methylated with thallous hydroxide and methyl iodide as described above. The second solid mixture was treated with water and the canary yellow thallous iodide was removed by centrifugation and washed with water. The solids obtained on solvent removal under reduced pressure from the aqueous solution and washings were then suspended in 15–20 ml. of methyl iodide and refluxed for 6 hr. with 28 g. of silver oxide.[8] The silver residues were removed by filtration and washed successively with hot chloroform, methanol and acetone. The solids obtained on solvent removal under reduced pressure from the combined methyl iodide solution and extracts were submitted to three more such methylations. The final methylated product was completely soluble in methyl iodide and chloroform and the latter solvent was employed as the sole extracting agent in the last methylation. The final combined methyl iodide solution and the chloroform extracts were freed of silver ion by treatment with hydrogen sulfide and the methylated product was obtained on solvent removal under reduced pressure as a frothed, light yellow solid; yield 260 mg., $[\alpha]^{26}\mathrm{D}$ $-54°$ (c 0.8, chloroform).

Anal. Calcd. for $C_6H_7O_5(OCH_3)_3$: OCH_3, 45.5. Found: OCH_3, 44.

Identification of the Products of Methanolysis and Hydrolysis of Tri-O-methylpneumogalactan.—Tri-O-methylpneumogalactan (100 mg.) was dissolved in 20 ml. of anhydrous methanol containing 1% hydrogen chloride and heated in a sealed tube at 98° for 15 hr. The cooled tube was then opened, 20 ml. of water added, the methanol removed by boiling and the resultant aqueous acid solution was heated at 98° for 3 hr. Chloride ion was removed from the cooled hydrolyzate with silver carbonate and any silver ion with hydrogen sulfide. Solvent was removed under reduced pressure to yield a sirup.

Portions of the above sirup were subjected to descending paper chromatography,[20] following the general technique of Hirst, Hough and Jones,[21] employing butanol–water development and Tollens reagent as indicator. Three spots of approximately the same order of size and intensity were found and were identified as 2,4-di-O-methyl-D-galactose, 2,3,4-tri-O-methyl-D-galactose and 2,3,4,6-tetra-O-methyl-D-galactose by comparison with concurrently run authentic specimens.[22]

An amount of 90 mg. of the above hydrolyzate was heated for 6 hr. in a sealed tube at 98° with 1 ml. of aniline (freshly distilled under reduced pressure) and 5 ml. of abs. ethanol. The cooled tube was opened and the sirup obtained on solvent removal was dissolved in benzene (thiophene-free) and chromatographed on a 150 × 35 (i.d.) mm. column of Magnesol[23]-Celite[23] (5:1 by wt.) employing 350 ml. of benzene as developer. The three widely separated zones, located by the alkaline permanganate indicator[23] on the extruded column, were sectioned and eluted with ethanol. Crystallization was effected with the same solvent. From the top zone there was obtained 2,4-di-O-methyl-D-galactose anilide of m.p. 214–217° (cor.); from the middle zone 2,3,4-tri-O-methyl-D-galactose anilide of m.p. 167–168° (cor.); and from the bottom zone 2,3,4,6-tetra-O-methyl-D-galactose anilide of m.p. 192–194° (cor.), $[\alpha]^{24}\mathrm{D}$ $-64° \rightarrow +36°$ (c 0.5, acetone). Mixed melting points with authentic samples[22] were undepressed in each case. Melting points were taken on the Fisher–Johns apparatus. Accepted[24] values are, respectively: 216°,[25] 167°,[25] 169°,[26] 192°,[25,27] and $-77° \rightarrow +38°$.[28]

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[20] Acknowledgment is made to Dr. G. N. Kowkabany of this Laboratory for advice and assistance in the techniques of paper chromatography.

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[22] We are indebted to Professors D. J. Bell (Cambridge), E. L. Hirst (Edinburgh), F. Smith (Minnesota), and M. Stacey (Birmingham) for kindly furnishing this material.

[23] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

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COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Reactions of Fatty Materials with Oxygen. XII. New Method for Concentrating Long-chain Peroxides[2,3]

BY JOSEPH E. COLEMAN, H. B. KNIGHT AND DANIEL SWERN

RECEIVED APRIL 25, 1952

Published procedures for the concentration of peroxides from autoxidized methyl oleate are generally small-scale procedures, they are tedious and time-consuming, and yields are low and difficult to duplicate. By precipitation of the non-peroxidic portion of methyl oleate autoxidation mixtures (containing 4–37% peroxides) as urea complexes, concentrates containing 70–90% peroxides have been isolated from the filtrates in 50–95% yields. The three isolation techniques developed are applicable on a large laboratory scale, no specialized equipment or chemicals are required, temperatures in the range of room temperature to the boiling point of methanol are employed, and the procedures are readily duplicated. Preliminary study indicates that the new techniques are applicable to the concentration of peroxides from autoxidized methyl elaidate and polyunsaturated acids.

Concentrating long-chain peroxides is one of the most important and difficult problems in studies on the autoxidation of fats and compounds derived from them. Although a few procedures have been published[4–8] to accomplish this, with the exception of the recent work on methyl linoleate hydroperoxide[8a] the techniques are generally tedious, they are small-scale operations, frequently yields are low, and the degree of concentration is usually not high. In concentrating peroxides formed during autoxidation of methyl oleate, some difficulty has been experienced in duplicating published procedures.

In view of these inadequacies and the importance of the peroxides from autoxidized methyl oleate in reaction mechanism and other investigations being

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] For paper XI, see *J. Am. Oil Chemists' Soc.*, **29**, 44 (1952).

[3] Presented in part at the Meeting-in-Miniature of the Philadelphia Section of the American Chemical Society, January 18, 1951, and at the Spring Meeting of the American Chemical Society, Boston, Massachusetts, April 5, 1951.

[4] E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 119 (1943).

[5] S. Bergström, *Arkiv Kemi, Mineral. Geol.*, **21A**, No. 14, 1 (1945).

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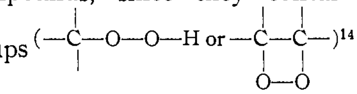
[8] L. R. Dugan, Jr., B. W. Beadle and A. S. Henick, *J. Am. Oil Chemists' Soc.*, **25**, 153 (1948).

[8a] K. T. Zilch, H. J. Dutton and J. C. Cowan, *ibid.*, **29**, 244 (1952).

conducted in this Laboratory, a simple procedure was sought which could be readily duplicated, was applicable on a large-size laboratory scale, could be conducted at reasonable temperatures, required no specialized equipment, chemicals or techniques, gave a high recovery of peroxide concentrate, and required the minimum of manipulation so that changes, if any, in the peroxide structure during handling would be held to a minimum.

Consideration was therefore given to the use of a new technique, discovered by Bengen[9] in 1940, in which a novel principle, namely, the size and shape of molecules, is the basis for separating organic compounds. Bengen[9] and subsequently others,[10–13] have shown that urea forms well-defined, easily handled crystalline complexes with many straight-chain compounds but generally not with cyclic or branched-chain compounds. Long-chain peroxides or hydroperoxides can be considered branched-chain compounds, since they contain relatively bulky groups



$(-\overset{|}{\underset{|}{C}}-O-O-H \text{ or } -\overset{|}{C}-\overset{|}{C}-)^{14}$ with $O-O$ bridging the two C below

along the straight chain. It seemed, therefore, that it should be possible to precipitate the non-peroxidic portion of a methyl oleate autoxidation mixture as urea complexes, leaving a peroxide concentrate in the filtrate.

The initial approach to the problem consisted in development of conditions for the substantially quantitative precipitation of methyl oleate as a urea complex, followed by determining whether non-peroxidic, oxygen-containing substances (oxirane, hydroxy, keto compounds), also formed during autoxidation, would form urea complexes in high yield. This approach was necessary because during the initial stages of autoxidation of methyl oleate, the reaction mixture consists mainly of unoxidized methyl oleate containing small amounts of peroxides, and as the oxidation continues the mixture becomes more complicated and also contains a variety of oxygen-containing molecules in small amounts.[15] In the model experiments, it was found that methyl oleate, low- and high-melting methyl 9,10-dihydroxystearates, low-melting 9,10-dihydroxystearic acid (but not the high-melting isomer),[16] 12-hydroxystearic, 12-ketostearic, and *cis*- and *trans*-9,10-epoxystearic acids readily formed urea complexes in high yield (75–100%).[13]

Application of this new separation technique to autoxidized methyl oleate containing 4–37% peroxides yields peroxide concentrates containing 70–90% peroxides, with a peroxide recovery of 50–95%. It meets the requirements outlined in the introductory paragraphs of this paper for a satisfactory isolation procedure. The procedure consists in treatment of the autoxidation reaction mixture with a methanol solution or slurry of urea for a sufficient time (2 to 24 hours) to precipitate most of the non-peroxidic constituents as urea complexes. These are filtered off at room temperature, and the peroxides are isolated from the filtrate by evaporation of methanol, addition of water to dissolve the excess urea, and solvent extraction. The peroxide concentrates are pale yellow oils.

In several instances, the crystalline urea complexes have been decomposed by addition of water, yielding the non-peroxidic material as a yellow oil consisting mainly of methyl oleate. After fractional distillation, this is suitable for re-oxidation.

Experimental

Materials Used.—The urea was reagent grade; the absolute methanol (synthetic) was A.C.S. reagent grade. Methyl oleate was prepared from the fatty acids of olive oil by multiple fractional distillation and low-temperature crystallization from acetone.[17–19]

Preparation of Urea Complex of Methyl Oleate in High Yield.—Five grams of methyl oleate was added to a boiling solution of 35 g. of urea in 100 ml. of methanol. The boiling was continued only until the solution became homogeneous; crystals of the complex began to form just below the boiling point. The mixture was allowed to stand overnight at room temperature, and the crystals of urea complex and urea were then filtered off and air-dried. These weighed 28.8 g. and contained 4.8 g. (96% yield) of methyl oleate, as determined by the saponification number of the complex (corrected for slight interference by urea).

Concentration of Peroxides from Autoxidized Methyl Oleate. (a) **Solution Method.**—A typical experiment is described. Two hundred grams of methyl oleate which had been autoxidized in the presence of ultraviolet light[15] until its peroxide content was 14.1%[20] (which usually required between 140–250 hours at 35°, about 20 hours at 70° and about six hours at 100°) was added, with mixing, to a warm solution of 1150 g. of urea (approximately 7:1 based on the non-peroxidic portion of the autoxidation mixture) in 3450 ml. of methanol contained in a 2.5-gallon Pyrex bottle. Crystals formed immediately, and the solution was allowed to stand overnight at room temperature and then filtered with suction. The precipitate of urea complexes weighed 690 g. and contained 165 g. of esters, which were substantially peroxide-free. The solvent was evaporated from the filtrate at room temperature, water was added to dissolve the excess urea, and the water-insoluble oily material was extracted with petroleum ether (boiling range, 35–60°). The petroleum ether solution was washed with water several times to remove residual urea, and the solvent was evaporated under vacuum at room temperature (nitrogen gas was used for agitation), yielding a pale yellow oil which weighed 34 g. This contained 75% peroxide[20]; the yield of peroxide recovered was 90%.

This experiment, repeated numerous times, gave 85–90% yields of 70–80% peroxide concentrates.

(b) **Slurry Method.**—This method was employed only in the larger scale operations, where it was desirable to reduce the quantity of urea and methanol. Three hundred grams of autoxidized methyl oleate (containing 14.3% peroxide) was added slowly to a well-mixed slurry of 950 g. of urea and 950 ml. of methanol in a 3-l. resin flask equipped with a stirrer, which scraped the sides of the container continuously. Since formation of the complex is exothermic, the autoxidized methyl oleate was added at such a rate that the internal temperature did not exceed 40°. After being stirred for eight hours, the slurry was filtered with suction, and the filtrate was handled as described under Solution

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(9) F. Bengen, German Patent Application O.Z.12438, March 18, 1940; Translation Book 319, Technical Oil Mission Reel 143, Frames 135–139.

(10) W. Schlenk, Jr., *Ann.*, **565**, 204 (1949).

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(14) Alternative structures are also possible.

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(16) D. Swern, L. P. Witnauer and H. B. Knight, THIS JOURNAL, **74**, 1655 (1952).

(17) J. B. Brown and G. Y. Shinowara, *ibid.*, **59**, 6 (1937).

(18) D. H. Wheeler and R. W. Riemenschneider, *Oil and Soap*, **16**, 207 (1939).

(19) D. Swern, H. B. Knight and T. W. Findley, *ibid.*, **21**, 133 (1944).

(20) D. H. Wheeler, *ibid.*, **9**, 89 (1932).

Method. The peroxide concentrate obtained weighed 24 g. and contained 89% peroxide (the yield of peroxide recovered was 50%).

Many repetitions of this experiment resulted in 50–70% yields of 80–90% peroxide concentrates. A single washing of the precipitate of urea complexes on the funnel with approximately 150 ml. of methanol saturated with urea resulted in an increased recovery of peroxide concentrate of about 15%, thus bringing the yields almost up to those obtained by the Solution Method.

(c) **Solution–Slurry Method.**—This is the preferred method at the present time. Slightly higher yields of 80–90% peroxide concentrate are obtained than in the Slurry Method, the quantity of urea and methanol is lower than in the Solution Method, and the reaction time is only two to six hours. To a stirred boiling solution of 1500 g. of urea in 3000 ml. of methanol in a 2.5-gallon Pyrex bottle, 350 g. of autoxidized methyl oleate (containing 15.2% peroxide) was added. The source of heat was removed *immediately*, and the mixture was stirred until it had reached room temperature. The peroxide concentrate obtained from the filtrate as already described weighed 44 g. and contained 83% peroxide; the yield of peroxide recovered was 69%.

Repetition of this experiment resulted in 60–75% yields of 80–90% peroxide concentrate. When autoxidized methyl oleate containing about 4% peroxide was employed as the starting material in the Solution–Slurry Method, somewhat lower yields of peroxide concentrate were obtained, probably because of difficulty in separating the non-complex fraction from the relatively large mass of urea complexes.

Concentration of Peroxides from Methyl Oleate Autoxidized to High Levels. Solution–Slurry Method.—Methyl oleate was autoxidized at 80° in the dark until the peroxide content was 37%. One hundred grams was processed by the Solution–Slurry Method; 380 g. of urea and 640 ml. of methanol were employed. The filtrate from the unwashed precipitate of urea complexes yielded 27 g. of peroxide concentrate containing 83% peroxide; peroxide recovery was 61%. When the precipitate of urea complexes was washed on the funnel with about 300 ml. of methanol saturated with urea, an additional 5.5 g. of peroxide concentrate containing 70% peroxide was obtained. This corresponded to an additional peroxide recovery of 10%, making the total yield of peroxide recovered 71%.

The peroxide concentrate was not completely soluble in carbon bisulfide whereas peroxide concentrates obtained from methyl oleate autoxidized to lower levels (15–20%) were usually completely soluble. The carbon bisulfide-insoluble material was a white solid which amounted to about 1% of the peroxide concentrate. Its melting point was 130–131°, and when it was mixed with authentic 9,10-dihydroxystearic acid (m.p. 130–131°) the melting point was 129–131°. It was tentatively identified as high-melting 9,10-dihydroxystearic acid, but insufficient material was available for confirmation.

Discussion

The best yields (85–95%) of peroxide concentrates were obtained by the Solution Method, but the concentration of peroxides rarely exceeded 75%. When the yield of peroxide was of greater importance than the degree of concentration, this method was preferred. Its main disadvantage was the large quantities of urea and methanol required, particularly when large quantities of the autoxidation mixture were to be processed. On the other hand, the Slurry Method required the minimum quantities of urea and methanol and was the most convenient for the largest scale laboratory operations, but the recovery of peroxides was frequently only fair (50–70%), even though the degree of concentration was high (80–90%). The Solution–Slurry Method was a compromise (60–75% yields of 80–90% concentrates) between the high yields and clean operation of the Solution Method and the small reagent requirements of the Slurry Method. In addition, with all the reactants in solution at the outset, reaction time was generally short, often two hours. Since the formation of complex is exothermic, the reaction was terminated when the internal temperature of the mixture reached room temperature, or nearly so. Yields of peroxide concentrate by the Slurry or Solution–Slurry Methods were increased almost to the levels of the Solution Method by a single washing of the precipitated urea complexes on the funnel with methanol saturated with urea. The peroxide concentrate isolated from the methanol wash had a slightly lower peroxide content than did the main portion of the product.

When the peak value for peroxide content in the autoxidation reaction mixture is passed, and the peroxide content is decreasing, the urea separation technique is unsatisfactory in all cases, both with respect to yield of peroxide recovered and degree of concentration achieved. For this reason, we always process autoxidation mixtures before they reach their maximum peroxide content to be sure that this interference is avoided.

Furthermore, in terms of the efficiency of utilizing methyl oleate, we autoxidized almost to the maximum peroxide level, which is about 38%, because yields of peroxide concentrate are approximately the same in the range of about 4 to 37% peroxide in the autoxidation mixture.

An important question which concerned us was the failure to obtain directly from the autoxidation mixture peroxide concentrates containing more than 90% peroxide. Furthermore, retreatment with urea of peroxide concentrates containing 75% peroxide also failed to yield concentrates containing more than 90% peroxide. Complete analysis[15,21] of the original autoxidation mixtures and, more particularly, of the peroxide concentrates furnished some information on this point. The original autoxidation mixtures contained approximately 1–2% of oxiranes, carbonyls and α-glycols, in addition to some free acid, probably cleavage or hydrolytic products. These minor components would undoubtedly fail to precipitate as urea complexes and would be concentrated in the filtrate containing the peroxide. Confirmation of this was the fact that peroxide concentrates (75% peroxide) contained approximately 5–10% of oxiranes, 5–10% of carbonyls and about 10% of α-glycols. Furthermore, some of the peroxide molecules may have other oxygen-containing functional groups, thus contributing to the failure to obtain an analytical value of 100% peroxide, based on methyl octadecenoate peroxide as the reference compound. Also, small amounts of methyl oleate, which is the main non-peroxidic component of the autoxidation mixture, or possibly methyl elaidate (formed as a result of an oxidatively induced *cis–trans* isomerization)[22] would pass into the peroxide fraction because even under the best conditions pure methyl oleate gives a maximum yield of urea complex of about 96%.

To demonstrate the generality of the peroxide concentration techniques, preliminary experiments

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(21) H. B. Knight and D. Swern, *J. Am. Oil Chemists' Soc.*, **26**, 366 (1949).

(22) H. B. Knight, C. R. Eddy and D. Swern, *ibid.*, **28**, 188 (1951).

were conducted with linoleic and linolenic acids autoxidized at 20° to a peroxide content of about 7-8% or methyl elaidate autoxidized at 35° to a peroxide content of 18%. With linoleic acid and methyl elaidate, a fourfold increase in peroxide content was achieved; with linolenic acid, the increase was twofold.

PHILADELPHIA 18, PENNA.

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Reactions of Orthoesters with Active Methylene Compounds

BY REUBEN G. JONES

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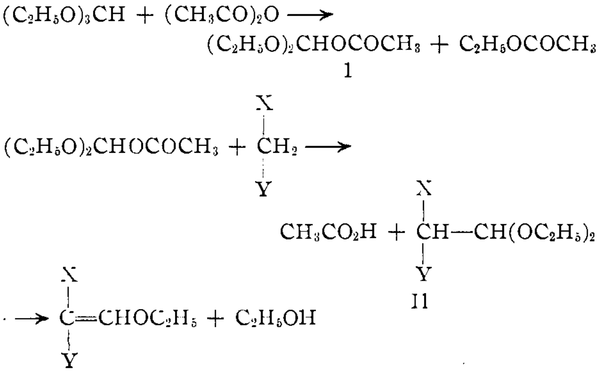
Ethyl orthoformate was found to react directly with a number of active methylene compounds in the absence of acetic anhydride to give the corresponding ethoxymethylene derivatives and ethanol. In the reaction with ethyl cyanoacetate, the presence of a little sulfuric acid decreased the yield, while the presence of a little sodium methylate appeared to increase the yield of ethyl ethoxymethylenecyanoacetate. Ethyl triethoxyacetate reacted with ethyl oxalacetate in the absence of acetic anhydride to give triethyl α-ethoxy-γ-ketoaconitate. The possible mechanism of the reaction is commented upon briefly.

Ethyl orthoformate in the presence of acetic anhydride reacts with a variety of compounds containing active methylene groups such as acetoacetic ester, acetylacetone, malononitrile, etc., to form the ethoxymethylene derivatives (III).[1] Post and Erickson[2] and more recently, Fuson, Parham and Reed[3] have presented good evidence that this reaction involves first a condensation of ethyl orthoformate with acetic anhydride to form diethoxymethyl acetate (I). This compound then alkylates the active methylene carbon to give the acetal (II), from which a mole of alcohol is finally eliminated to yield III.



$$(C_2H_5O)_3CH + (CH_3CO)_2O \longrightarrow \underset{\text{I}}{(C_2H_5O)_2CHOCOCH_3} + C_2H_5OCOCH_3$$

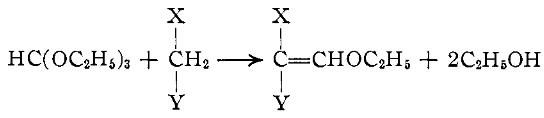
$$(C_2H_5O)_2CHOCOCH_3 + \underset{Y}{\overset{X}{CH_2}} \longrightarrow CH_3CO_2H + \underset{\text{II}}{\underset{Y}{\overset{X}{CH}}-CH(OC_2H_5)_2}$$

$$\longrightarrow \underset{Y}{\overset{X}{C}}{=}CHOC_2H_5 + C_2H_5OH$$

III X and Y = CO_2R, $COCH_3$, CN, etc.

That this may not be the only mechanism by which ortho esters can react with active methylene compounds, has become evident from a number of observations in this Laboratory and elsewhere.[4]

The purpose of this paper is to report that ethyl orthoformate will undergo reaction with a number of active methylene compounds *in the absence of acetic anhydride* to give the ethoxymethylene derivatives (III). The two reactants are simply heated together at about 140° for several hours. This reaction can be represented by the equation



$$HC(OC_2H_5)_3 + \underset{Y}{\overset{X}{CH_2}} \longrightarrow \underset{Y}{\overset{X}{C}}{=}CHOC_2H_5 + 2C_2H_5OH$$

III

Thus, when ethyl acetoacetate and ethyl orthoformate were heated at 140–150° for eight hours, an 18% yield of ethyl ethoxymethyleneacetoacetate[5] was isolated. The only other product, aside from the unchanged starting materials, was ethanol. In a like manner, ethyl orthoformate and ethyl cyanoacetate underwent reaction on heating at 140° for several hours to give ethanol and ethyl ethoxymethylenecyanoacetate[6] (20% yield). Ethyl oxalacetate and ethyl orthoformate gave a 30% yield of ethyl ethoxymethyleneoxalacetate.[1] Malononitrile and ethyl orthoformate gave a 66% yield of ethoxymethylenemalononitrile.[7] In this latter condensation an interesting side reaction took place. In addition to ethanol, large quantities of diethyl ether and ethyl formate were obtained, and only a little unchanged ethyl orthoformate was recovered. It is surprising that malononitrile can cause this decomposition of ethyl orthoformate into ether and ethyl formate, although it is well known that such strongly acidic substances as hydrogen chloride[8] and boron trifluoride[9] can do so. Diethyl malonate failed to react with ethyl orthoformate even after prolonged heating at 150°.

The yields of ethoxymethylene compounds are considerably lower when no acetic anhydride is used in the reactions. At first thought this may seem to indicate that an equilibrium is established so that the reaction proceeds only part way, but if acetic anhydride is added the equilibrium is shifted by removal of the alcohol with formation of ethyl acetate, and the reaction goes to completion

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(1) For leading references see R. G. Jones, THIS JOURNAL, **73**, 3684 (1951).

(2) H. W. Post and E. R. Erickson, *J. Org. Chem.*, **2**, 260 (1937).

(3) R. C. Fuson, W. E. Parham and L. J. Reed, *ibid.*, **11**, 194 (1946).

(4) J. Pascual Vila and M. Ballester, *Anales real soc. fis. y quim.* **45B**, 87 (1949) [*C. A.*, **44**, 3884 (1950)], have found that ethyl orthoacetate reacts directly with malononitrile to yield methylethoxymethylenemalononitrile.

(5) L. Claisen, *Ann.*, **297**, 1 (1897).

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