$$(R_2Mg)_2 \rightleftharpoons 2R_2Mg; \quad (18a)$$

$$(MgX_2)_2 \rightleftharpoons 2MgX_2; \quad (18b)$$

$$R_2Mg + MgX_2 \rightleftharpoons R_2Mg{\cdot}MgX_2; \quad (18c)$$

$$R_2Mg{\cdot}MgX_2 \xrightarrow{\text{electrolysis}} RMg^+ + RMgX_2^-(?) \quad (18d)$$

These equations satisfactorily account for the nonequivalency of magnesium,[4] the increase in apparent molecular weight of the Grignard reagent with rising concentration,[26] the dissociation products on electrolysis,[5] the independence of the ratio of diethylmagnesium to "RMgX" as a function of the total Grignard reagent present,[3] and the presence of magnesium halide in its dimeric form.[22] The hypothesis that dialkylmagnesium exists in part as a dimer is also included in these equations.

It seems reasonable to assume that if diethylmagnesium is present in a Grignard reagent, at least part of the reaction should proceed through this intermediate. Examination of Figure 2 suggests that this must be the case since, if it were absent, a straight line should have been obtained.

On the other hand, it is doubtful that I is the sole reactive species, since about a threefold increase in k was found with an increase in the $[Br_0/(C_2H_5)_0]$ ratio from zero to one. This rise cannot be attributed solely to an enhancement in reactivity of benzonitrile by magnesium bromide since excess magnesium bromide did not cause any further increase in the rate constant. Possibly, the rise in the rate constant may come from a shift in equilibrium from $[(C_2H_5)_2Mg]_2$ to $(C_2H_5)Mg.MgBr_2$ (VIII) or to changes in dielectric constant of the medium as the reaction proceeds. These alternatives have not been differentiated in the present study.

Acknowledgment. We wish to thank the Eastman Kodak Co., Inc., for generous support for one of us (S.J.S.).

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[26] J. Meisenheimer and W. Schlichenmaier, *Ber.*, **61**, 720 (1928).

A Study of Alkyl Nitratocarbonates. An Improved Synthesis of Nitrate Esters

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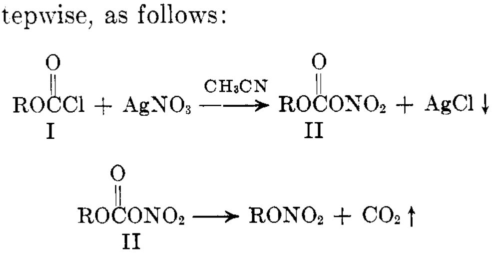
An alkyl nitratocarbonate, postulated as an unstable intermediate in the reaction of silver nitrate with an alkyl chloroformate, has been prepared in solution by using a catalyst in the cold. It decomposes completely upon warming to room temperature to give an alkyl nitrate and carbon dioxide. The pyridine-catalyzed reaction of silver nitrate with alkyl chloroformates constitutes a quick, mild, quantitative synthesis of alkyl nitrate esters.

In connection with studies of this laboratory, it became of interest to attempt the preparation and isolation of alkyl nitratocarbonates (II). After this work had been begun, Boschan's[1] work was published in which he shows that the nitratocarbonate structure is unstable and decomposes by an intramolecular cyclic mechanism to give alkyl nitrate and carbon dioxide. The synthesis and decomposition of a nitratocarbonate appeared to be stepwise, as follows:



$$\underset{\text{I}}{RO\overset{\overset{O}{\|}}{C}Cl} + AgNO_3 \xrightarrow{CH_3CN} \underset{\text{II}}{RO\overset{\overset{O}{\|}}{C}ONO_2} + AgCl\downarrow \quad (1)$$

$$\underset{\text{II}}{RO\overset{\overset{O}{\|}}{C}ONO_2} \longrightarrow RONO_2 + CO_2\uparrow \quad (2)$$

Step 1 involved the metathesis of an alkyl chloroformate (I) with silver nitrate to form the nitratocarbonate as an unstable intermediate (II) which then decomposed in step 2. Boschan believed that II had a finite lifetime since the kinetics of the over-all reaction were slightly less than second order.

In order to be able to prepare II, it seemed advisable to separate kinetically the two proposed steps of the reaction and to determine their relative rates. One way of determining the rate of step 1 is to follow the disappearance of chloroformate I in the reaction mixture. This could be done by vapor chromatography. The over-all rate of steps 1 and 2 could be followed by evolution of carbon dioxide. In addition to the rate information, vapor chromatography would also give a product analysis.

Using this approach, some preliminary experiments were carried out in acetonitrile using n-propyl chloroformate. Boschan's results were confirmed. In addition, it was found that reaction 2 roughly paralleled reaction 1 at high temperatures (40°), but was much slower than reaction 1 at temperatures below zero. However, reaction 1 was too slow to be useful at these temperatures. It was reasoned that if step 1 could be made to proceed more rapidly at low tempera-

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[1] R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

tures, isolation of the nitratocarbonate might be possible.

Pyridine was found to be an excellent catalyst for the metathesis step. In one reaction run at −17°, vapor chromatography indicated that only 40% of the chloroformate was left after two hours, but no carbon dioxide had been evolved. Plainly, reaction 1 was taking place, but reaction 2 was not. *n*-Propyl nitratocarbonate was therefore building up in the reaction mixture. The vapor chromatogram showed, in addition to chloroformate, *n*-propyl nitrate, and a very strong carbon dioxide band. It therefore appears that the nitratocarbonate was completely destroyed on the column. The reaction mixture was allowed to come to room temperature gradually overnight. In the morning, vapor chromatography showed 100% *n*-propyl nitrate. There were no by-products and no starting material. *The reaction had given a quantitative conversion to nitrate ester.*

With these results the study of the nitratocarbonate itself was terminated. Further work was confined to the use of this method as a synthetic tool.

These results indicate that the catalyzed reaction of chloroformates with silver nitrate to give alkyl nitrates is mild, quick, and quantitative. As such, it represents an extremely valuable synthetic tool.

In most of the experiments a single impurity was formed. This impurity was identified as *n*-propyl alcohol from its elution time in the vapor chromatogram. Its formation is hardly surprising since the solvents were redistilled but not dried, and no effort was made to dry the glassware or to exclude atmospheric moisture. Such precautions would unquestionably have eliminated alcohol formation and allowed the reaction to proceed quantitatively near room temperature. Even without such precautions, alcohol formation was not observed for the catalyzed reaction at −20°.

In an effort to define the scope and applicability of this synthetic method, several modifications in reaction conditions and reactants were tried. When triethylamine was substituted for pyridine at 32°, a slight acceleration of rate was observed. The amine removed silver from solution as a dark precipitate reminiscent of silver oxide. The reaction was not clean: build-up of three by-products was noted in the vapor chromatograms.

Substitution of another cation for the silver was also attempted, but with limited success. Thus, ammonium nitrate in *N*,*N*-dimethylformamide solution at room temperature gave only a low yield of nitrate ester with ethyl chloroformate. A very complex reaction mixture resulted. However, a reaction was found to take place between ethyl chloroformate and dimethylformamide alone at room temperature. Much of the chloroformate was lost as gaseous products, and a complex mixture of liquids was formed. To suppress this competing reaction, the metathesis with ammonium nitrate was attempted at −10°. When nothing appeared to happen, a little pyridine was added. Some ethyl nitrate was formed, but most of the chloroformate was lost as gaseous products.

Replacement of silver nitrate by pyridinium nitrate was attempted with *n*-propyl chloroformate in acetonitrile at 25° using excess pyridine as a catalyst. Within fifteen minutes, the vigorous evolution of gas had ceased, and the reaction was sampled. Unexpectedly, the vapor chromatogram disclosed that the only substance present in addition to solvent was a trace of *n*-propyl alcohol. Apparently the chloroformate had completely decomposed to gaseous products.

The pyridine catalyst was usually used at a concentration of about 2% by volume. One experiment using silver nitrate at 25° was conducted with only one tenth of the usual pyridine concentration. The rate of reaction under these conditions was much slower, but was faster than for the uncatalyzed reaction. Gradual build-up of at least two impurities was observed.

It was also observed in controlled experiments that evolution of carbon dioxide from the reaction began at about 15° and was very slow below about 20°, but that when the temperature was raised to about 25°, violent evolution of carbon dioxide commenced with local overheating, in spite of vigorous stirring, and became uncontrollable. When addition of reactants was carried out at 25° or above, the reaction mixture always turned yellow. If the reactants were mixed at 20° or lower, with effective cooling, this yellowing was usually avoided. This behavior is another indication of the temperature sensitivity of nitratocarbonates.

From this study several generalizations can be drawn. For best synthetic results, the reaction should be conducted in such a way that formation of the nitratocarbonate is rapid and essentially complete before its decomposition begins. This requirement is partially met when the cation of the nitrate salt will precipitate as its chloride. Catalyzing the reaction of the nitrate salt and chloroformate allows the metathesis to take place at low temperatures where the decomposition of the intermediate nitratocarbonate does not occur. Combination of low temperature catalysis and the proper cation nitrate in a suitable solvent gives quantitative conversion to nitrate ester.

Experimental

n-Propyl chloroformate was prepared from 1-propanol and phosgene by the procedure of Strain,[2] b.p. 111–112°. An authentic sample of *n*-propyl nitrate was prepared by treating 1-propanol with nitric and sulfuric acids,[3] b.p.

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[2] F. Strain, *et al., J.Am.Chem.Soc.*, **72**, 1254 (1950), procedure B.

[3] R. Boschan, R. T. Merrow, and R. W. Van Dolah, *Chem. Revs.*, **55**, 485 (1955).

108–109°. Acetonitrile was Eastman White Label, redistilled, b.p. 79.5–81.5°.

Analytical Precedures.—The composition of the reaction mixtures was determined by vapor chromatography at 100° using a 4-ft. commercial Narcoil column with helium at 10 p.s.i. as the carrier. Components of the mixture were identified by comparison of retention times with those of authentic samples. Quantitative information, especially for the disappearance of chloroformate, was obtained by comparison of peak areas.

Reaction of *n*-Propyl Chloroformate and Silver Nitrate at 40°.—Into a 200-ml. three-necked flask which, in addition to a stirrer, was fitted with a gas addition tube and water-cooled reflux condenser connected to a gas train consisting of a Dry Ice trap, Ascarite tube, and mineral oil bubbler vented to atmosphere, were placed 22.60 g. (0.133 mole) of silver nitrate and 75 ml. of acetonitrile. The stirrer was started, and argon was passed through the system overnight. The bath was then brought to 40.0 ± 0.3°, and 15.0 ml. (0.133 mole) of *n*-propyl chloroformate was pipetted into the flask. Silver chloride began to precipitate almost at once.

Disappearance of the chloroformate and appearance of *n*-propyl nitrate paralleled the evolution of carbon dioxide. Two small by-product bands appeared in the vapor chromatogram; their intensities were unchanged by flash distillation of the total liquids. One by-product was identified as 1-propanol.

The reaction was stopped at 28 hr. Carbon dioxide evolution amounted to 4.91 g. (84%). The silver chloride weighed 16.94 g. (89%). Residual chloroformate amounted to about 9%.

Reaction of *n*-Propyl Chloroformate and Silver Nitrate at −10°.—This experiment was carried out in exactly the same manner as the previous experiment except that the reaction temperature was maintained at −10° ± 7° by a cooling bath. The reaction was terminated at 48.5 hr. by suction filtration in the cold and flash distillation of the filtrate in the cold at reduced pressure. Chromatography indicated *ca.* 10% *n*-propyl chloroformate consumed although only 5.3% carbon dioxide was evolved. Silver chloride amounted to 2.07 g. (10.9%). The same two by-products as observed at 40° were present in both the crude reaction mixture and the flash distillate. *n*-Propyl nitrate was the major product.

Catalyzed Reaction of *n*-Propyl Chloroformate and Silver Nitrate at 25°.—The apparatus and reactants were as in the previous two runs except that no temperature-controlling bath was used. Two milliliters of pyridine was added with stirring. Before the addition could be completed, an extremely vigorous evolution of gas commenced and a copious precipitation took place. The reaction mixture became quite warm and turned yellow. No measure of the rate of carbon dioxide evolution was possible. Although the reaction appeared to be over within 5 min., the mixture was stirred for 1 hr. before an aliquot was chromatographed. The chromatogram showed the complete absence of starting chloroformate, over 90% *n*-propyl nitrate, less than 10% 1-propanol, and none of the second by-product.

Catalyzed Reaction of *n*-Propyl Chloroformate and Silver Nitrate at −17°.—In the 200-ml. flask were placed 22.60 g. (0.133 mole) of silver nitrate, 50 ml. of acetonitrile, and 2.0 ml. of pyridine. The mixture was stirred to solution, cooled to −17°, and maintained at −17 ± 2° while 15.0 ml. (0.133 mole) of *n*-propyl chloroformate in 30 ml. of acetonitrile was added dropwise over a period of 1 hr. Two hr. after the addition had been completed, the Ascarite tube showed no weight gain. Vapor chromatography indicated that 60% of the starting chloroformate had disappeared. Strong *n*-propyl nitrate and carbon dioxide bands were also present in the chromatogram.

The reaction mixture was allowed to warm to room temperature overnight. The vapor chromatogram then showed (other than an acetonitrile band) a single peak corresponding to *n*-propyl nitrate. No other peaks were observable, even at high detector sensitivity.

Notes

Synthesis of Fatty Acid Diesters of the Sulfur Analogs of Batyl and Chimyl Alcohols

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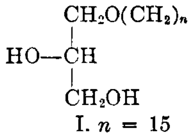
The α-glyceryl ethers are widely distributed materials in animal lipid systems with chimyl alcohol (I) and batyl alcohol (II) being the most important saturated members of the α-glyceryl ethers. In all natural sources the α-glyceryl ethers are found to be esterified with fatty acids.[2] Therefore we have prepared the sulfur analogs of these two important saturated alkoxy diglycerides, which correspond to the triglycerides tristearin and tripalmitin. These sulfur analogs of α-glyceryl ether esters are being used as part of our search of potential tuberculostatic agents and also in connection with their associated hemopoietic effects.[3,4] The results of this study will be reported elsewhere.



$$\begin{array}{l} \quad\;\; CH_2O(CH_2)_nCH_3 \\ \quad\;\; | \\ HO{-}CH \\ \quad\;\; | \\ \quad\;\; CH_2OH \end{array}$$

I. $n = 15$
II. $n = 17$

The diesters are synthesized by interaction of

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(2) D. C. Maline, *Chem. & Ind.*, 1359 (1960).

(3) A. Brohult and J. Holmberg, *Nature*, **174**, 1102 (1954).

(4) J. W. Linman, *Proc. Soc. Exper. Biol. and Med.*, **401**, 703 (1960).