The Reaction of Formaldehyde with Methyl- and Ethylxanthates

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Formaldehyde is a well-known component of viscose rayon spinning baths. This paper reports the results of work aimed at elucidating the chemistry of its action through study of its reaction with model xanthates. The product of the reaction of formaldehyde with ethylxanthic acid is S-hydroxymethyl O-ethylxanthate, $C_2H_5OCSSCH_2OH$, as shown by its preparation, elemental analysis, and molecular weight. The infrared spectrum is consistent with this formula. On pyrolysis at 70° the product decomposes into CS_2, $(C_2H_5O)_2CH_2$, HCHO, and H_2O. The experimental results show the existence of the equilibrium: $ROCSS^- + HCHO + H_3O^+ \rightleftharpoons ROCSSCH_2OH + H_2O$. The formation equilibrium constants, calculated from pH and ultraviolet absorbance data for $C_2H_5OCSSCH_2OH$, are 2.75×10^5 in water and 3.38×10^5 in water–acetone (82.5:17.5). The corresponding constants for $CH_3OCSSCH_2OH$ are 1.23×10^5 and 2.24×10^5. The values of the constants are nearly independent of temperature in the range 3–11°.

Formaldehyde as a component of viscose rayon spinning baths makes possible the stretching of the newly spun fibers to a greater degree with resulting increased tensile strength. The mechanism of its action has not been clear. Alles[2] studied the reaction of aldehydes with cellulose xanthate and named the reaction products cellulose xanthate aldehydes. His patent does not discuss the formulas of these products, but states that they are unstable in mild alkali. That a definite chemical compound is produced by the reaction of cellulose xanthate with formaldehyde in aqueous acid was first demonstrated by means of ultraviolet spectroscopy by Phifer and Ticknor[3] in our laboratories.

This paper describes some experiments with simpler model xanthates which led to the suggested equilibrium expression (eq. 1) between the proposed product and the reactants. The equilibrium constant is calculated from titration data and from ultraviolet absorbance data. The existence of such a compound is finally substantiated by the preparation and isolation of S-hydroxymethyl ethylxanthate, its elemental analysis, measurement of some of its physical properties, and identification of the products of its pyrolysis.

$$ROCSS^- + HCHO + H_3O^+ \rightleftharpoons ROCSSCH_2OH + H_2O \quad (1)$$

Experimental

Materials.—Reagent grade 36–38% formaldehyde containing 10–15% methanol was used without further purification. Stock solutions were analyzed polarographically. Eastman code 1568 potassium ethylxanthate (KEX) was used as obtained. Potassium methylxanthate (KMX) was prepared following the method of Trieber.[4] Sulfur analysis of KMX indicated 92% purity. Weights used were on this basis. All other chemicals were reagent grade.

Measurements.—Conductances were measured by means of a Serfass conductivity bridge Model RC M15, using platinized platinum electrodes with a cell constant of 0.1.

Acid–base titrations were followed by use of a Leeds and Northrup No. 7664 pH meter in conjunction with a Varian G-11 recorder adjusted to read pH with a sensitivity better than 0.1 unit. During automatic titrations, acid or base was added at a constant rate by use of a 50-ml. hypodermic syringe attached to a Harvard Apparatus Company infusion withdrawal pump, Model 600–900. The rate was calibrated for each syringe by weight of water infused in 1 min.

Ultraviolet absorbance measurements were made with a Beckman Model D.U. spectrophotometer. The accuracy of the wavelength scale was within 0.5 mμ by comparison with a holmium oxide glass filter. The cell housing was equipped with a cooling jacket for circulation of cold water. Absorbance measurements were made on solutions at 9° or lower.

Procedure.—When 4.7 mmoles of HCHO in the form of a 37% aqueous solution was added to a solution of 3.1 mmoles of KEX in 6 ml. of water, no observable reaction occurred. On acidification with dilute H_2SO_4 a white emulsion formed from which an oil gradually settled to the bottom. The heavy oil was nonvolatile, and was soluble in 10% NaOH, from which it could be reprecipitated by H_2SO_4 with some loss in yield.

In order to study the properties and composition of the product it was prepared on a larger scale as follows. To a 1000-ml. beaker placed in an ice bath were charged 80 g. (0.5 mole) of potassium ethylxanthate and 160 g. of formalin (approximately 2.1 moles of CH_2O). The charge was stirred and cooled to 5°, and an ice-cold solution of 15 ml. of concentrated H_2SO_4 in 50 ml. of water was added dropwise over about 30 min. to pH 4. Stirring at 5–10° was continued 0.5 hr. The entire reaction mass was then transferred to a separatory funnel and extracted with five 100-ml. portions of cold ether. The combined ether extracts were dried over Na_2SO_4, filtered, and concentrated in a rotating film evaporator at 200 mm. and a bath temperature of 25°. The oily residue was further concentrated *in vacuo* and finally evacuated 3 hr. at 0.03 mm. with shaking. The residue weighed 67 g. and had $n^{23}{}_D$ 1.5473.

A portion of the crude product was distilled *in vacuo* and yielded a major fraction boiling at 43° at 0.04 mm. This product had $d^{22}{}_4$ 1.2480, $n^{22}{}_D$ 1.5673, M_D 39.9 (calculated 40.1, Condon), and m.p. −5°. The infrared spectrum showed an abundance of hydroxyl and absorption in the same region as CS_2.

Anal. Calcd. for $C_4H_8O_2S_2$: C, 31.6; H, 5.27; S, 42.1; mol. wt., 152. Found: C, 31.6; H, 5.48; S, 42.3; mol. wt. (cryoscopically in benzene), 151.

Pyrolysis of the product from a similar run yielded formaldehyde (as a gas) and a condensate which separated into two layers. The lower layer was identified as CS_2 by density, boiling point, solubilities, and odor. The upper layer was soluble in water, had a strong odor of formaldehyde, and gave on distillation a CS_2 fraction at 44–46°, a principal fraction at 70–80°, and a smaller fraction at 80–90°. The 70–80° fraction on redistillation came over at 75° and its $n^{23}{}_D$ was 1.3710. Derivatives of this material were identified as ethyl 3,5-dinitrobenzoate, m.p. 93–93.5°, and α-naphthylurethane, m.p. 75–78°, plus some di-α-naphthylurea. Diethylformal forms an azeotrope with water boiling at 75.2°.[5] Anhydrous diethylformal boils at 89°, as did the 80–90° fraction on redistillation after drying over Na_2SO_4. Diethylformal was prepared[5] and both the azeotrope (with water) and the anhydrous material were isolated. These products corresponded in all respects, including the position of the peaks in a gas chromatogram, with the corresponding fractions of the pyrolysis product.

In order to study the equilibrium reaction between formaldehyde and simple xanthates, titration of the xanthates against standard acids were carried out, both in the absence and in the presence of formaldehyde. The solutions, cooled to 10–11°, were brought to a pH of approximately 2 by the addition of acid, and

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[1] To whom inquiries should be addressed.

[2] F. P. Alles, U. S. Patent 2,123,493 (1938).

[3] L. H. Phifer and L. B. Ticknor, paper presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[4] E. Trieber, *Monatsh.*, **82**, 53 (1951).

[5] A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 66–68.

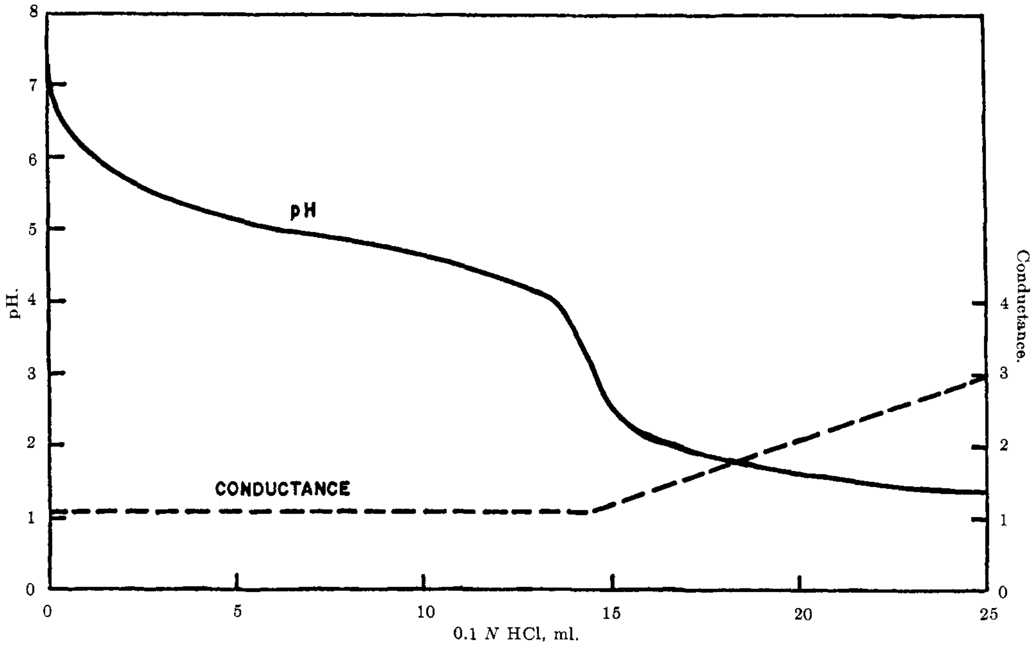


Fig. 1.—Titration of potassium ethylxanthate in the presence of formaldehyde; initial solution consisted of 2.5 g. of potassium ethylxanthate, 100 ml. of water, and 14.8 ml. of formalin.

were then back-titrated to the original pH by the addition of standard alkali. The amount of the xanthate decomposing during the titration was calculated from the difference between the titers, since any decomposition would result in the disappearance of hydronium ion, in accordance with eq. 4 (see Discussion). Titrations of KEX and KMX were carried out in water, and, because of the limited solubility of hydroxymethyl ethylxanthate (HMEX) in water, also in a water-acetone mixture containing 17.5% acetone by volume. It was determined that 0.001 M HCl gave the same pH in this mixed solvent as in water, so that the mixed-solvent titrations were considered valid.

Equilibrium data in very dilute aqueous solutions were also obtained by means of ultraviolet spectrophotometry. A series of solutions was made up containing buffers of 0.1 M sodium acetate with enough glacial acetic acid to give the desired pH. The buffer was mixed with the required amount of CH_2O and cooled to 4° before the required amount of a cold 0.001 M KEX solution in 0.01 M NaOH was added. The absorbances of the resulting solutions were measured against a reference cell containing formaldehyde and the buffer solution at the concentrations used in the experimental mixtures. Since the absorbance of formaldehyde is much lower than that of any of the other components present at the wave lengths of the measurements, the difference due to the amount combined in the reaction product would not affect the result significantly.

Results

Titration of KEX in the absence of formaldehyde was very unsatisfactory because the pH was not stable. Upon addition of a drop of acid, the pH of the solution would fall, but would then creep up over a period of several minutes toward the original value. However, titration, with 0.1 N HCl, of a solution of 2.5 g. of KEX and 14.8 ml. of formalin in 100 ml. of water gave a titration curve (see Fig. 1) typical of that of a weak base, with a slight plateau about pH 5 and a pseudo-equivalence point corresponding to the amount of KEX present.

Data collected on the effect of the CH_2O–total xanthate mole ratio on the decomposition of xanthate during acidification and back-titration is shown in Table I. The influence of excess CH_2O is clear. The increase in per cent decomposition at the 50:1 mole ratio over the 20:1 ratio may indicate that at very low pH values the product, $ROCSSCH_2OH$, suffers decomposition, although at pH 2.9 it is quite stable.

Table I

Xanthate Decomposition during Titration

HCHO-MX^-,[a] mole ratio	Temp., °C.	Lowest pH	% dec.
0	10	2.2	94
2	10	2.2	55
10	10	2.1	5.3
20	11	2.9	1.0
50	10	2.1	4.0

[a] MX^- is the methylxanthate ion, CH_3OCSS^-

The equilibrium constant, $K = [HMMX]/[MX^-][CH_2O][H^+]$, where HMMX is the hydroxymethyl methylxanthate and MX^- is the methylxanthate ion, was calculated from pH values obtained from titration of 0.025 M potassium methylxanthate in aqueous solutions containing 0.05, 0.25, 0.5, and 1.25 M CH_2O, respectively, using 0.25 M H_2SO_4 as titrant. It was assumed that there were no significant side reactions, and that 1 mole of HMMX formed from each mole of H^+ added, using 1 mole of CH_2O and 1 mole of the xanthate. Values of pK and of K with their 95% confidence limits at four CH_2O–KMX ratios as well as values at 3 and 11° at a 20:1 ratio are given in Table II.

Table II

Effect of CH_2O-MX Ratio on HMMX Equilibrium Constant (in water)

Mole ratio, CH_2O-MX^-	Temp., °C.	pK	$K \times 10^{-5}$
2	10	-4.99 ± 0.10	0.98
10	10	-5.25 ± 0.08	1.78
20	3	-5.03 ± 0.05	1.07
20	11	-5.04 ± 0.05	1.10
50	10	-5.14 ± 0.07	1.38
Mean		-5.09 ± 0.04	1.23

Data for the titration of hydroxymethyl ethylxanthate in 17.5% acetone and 82.5% water at a CH_2O–KEX ratio of 10 are shown in Table III. For comparison, data obtained with KMX in water–acetone are also shown. It will be noted that the value of K for KEX is greater than that for KMX in the same medium.

Table III

Equilibrium Constants in Water–Acetone Mixtures

[Xanthate ion] / [derivative]	KMX in water–acetone pH	KMX in water–acetone pK	KEX in water–acetone pH	KEX in water–acetone pK
18.38	5.95	−5.28	6.18	−5.51
8.69	5.58	−5.25	5.83	−5.51
5.45	5.40	−5.38	5.59	−5.57
4.84	5.25	−5.29	5.45	−5.49
2.22	5.00	−5.28	5.20	−5.48
1.42	4.85	−5.34	5.02	−5.51
0.93	4.72	−5.40	4.85	−5.53
0.61	4.55	−5.42	4.69	−5.56
0.38	4.45	−5.54	4.51	−5.60
Mean pK		−5.353		−5.529
K		2.25×10^5		3.38×10^5

The extinction coefficients for the ethylxanthate ion (EX^-) in 0.01 *M* NaOH and for $C_2H_5OCSSCH_2OH$ (HMEX) are shown in Table IV. One solution of KEX in a buffer at pH 6 gave the same extinction coefficient as found in 0.01 *M* NaOH. The values for $C_2H_5OCSSCH_2OH$ were obtained on aliquots of solutions containing a large excess of CH_2O and, hence, essentially only the reaction product. Concentrations and equilibrium constants calculated by the application of the Beer-Lambert law are shown in Table V.

Table IV

	Wave length (mμ) 310	301	276.5	270
ϵ_{EX^-}	11490	17400	1965	875
Number of determinations	8	8	8	8
Standard deviation	500	343	107	100
ϵ_{HMEX}	368	980	11180	9700
Number of determinations	4	4	4	4
Standard deviation	144	120	142	201

Table V

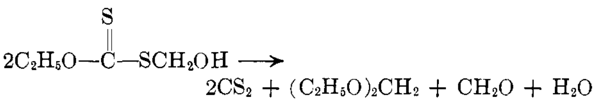
K = equilibrium constant = $[HMEX]/[EX^-][CH_2O][H^+]$[a]

Total xanthate, μmoles/l.	HCHO, *M*	pH	Mean $[EX^-]$, μmole/l.	Mean $[HMEX]/[EX^-]$, μmole/l.	$K \times 10^{-5}$
97.3	0.075	4.00	31.5	2.09	2.79
97.3	0.075	3.70	18.7	4.21	2.82
97.3	0.075	4.37	52.0	0.87	2.72
97.3	0.0375	4.00	45.3	1.15	3.07
97.3	0.150	4.00	20.4	3.77	2.51
48.7	0.075	4.00	16.4	1.97	2.63
146.0	0.075	4.00	49.9	1.93	2.58
97.3	0.075	4.55	60.7	0.603	2.85
			Mean K		2.75
			pK		−5.44

[a] KEX in water. Ultraviolet absorbance method.

Discussion

The Reaction Product.—It was concluded that, considering the pyrolysis products and the method of preparation, a likely structure would be $C_2H_5OCSSCH_2OH$. The elemental analysis, molecular weight, and infrared spectrum served to support the structure. Pyrolysis of this compound could be expected to proceed according to eq. 2.



$$2C_2H_5O{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SCH_2OH \longrightarrow 2CS_2 + (C_2H_5O)_2CH_2 + CH_2O + H_2O \quad (2)$$

Equilibrium Constant.—The solubility of the product in aqueous alkali and partial recovery on acidification suggests that an equilibrium exists, possibly according to eq. 1. In an acidic reaction medium there would be two competing reactions—the formation of ethylxanthic acid (eq. 3) and the acid decomposition of the xanthate (eq. 4). If the reaction went *via* eq. 3, then adding CH_2O reversibly one would obtain eq. 1.

$$ROCSS^- + H_3O^+ \rightleftharpoons ROCSSH + H_2O \quad (3)$$

$$ROCSS^- + H_3O^+ \longrightarrow ROH + CS_2 + H_2O \quad (4)$$

The unstable pH values observed on titration of potassium ethylxanthate (KEX) in the absence of formaldehyde would be predicted on the basis of the decomposition of the xanthate ion, as in eq. 4. On the other hand, titrations in the presence of formaldehyde gave quite different results, the solutions behaving like those of a weak base. In a series of titration curves with varied CH_2O–xanthate ratios, the midpoint pH increased with increased formaldehyde concentration. This result indicates that formaldehyde must be involved in the equilibrium reaction. The bottom curve in Fig. 1 resulted from the simultaneous measurement of conductance. The two curves break at the same point, indicating that reaction 1 is stoichiometric, and that there is no major reaction afterward.

The presence of excess formaldehyde should, if the equilibrium (eq. 1) exists, shift it to the right, so that when acid is added the xanthate is converted to $ROCSSCH_2OH$ to an extent dependent on the concentration of CH_2O and H_3O^+. Since eq. 4 is not reversible to any appreciable extent, any acid used in that reaction would not be available for back-titration with alkali, while acid used to form the reaction product (eq. 1) or xanthic acid (eq. 3) could be measured by back-titration, which thus served as a method of measuring the amount of decomposition (eq. 4 and Table I).

The equilibrium constants obtained for the formation of the hydroxymethyl ethylxanthate (Table V), were about twice those obtained for the hydroxymethyl methylxanthate (Table II). Also the presence of acetone in the solution raised the values of the formation equilibrium constants (Table III).

In the methylxanthate titration runs, the ionic strength of the solution was about 0.025. The ethylxanthate solutions observed with the spectrophotometer had an ionic strength of about 0.1. It would be expected, then, that the activity coefficients of the ions might be in the order of 10% higher in the titration runs, making the true equilibrium constant about 10% lower (since f_{H^+} is already included in the pH). The salt effect should be too small, then, to be responsible for much of the difference in equilibrium constants.

Since the presence of 17.5% acetone in the solution increased the equilibrium constant about 80% in the case of the KMX–HCHO reaction, a similar effect for the KEK–HCHO reaction would predict a higher value in the water–acetone mixture, minus 10% for the ionic strength effect, or about 4×10^5. We actually found 3.4×10^5. With the combination pH meter and recorder it is difficult to ensure accuracy to 0.1 pH unit; thus the predicted and observed values agree within the limits of experimental accuracy.

Conclusions

The reaction product of formaldehyde and a simple xanthate in slightly acid solution is an S-hydroxymethyl alkylxanthate. In the absence of water, the reaction product is stable at room temperature and up to about 70°. In aqueous solution an equilibrium exists between the xanthate ions, formaldehyde, hydrogen ions, and the reaction product. In the case of the ethylxanthate, the equilibrium favors a larger fraction of the reaction product than in the case of the methylxanthate. The presence of acetone in the equilibrium solution favors a larger fraction of the reaction product than is present in a pure water solution.

Reaction of Benzoyl Isocyanate with a Phospholene Oxide Catalyst

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Benzoyl isocyanate with catalytic amounts of 1-ethyl-3-methyl-3-phospholene 1-oxide gives a product of empirical formula $C_{22}H_{15}N_3O_2$. Evidence indicates that the compound is 2,6-diphenyl-4-dehydrobenzamido-1,3,5-oxadiazine (I).

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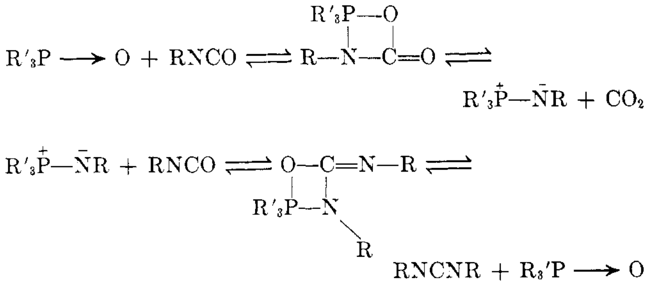
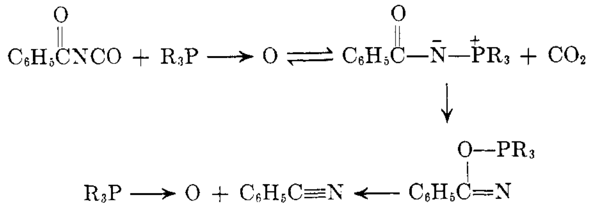
The conversion of aryl isocyanates to carbodiimides through the use of phospholene oxide catalysts has been described recently[1a-d] in the literature. The reaction proceeds cleanly and rapidly, with or without the use of a solvent, and the carbodiimide product can be isolated in nearly quantitative yield. The most active catalyst is 1-ethyl-3-methyl-3-phospholene 1-oxide. The kinetics of the reaction have been studied, and they support the formation of a phosphinimide intermediate, as described by the following mechanism.



On the basis of this mechanism, it was reasoned that a reaction of benzoyl isocyanate with the phospholene oxide catalyst should yield benzonitrile by the following route.

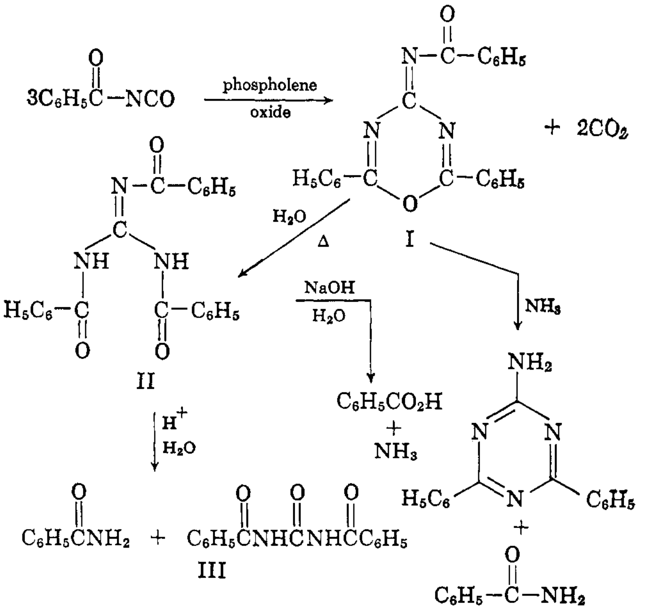


In ether solution[1b] or in xylene, however, benzoyl isocyanate reacted with 1-ethyl-3-methyl-3-phospholene 1-oxide to give a good yield of a solid product which could be decomposed subsequently into benzonitrile, carbon dioxide, and other products, but only at temperatures as high as 200°. Evidence is now presented to show that the compound, $C_{22}H_{15}N_3O_2$, is 2,6-diphenyl-4-benzoylimino-1,3,5-oxadiazine (I).

The reactions and structures discussed in this section are summarized in Chart I. Structure I is supported by elemental analysis, infrared spectrum (Fig. 1a), molecular weight measurements, and the degradative products subsequently described. Carbon dioxide was produced in the preparation, and the amount was quantitative for the stoichiometry of the reaction.

Chart I

Preparation and Structure Determination of 2,6-Diphenyl-4-benzoylimino-1,3,5-oxadiazine



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[1] (a) T. W. Campbell and J. J. Monagle, *J. Am. Chem. Soc.*, **84**, 1493 (1962); (b) T. W. Campbell, J. J. Monagle, and V. S. Foldi, *ibid.*, **84**, 3673 (1962); (c) T. W. Campbell, J. J. Monagle, and H. F. McShane, *ibid.*, **84**, 4288 (1962); (d) J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).