimental Section

Trithioorthoacetates. All trithioorthoacetates were prepared by heating corresponding thiolacetates (5 mmol) and thiophenols (10 mmol) for 2 hr at 50° using a small amount of *p*-toluenesulfonic acid as a catalyst and recrystallized from benzene or *n*-hexane. $(C_6H_5S)_3CCH_3$: mp 147°.[5] $(p\text{-}CH_3OC_6H_4S)_3CCH_3$: mp 158°; NMR ($CDCl_3$) τ 2.80 (q, 12 H), 6.17 (s, 9 H), 8.68 (s, 3 H). $(p\text{-}CH_3C_6H_4S)_3CCH_3$: mp 147°; NMR ($CDCl_3$) τ 2.67 (q, 12 H), 7.63 (s, 9 H), 8.64 (s, 3 H). Anal. Calcd for $C_{23}H_{24}S_3$: C, 69.65; H, 6.10; S, 24.25. Found: C, 69.52; H, 6.16; S, 24.04. $(p\text{-}ClC_6H_4S)_3CCH_3$: mp 111°; NMR ($CDCl_3$) τ 2.60 (q, 12 H), 8.62 (s, 3 H). Anal. Calcd for $C_{20}H_{15}S_3Cl_3$: C, 52.46; H, 3.30; S, 21.01; Cl, 23.25. Found: C, 52.31; H, 3.36; S, 20.99; Cl, 23.42.

Acylation of Trithioorthoacetates. In a typical experiment 3 g (14.3 mmol) of trifluoroacetic anhydride was added to a solution of $(p\text{-}CH_3C_6H_4S)_3CCH_3$ (3 g, 7.58 mmol) in $CHCl_3$ (8 ml) and the mixture was stirred for 20 hr at room temperature or for 2 hr at 40°, and gave after evaporation of the solvent 2.74 g (98% yield) of $(p\text{-}CH_3C_6H_4S)_2C{=}CHCOCF_3$ as white needles, mp 160°. If necessary, the raw products were submitted to column chromatography on silica gel and then purified by recrystallization from appropriate solvents. All spectroscopic and analytical data are tabulated in Table I.

H–D Exchange Experiments. For example, a solution of $(C_6H_5S)_3CCH_3$ (0.1 g) in $CDCl_3$ (0.3 ml) was mixed with 0.5 ml of CF_3CO_2H in a NMR tube and its NMR spectrum was recorded immediately at 35°. A peak for methyl at δ 1.40 in $CDCl_3$ shifted to δ 2.93 and disappeared almost completely when CF_3CO_2D was used instead of CF_3CO_2H. In an isolation experiment, evaporation of the solvent gave $(PhS)_3CCD_3$ almost quantitatively. This material, the deuterium content of which was estimated to be more than 90% by NMR integration in $CDCl_3$ was converted back to $(PhS)_3CCH_3$ by dissolving it into CF_3CO_2H and confirmed by mixture melting point.

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Registry No.—$(C_6H_5S)_3CCH_3$, 14859-20-2; $(p\text{-}CH_3OC_6H_4S)_3CCH_3$, 39141-48-5; $(p\text{-}CH_3C_6H_4S)_3CCH_3$, 35446-98-1; $(p\text{-}ClC_6H_4S)_3CCH_3$, 39141-50-9; $(CF_3CO)_2O$, 407-25-0; $(CCl_3CO)_2O$, 4124-31-6; $CHCl_2COCl$, 79-36-7; $CH_2ClCOCl$, 79-04-9; $(p\text{-}CH_3C_6H_4S)_2PhCCH_3$, 54083-69-1; thiophenol, 108-98-5; *p*-methoxythiophenol, 696-63-9; *p*-methylthiophenol, 106-45-6; *p*-chlorothiophenol, 106-54-7; dithioacetic acid, 594-03-6.

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(3) H. Boehme and J. Roehr [*Justus Liebigs Ann. Chem.*, **648**, 21 (1961)] reported a reaction of triethyl trithioorthoacetate with acetyl chloride to form ketene diethyl dithioacetal and thiolacetate. In our experiment with $(ArS)_3CCH_3$ and acetyl chloride, no reaction occurred. However, if a small amount of acetic acid was present, resinous materials were produced, probably derived from the ketene dithioacetal.
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Homobenzylic and Homoallylic Spin–Spin Coupling Interactions in Some Octahydro- and Hexahydrophenanthridines

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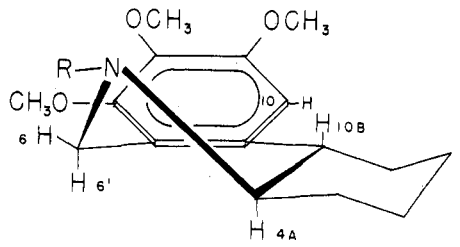
In a previous communication[1] we reported that the signals assigned to H-6′ in the NMR spectra of **1** showed splittings of ca. 1.5 Hz in addition to those expected from geminal coupling between H-6 and H-6′. The conformation of **1** is believed to be that shown here and was derived[1] mainly



1 a R = Me

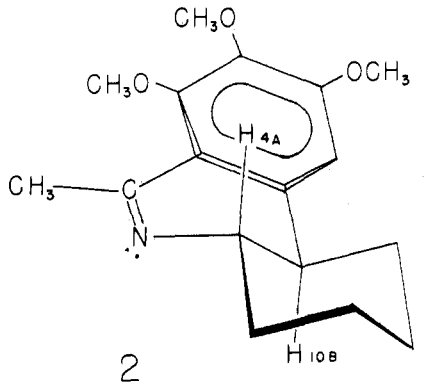
b R = Et

from nmr data. It can be seen that the protons most likely to be responsible for the additional splitting are H-10 (benzylic coupling),[2] H-4a (coupling across four single bonds),[2] or H-10b (homobenzylic coupling).[2] The original suggestion[1] of long-range coupling between H-6′ and H-4a would represent an unusual case of substantial coupling across four single bonds in non-W configuration.[2] An earlier report proposing such a case[3] has been shown to be incorrect.[4]

We now present conclusive evidence from 100-MHz multiple resonance studies and from studies on the 4a-deuterio derivative of **1a** that the observed interaction results from homobenzylic coupling between H-6′ and H-10b. The spectra of **1** have been reexamined in $CDCl_3$ at 100 MHz[5] by the Sydney group and, with the aid of multiple resonance experiments, it was established that the proton responsible for the long-range interaction with H-6′ (multiplet, δ 2.52 in **1a**) also interacts with H-10 ($J \simeq 0.8$ Hz, benzylic coupling).[2] Clearly, the resonance at δ 2.52 must be due to H-10b and the long-range interaction responsible for the additional splitting of the signals due to H-6′ is a homobenzylic coupling.[2] An analogous series of results was also obtained for **1b**. A careful measurement of the splittings in the signals due to H-6′, while the residual broadening due to interaction with H-10 was removed by decoupling, showed $J_{6',10b} = 1.88 \pm 0.03$ Hz in **1a** and 1.69 ± 0.03 Hz in **1b**, the largest homobenzylic interactions reported so far.[2,6] The assignment is confirmed by the spectrum of 5-methyl-7,8,9-trimethoxy-4a,10b-*trans*-1,2,3,4,4a,5,6,10b-octahydrophenanthridine-*4a-d*, in which the signal of H-6′ has the same multiplicity as seen with the undeuterated **1a**.

It is significant that these interactions and the similar, slightly smaller, spin–spin coupling in some sterically analogous steroids with ring A aromatic[4] are between trans disposed pseudo-axial protons, which is a particularly favorable juxtaposition for cisoid homoallylic coupling,[7] a related long-range spin–spin interaction.

In a previous communication[8] we have also reported homoallylic coupling constants of about 2 Hz between H-4a and the C-6 methyl protons in 6-methyl-7,8,9-trimethoxy-4a,10b-*trans*- (**2**) and -4a,10b-*cis*-1,2,3,4,4a,10b-hexahydrophenanthridine (**3**). These two compounds represent examples of transoid homoallylic coupling where a methyl group



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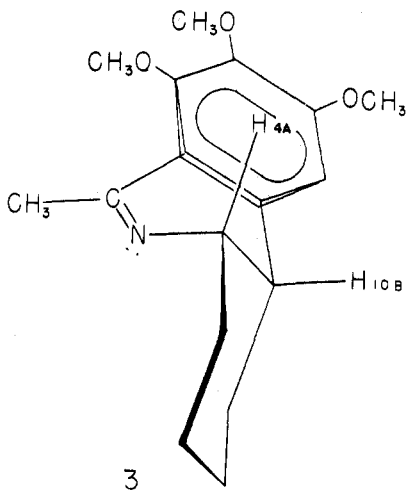

3

assumes the equilibrium conformation in systems where one sp^2 carbon is replaced by an sp^2-hybridized nitrogen atom. In view of the conformational dependence of homoallylic coupling constants,[7] the similarity of the observed homoallylic coupling constants in the trans and cis isomers indicates that H-4a must have essentially the same conformational relationship to the double bond in the two isomers, that is, one in which the dihedral angle between H-4a and the plane of the double bond approaches 90°. This requires that the predominant solution conformation of the cis isomer **3** be that in which the cyclohexane ring has the chair conformation with H-4a in equatorial and H-10b in axial orientations, contrary to what was previously proposed[8] on the basis of chemical shift arguments. The 100-