Hard Acid and Soft Nucleophile System. New Efficient Method for Removal of Benzyl Protecting Group

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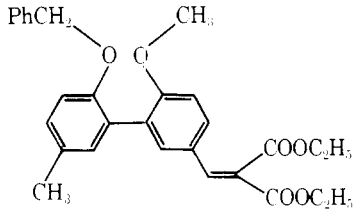
Aliphatic and aromatic benzyl ethers have been easily cleaved on treatment with a hard acid, boron trifluoride etherate, and a soft nucleophile, EtSH or ethanedithiol, to give parent alcohols and phenols, respectively. Competitive debenzylation experiments demonstrated that the coordination of a hard acid (pulling factor) is more important than the nucleophilic attack of a soft nucleophile to the carbon atom (pushing factor) in this reaction.

In the course of our synthetic studies of Lythraceous alkaloids,[1] we needed an efficient method of removing the benzyl protecting group in the biphenyl derivative 1 which could be an important synthetic intermediate for lythranidine (2).[2] Among the reported methods for removal of the benzyl protecting group, catalytic hydrogenolysis[3] or reductive cleavage with sodium in ethanol[4] or in liquid ammonia[5] seemed unsuitable because of the structural limitations. Attempted debenzylation of compound 1 with concentrated hydrochloric acid in refluxing ethanol[6] gave a complex mixture of products. Trifluoroacetic acid has been used to cleave a number of aromatic benzyl ethers when the aromatic ring contains either meta-directing or ortho- and para-directing groups.[7] Applying this reagent to the compound 1 also resulted in the formation



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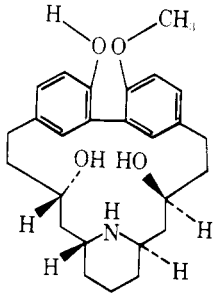

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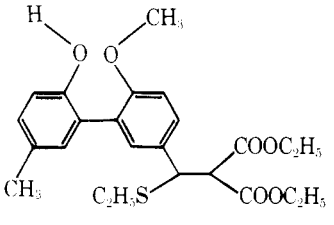

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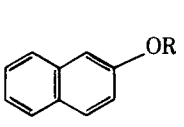
of a complex mixture whose ^{1}H-NMR spectrum indicated considerable migration of the benzyl group onto the aromatic ring. Although several other methods are available in the literature, they have not been tested by us because of their drastic conditions[8-10] or insufficient data.[11]

We have published that the methyl ethers of primary and secondary alcohols are easily cleaved by the combination of a hard acid, boron trifluoride etherate, and soft nucleophiles, thiols, to give the parent alcohols.[12] Consideration of the probable mechanism for the reaction led to the anticipation that this system could be useful also for cleavage of benzyl ethers.

Results and Discussion

As expected, debenzylation of compound 1 was easily accomplished by treatment with boron trifluoride etherate in EtSH at room temperature, but a simultaneous addition of EtSH to the Michael acceptor in the molecule was accompa-



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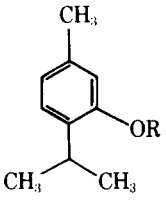

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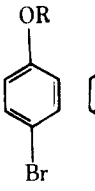

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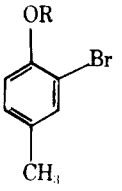

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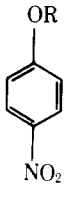

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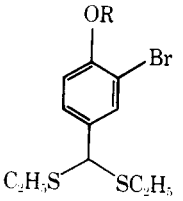

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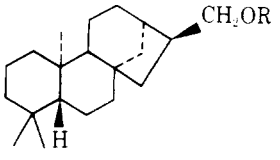

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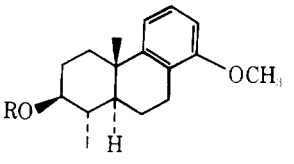

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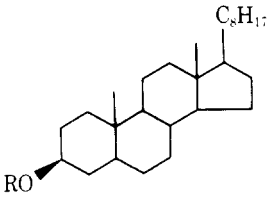

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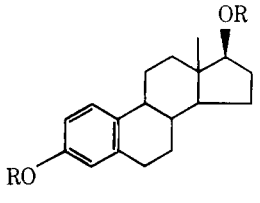

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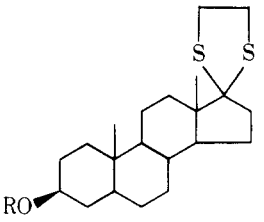

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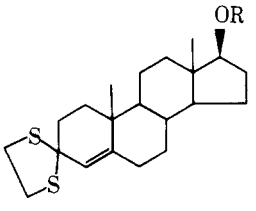

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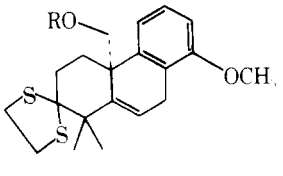

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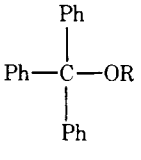

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4-17, R = CH_2Ph

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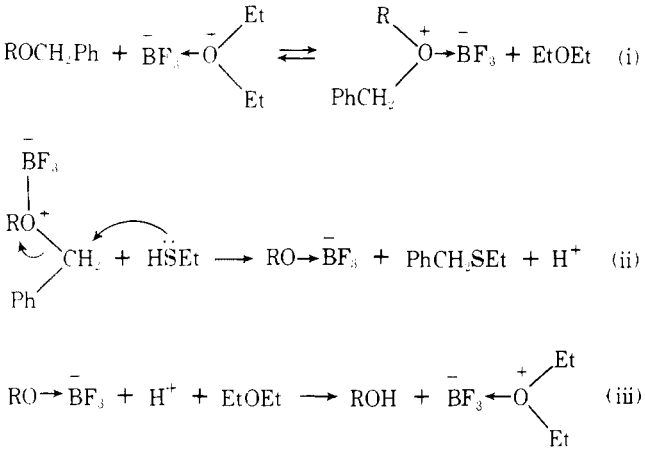
Table I. Debenzylation of Aromatic and Aliphatic Benzyl Ethers

Compd (mmol)	BF_3–Et_2O, mmol	EtSH, mL	reaction time, h	yield (%) of the parent phenol or alcohol
4 (0.5)	4	1.0	0.8	92
5 (1.0)	8	2.0	1.0	93
6 (0.5)	4	1.0	1.0	92
7 (1.0)	8	2.0	1.0	90
8 (0.5)	4	1.0	0.5	94
9 (0.3)	4	1.0	1.5[a]	86
10 (0.13)	0.47	0.5	24	93
11 (0.1)	0.8	0.5[b]	19	99
12 (0.1)	0.8	0.5[b]	20	90
13 (0.1)	1.6	1.0[b]	18	96
14 (0.1)	0.8	0.5[b,c]	2	87
15 (0.07)	0.56	0.3[b,c]	2	94
16 (0.1)	0.8	0.5[b,c]	3.5	47
17 (0.5)	13	1	18	0[d]

[a] After an hour sodium sulfate (500 mg) was added. [b] Dichloromethane (1.0 mL) was used as the cosolvent. [c] Ethanedithiol was used for ethanethiol. [d] Starting material was recovered quantitatively.

Scheme I. Possible Mechanism of Debenzylation



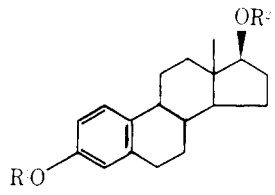
nied giving rise to 3 as the product in 88% yield. Nevertheless, this new debenzylation method was expected to have a wide range of synthetic utility, hence the scope and limitation of the reaction was studied.

The benzyl protecting group of phenols was effectively removed with boron trifluoride etherate in EtSH at room temperature. Dichloromethane was used as the cosolvent in the case of aliphatic benzyl ethers. The results are summarized in Table I.

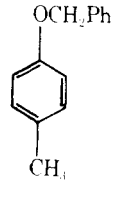
In the case of the reaction with the compound **9**, a small amount of 3-bromo-4-hydroxybenzaldehyde was detected as a minor product with TLC after an hour. Hence, sodium sulfate was added to remove a small amount of water causing the hydrolysis of a dithioacetal moiety and an additional stirring was continued for 30 min to afford the corresponding phenol in 86% yield. It is worthy to note that the debenzylation with the compound having a labile dithioacetal group on the benzene ring proceeds smoothly. Dithioacetals **14** and **15** were converted to the corresponding alcohols also in high yields without touching dithioacetal moiety by using ethanedithiol for EtSH. Debenzylation of compound **15** is illustrative of synthetic utility of this method, because other effective methods for such a material bearing a double bond and a dithioacetal moiety in the molecule as compound **15** are not found in the known procedures. The low yield (47%) in the debenzylation of **16** lies in susceptibility to the autoxidation of the resulting alcohol.

The reactions of 0.05 mmol of cholestan-3β-yl benzyl ether (**12**) in 1 mL of anhydrous dichloromethane and 0.5 mL of EtSH with a drop of (condition a), 0.8 mmol of (condition b), and 8 mmol of (condition c) boron trifluoride etherate were followed by TLC. Debenzylation was completed within 15 min and 150 min with conditions c and b, respectively, whereas in condition a, about 50% of starting ether (**12**) remained unchanged even after 100 h, which shows the rate of the reaction depends on the concentration of boron trifluoride etherate. The necessity of a soft nucleophile (a thiol) in this reaction was verified by the fact that no debenzylation proceeded at all within 15 h when EtOH was used for EtSH in condition b. Benzyl ethylsulfide was obtained from every reaction using EtSH as a soft nucleophile. Although detailed mechanistic studies have not been carried out, the plausible pathway shown in Scheme I agrees with the above observations. Thus, the benzyl ether oxygen coordinates to BF_3 to form an oxonium species (eq i), then a soft nucleophile, thiol, attacks the soft benzyl carbon atom in an S_N2 sense to complete the cleavage of benzyl ether (eq ii).

A mixture of 0.1 mmol of estradiol dibenzyl ether (**13**), 1 mL of EtSH, and 1 mL of dichloromethane was treated with 1 mmol of boron trifluoride etherate for 3 h. Product analysis of the resulting mixture showed that estradiol (**18**) and monobenzyl ethers, **19** and **20**, were obtained in 30, 12, and 18% yield, respectively, with recovery of 26% of the starting material (**13**). The easier cleavage of aliphatic benzyl ether is well explained by assuming that BF_3 could be coordinated more easily by the aliphatic benzyl ether than aromatic benzyl ether owing to their inductive effect. From the same reasoning *p*-benzyloxytoluene (**21**) suffered debenzylation more easily than *p*-benzyloxybromobenzene (**6**). The electronegative bromine atom on the para position in **6** would reduce the coordinating



18, $R^1 = R^2 = H$
19, $R^1 = H$; $R^2 = CH_2Ph$
20, $R^1 = CH_2Ph$; $R^2 = H$



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power with BF_3, so that the rate of debenzylation of **6** should be slower than that of **21**.

When the reaction conditions are displaced toward the S_N2 end of the mechanistic spectrum in the debenzylation reaction of **13**, or the nucleophilicity of a nucleophile is increased and the Lewis acid is removed, monobenzyl ether **19** should be obtained as the major product. Actually, monobenzyl ether **19** was obtained in 72% yield from the reaction of estradiol dibenzyl ether (**13**) with EtSNa in DMF.

Cleavage of the C–O bond with the BF_3 and thiol system is based on the balance between the coordination of a hard acid with the oxygen atom in benzyl ethers (pulling factor) and the nucleophilic attack of a soft nucleophile to the carbon atom (pushing factor). It should be possible to apply this system for selective cleavage of a variety of C–O bonds by moving the balance between the pulling factor and the pushing factor, or by changing the hardness of Lewis acids and/or the softness of nucleophiles.

Experimental Section

Melting points are uncorrected. The IR spectra were recorded with a Hitachi EPI-S2 spectrometer and the NMR spectra were obtained with either a Varian T-60 spectrometer or a JEOL JNM-FX100

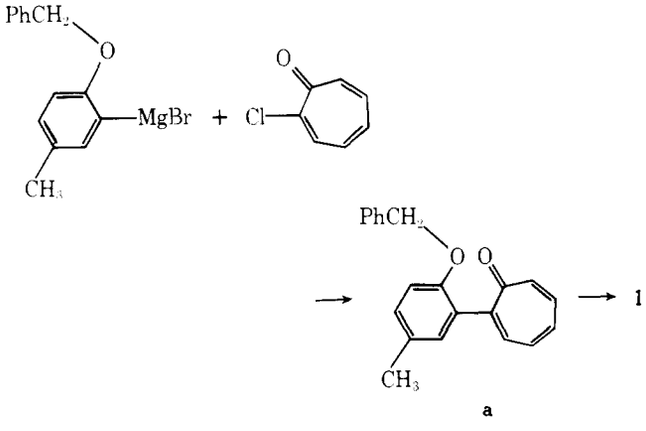
spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. GLC analyses were performed with a Shimadu Model GC-4CM instrument.

Materials. Benzyl ethers 4–17 except 9 were prepared from the parent phenols or alcohols according to the standard method.[13] Melting points, chemical shifts of benzylic protons, and analyses are given in Table II. Data of benzyl ether 8 do not appear in Table II since it is the known compound.[14]

Synthesis of 9. To a stirred solution of 3-bromo-4-hydroxybenzaldehyde (1.0 g) in DMF (5 mL) was added NaH (50% in mineral oil, 360 mg) portionwise with ice cooling and stirring. After addition of benzyl chloride (1.5 g), the stirring was kept for 24 h at room temperature. The reaction mixture was poured into water and extracted in ether. The extract was washed successively with aqueous Na_2CO_3 and brine, dried (Na_2SO_4), filtered, and evaporated in vacuo to afford a crude product which was recrystallized from CCl_4–hexane to give 3-bromo-4-benzyloxybenzaldehyde (1.1 g, 75%): mp 78–80 °C; NMR ($CDCl_3$) δ 5.20 (s, 2 H), 7.00, (d, J = 8.4 Hz, 1 H), 7.38 (br s, 5 H), 7.75 (dd, J = 8.4, 1.8 Hz, 1 H), 8.08 (d, J = 1.8 Hz, 1 H), 9.82 (s, 1 H); IR ($CHCl_3$) ν 1690, 1590, 1489 cm^{-1}. Anal. Calcd for $C_{14}H_{11}O_2Br$: C, 57.76; H, 3.81. Found: C, 57.26; H, 3.83.

To a stirred solution of 3-bromo-4-benzyloxybenzaldehyde (500 mg) in dichloromethane (5 mL) was added $ZnCl_2$ (0.1 g), EtSH (2 mL), and anhydrous Na_2SO_2 (1.0 g). After stirring for 4 h at room temperature, inorganic material was removed by filtration and the filtrate was evaporated to dryness followed by chromoatography over silica gel. Elution with petroleum ether–benzene afforded a pure compound 9 (607 mg, 89%) as an oil: NMR ($CDCl_3$) δ 1.20 (t, J = 7.0 Hz, 6 H), 2.56 (q, J = 7.0 Hz, 4 H), 4.84 (s, 1 H), 5.10 (s, 2 H), 6.85 (d, J = 9.0 Hz, 1 H), 7.15–7.57 (m, 6 H), 7.65 (d, J = 2.2 Hz, 1 H); IR ($CHCl_3$) ν 2895, 1597, 1488, 1453 cm^{-1}. Anal. Calcd for $C_{18}H_{21}OBrS_2$: C, 54.50, H, 5.33. Found: C, 54.29; H, 5.43.

Synthesis of 1. Compound 1 was synthesized from 7 and 2-chlorotropone according to the following scheme.[15]



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A Grignard solution, made from 7 (2.77 g) and metallic magnesium (0.26 g) in anhydrous ether (10 mL) under nitrogen, was added to a solution of 2-chlorotropone (1.05 g) in anhydrous ether (10 mL) in one portion. After being refluxed for 15 min, 5% aqueous NH_4Cl was added to the reaction mixture which was extracted with ether. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and evaporated to give an oily residue (2.9 g). Chromatography over a silica gel column with benzene followed by recrystallization from ether gave phenyltropone a as yellow needles (1.1 g, 49.5%): mp 75–77 °C; NMR (CCl_4) δ 2.21 (s, 3 H), 4.86 (s, 2 H), 6.34–7.50 (br, 13 H); IR ($CHCl_3$) ν 1628, 1587, 1497 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.09; H, 5.97.

To a stirred solution of phenyltropone a (115 mg) in dichloromethane (5 mL) was added magic methyl (276 mg) under nitrogen. After stirring for 18 h at room temperature dimethylsulfonium bis(carbomethoxy)methylide (450 mg) was added portionwise to the solution with stirring for 7 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and evaporated to give a crude oil. Chromatography over a silica gel column with benzene afforded 1 (122 mg, 67.7%) as a pure oil: NMR (CCl_4) δ 1.20 (t, J = 7.4 Hz, 3 H), 1.28 (t, J = 7.4 Hz, 3 H), 2.28 (s, 3 H), 3.61 (s, 3 H), 4.20 (q, J = 7.4 Hz, 4 H), 4.90 (s, 2 H), 6.46–7.60 (m, 13 H); IR ($CHCl_3$) ν 1718, 1622, 1600, 1498 cm^{-1}. Anal. Calcd for $C_{29}H_{30}O_6$: C, 73.40; H, 6.37. Found: C, 73.07; H, 6.25.

Debenzylation of 1. To a solution of 1 (170 mg, 0.36 mmol) in EtSH (1 mL) was added boron trifluoride etherate (4 mmol). After stirring for 40 min at room temperature, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuo to yield an oil (169 mg), which was chromatographed over silica gel with benzene–dichloromethane to yield 3 as a pure oil (141 mg, 88%): NMR (CCl_4) δ 0.96 (t, J = 6.6 Hz, 3 H), 1.17 (t, J = 7.4 Hz, 3 H), 1.30 (t, J = 7.4 Hz, 3 H), 2.18–2.62 (m, 2 H), 2.30 (s, 3 H), 3.55–4.50 (m, 6 H), 3.80 (s, 3 H), 5.74 (br s, 1 H), 6.60–7.54 (m, 6 H); IR ($CHCl_3$) ν 2890, 1725, 1493 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_6S$: C, 64.55; H, 6.77. Found: C, 64.37; H, 6.84.

Table II. Physical Data of Benzyl Ether[a]

compd (mp, °C)	recrystn solvent	^1H NMR (in $CDCl_3$), δ ($-OCH_2Ph$)
4 (102–103)	petroleum ether–CH_2Cl_2	5.10 (s, 2 H)
5 (oil[b])		5.02 (s, 2 H)
6 (59–60)	petroleum ether	4.94 (s, 2 H)
7 (29–30)	MeOH	4.95 (s, 2 H)[c]
10[d] (80–82)	EtOH–EtOAc	4.50 (s, 2 H)
11 (87–89)	Et_2O–hexane	4.42, 4.68 (AB q,[e] 2 H)
12 (104–105)	acetone	4.53 (s, 2 H)
13 (81–82)	EtOH–acetone	4.56 (s, 2 H), 5.01 (s, 2 H)
14 (104–106)	EtOAc	4.55 (s, 2 H)
15 (135–136)	EtOH–Et_2O	4.53 (s, 2 H)
16 119–120)	Et_2O–hexane	4.19 (s, 2H)
17 (100–102)	petroleum ether	4.18 (s, 2 H)

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all new compounds. [b] Bp 140–141 °C (8 mm). [c] Measured in CCl_4. [d] A slight deviation (−0.42) in the analysis for H was found. [e] J = 12 Hz.

General Procedure for Debenzylation. (a) For Aromatic Benzyl Ethers. A mixture of substrate, EtSH, and boron trifluoride etherate was stirred at room temperature under the conditions described in Table I. The reaction mixture was poured into water and extracted with ether. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and evaporated to leave crude material which was purified by recrystallization and/or chromatography over a silica gel column. All products except for the one[16] from 9 were identified with the parent phenols. The yields are given in Table I.

(b) For Aliphatic Benzyl Ethers. The crude alcohol was obtained from the same procedure as aromatic benzyl ethers except that dichloromethane was used as the cosolvent. The crude alcohol was recrystallized from the appropriate solvent system. Mother liquor was chromatographed over a silica gel column to give a further crop of crystals. The combined yield is given in Table I.

Partial Debenzylation of Estradiol Dibenzyl Ether (13). A mixture of 13 (171 mg, 0.37 mmol), EtSH (116 mg, 1.85 mmol), and boron trifluoride etherate (254 mg, 1.85 mmol) in dichloromethane (4 mL) was stirred for 3 h at room temperature. Usual workup as described above gave a crude product which was chromatographed over a silica gel column. Elution with benzene gave the starting benzyl ether 13 (45 mg, 26.39%), monobenzyl ether 19 (16 mg, 11.7%), mp 193–194 °C, monobenzyl ether 20 (24 mg, 17.5%), mp 85–87 °C from benzene (lit.[17] mp 95.5–98 °C from light petroleum, lit.[18] mp 82–84 °C from EtOH), and estradiol (31 mg, 30.1%) successively.

Monobenzyl Ether 19. To a stirred solution of EtSH (0.7 mL) and NaH (50% in mineral oil, 600 mg) in DMF (5 mL) was added a solution of 13 (88 mg, 0.19 mmol) in DMF (1 mL) in one portion, and the mixture was refluxed for 4 h and then stirred overnight at room temperature. The reaction mixture was poured into 5% aqueous HCl and extracted with ether. Usual workup gave a crude material. Purification by chromatography over a silica gel column afforded monobenzyl ether 19 (51 mg, 72%). Recrystallization from EtOH gave an analytical sample: mp 195–196 °C; NMR ($CDCl_3$) δ 0.86 (s, 3 H), 3.49 (t, J = 7.5 Hz, 1 H), 4.56 (s, 2 H), 6.52–7.36 (m, 8 H); IR ($CHCl_3$) ν 3610, 1610, 1585, 1505 cm^{-1}. Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.48; H, 8.39.

Debenzylation of a 1:1 Mixture of 6 and 21. To a stirred mixture of 6 (132 mg, 0.05 mmol), 21 (99 mg, 0.5 mmol), and EtSH (37.4 μL, 0.5 mmol) in dichloromethane (5 mL) was added boron trifluoride etherate (126.2 μL, 1 mmol). After being stirred for 19 h at room temperature, the reaction mixture was diluted with dichloromethane and washed successively with 5% aqueous NaOH and brine. Most of dichloromethane was removed by distillation, and the residual solution was analyzed by GLC on a 20% silicon DC 200 (1 m × 3 mm)

column at 200 °C. The ratio of the remaining **6** and **21** was observed to be 2:1.

Registry No.—**1**, 69455-09-0; **3**, 69455-10-3; **19**, 55561-42-7; **20**, 14982-15-1; **21**, 834-25-3; phenyltropone a, 69455-11-4; 3-bromo-4-hydroxybenzaldehyde, 2973-78-6; benzyl chloride, 100-44-7; 3-bromo-4-benzyloxybenzaldehyde, 69455-12-5; 2-chlorotropone, 3839-48-3; ethanethiol, 75-08-1.

References and Notes

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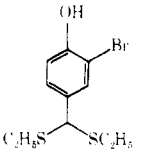
(16) The structure of the oily phenol obtained from **9** was fully characterized as follows: NMR ($CDCl_3$) δ 1.22 (t, J = 7.4 Hz, 6 H), 2.35 (q, J = 7.4 Hz, 4 H), 4.60 (s, 1 H), 5.40 (br s, 1 H), 6.70 (d, J = 8.4 Hz, 1 H), 7.07 (dd, J = 8.4, 2.4 Hz, 1 H), 7.34 (d, J = 2.4 Hz, 1 H); IR ($CHCl_3$) ν 2880, 1596, 1486 cm^{-1}. Anal. Calcd for $C_{11}H_{15}OS_2Br$: C, 43.00; H, 4.92. Found: C, 42.77; H, 4.89.



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General Acid-Catalyzed Decomposition of Alkyl Xanthates

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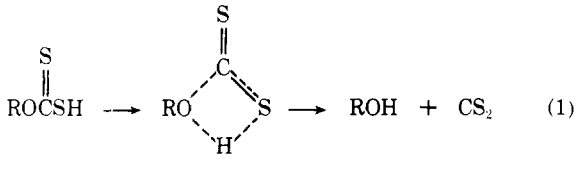
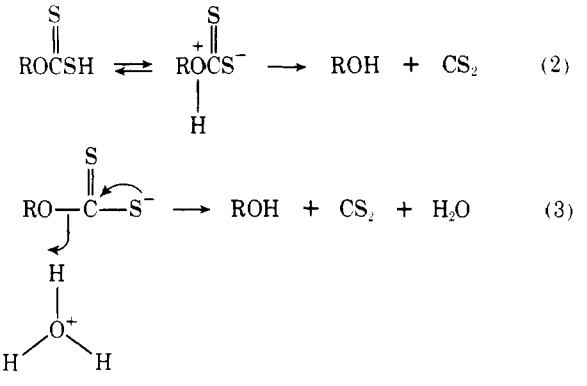
Xanthates of 2,2,2-trifluoroethanol, methoxyethanol, and ethanol have been prepared, and their decomposition in aqueous carboxylic acid buffers has been studied. pH–rate profiles reveal that the pK_a values for the ionization of the xanthic acids are 1.60 for ethyl, 1.30 for trifluoroethyl, and 1.45 for methoxyethyl. Brønsted α values for the general acid catalysis of the breakdown of xanthates are 0.96 for ethyl, 0.88 for methoxyethyl, and 0.79 for trifluoroethyl. These results are interpreted in terms of a concerted process for proton transfer and carbon–oxygen bond breaking. Positive deviations from linearity were observed at high values of mole fraction of the catalyzing acid in plots of k_{BT} vs. mole fraction of HA. These results have been discussed in terms of a general acid-catalyzed breakdown of xanthic acids and solvent-assisted breakdown of xanthate anion.

Monoalkyl xanthates have found important applications in the cellulose industry and in mineral flotation processes.[1] The breakdown of ethyl xanthate catalyzed by hydronium ion has been extensively studied.[2] At pH greater than 2 the first-order rate constant was proportional to the concentration of ethylxanthic acid. The acid-catalyzed hydrolysis of *n*-butyl xanthate and *tert*-butyl xanthate in solutions of hydrochloric acid and perchloric acid has also been studied, and similar dependence on the concentration of xanthic acid has been noted.[3] Further, the effect of cationic micelles, anionic micelles, and nonionic micelles on the hydrolysis of ethyl, *n*-butyl, and *n*-octyl xanthates has been investigated.[3] It was found that the decomposition of the xanthate to the alcohol and carbon disulfide was inhibited by cationic micelles of cetyltrimethylammonium bromide and catalyzed by anionic micelles of Triton X-100A at pH > 2. These results were explained in terms of micellar effects upon the protonation of the xanthate ion.

Previous workers have suggested a variety of mechanisms to account for xanthate decompositions in acid solution. These are summarized in eq 1–3.



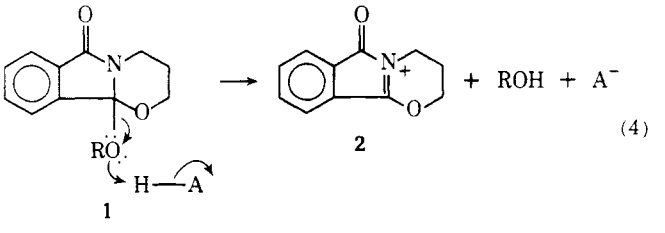
(1)



(2)

(3)

We wished to know whether carboxylic acid catalysts would lead to the breakdown of xanthates. Thus, we initiated the present structure–reactivity study for the purpose of determining whether general acid catalysis exists, and if so, whether the reactions are stepwise or concerted.[4–6]



(4)

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