As can be seen from this table the stability of this type of *aci*-nitro compound is dependent to a considerable extent on the position and nature of the substituents on the benzene rings.

Since the preparation of the diarylalkyl nitro compounds of the type used is rather simple, the *aci*-nitro compounds described and other similar ones are probably more readily available than any previously described compounds of this class.

The formation of the oxime by the action of methanol is believed to take place through the intermediate formation of the ester of the *aci*-nitro compound. Such esters are known to decompose to oximes.[6] The other product from this decomposition would be formaldehyde. This would be expected to react to some extent at least with methanol to form methylal. The presence of methylal in one of the reaction mixtures was demonstrated by the formation of formaldehyde 2,4-dinitrophenylhydrazone after hydrolysis of a distillate from the reaction mixture.

Experimental

Preparation of Nitro Compounds.—The nitro compounds were all prepared in about the same manner. The preparation of 1-*o*-chlorophenyl-1-*p*-chlorophenyl-2-nitropropane will be given as an example.

To a stirred mixture of 125 g. (1.11 moles) of chlorobenzene and 200 g. of 96% sulfuric acid held at about 25° by water cooling was added dropwise 100 g. (0.465 mole) of 1-*o*-chlorophenyl-2-nitro-1-propanol. The addition took 33 minutes and stirring was continued for another 27 minutes. Then 50 ml. of chlorobenzene was added (to prevent crystallization) and the organic layer was separated and washed with 200 g. of 5% sodium carbonate solution. It was then distilled in the presence of water to a vapor temperature of 99° and the organic residue was cooled and stirred for one-half hour with 300 ml. of petroleum ether. Filtration gave 99.1 g. (68%) of white solid; m.p. 101–110°. Recrystallization from a methanol–benzene mixture gave 68.1 g. (47%); m.p. 115–116°. One further crystallization from benzene raised the m.p. to 117–118°.

In condensations in which xylene and toluene took part, 85% and 90% sulfuric acids were used, respectively.

Preparation of *aci*-Nitro Compounds.—The preparation of the *aci*-nitro compounds will be illustrated by a description of the preparation of the *aci*-form of 1-*p*-bromophenyl-1-*o*-chlorophenyl-2-nitropropane.

To a solution of 4.4 g. (0.012 mole) of 1-*p*-bromophenyl-1-*o*-chlorophenyl-2-nitropropane and 0.75 g. (0.013 mole) of potassium hydroxide in 10 ml. of methanol was added 20 ml. of water. This solution was then added dropwise with stirring to a solution of 5 ml. of concentrated hydrochloric acid in 40 ml. of water which was held at 20°. The white precipitate was filtered and washed with 10 ml. of water. After two hours in a vacuum desiccator and further drying in the air overnight, there were 4.5 g. of white solid.

Anal. Calcd. for $C_{15}H_{13}BrClNO_2$: Br, 22.54; Cl, 10.00; N, 3.95. Found: Br, 22.85; Cl, 10.14; N, 3.73.

Preparation of Oximes.—These were also all prepared in the same manner. Their preparation will be illustrated by a description of the conversion of 1-*p*-bromophenyl-1-*o*-chlorophenyl-2-nitropropane to 1-*p*-bromophenyl-1-*o*-chlorophenyl-2-propanone oxime.

The *aci*-nitro compound was prepared as described in the preceding example, but was dried only the two hours in a vacuum desiccator. Then it was added to 25 ml. of methanol and the mixture was heated on a steam-bath for one-half hour. It was then left standing in an open erlenmeyer flask. After three weeks the residue in the flask was crystallized three times from methanol to give 1.3 g. (16%) of the oxime.

The yield given is about typical for the series. All of the oximes were impure as first recovered and some required as many as five crystallizations to give pure compounds.

Identification of Formaldehyde.—Thirty-seven grams (0.12 mole) of the *aci*-form of 1-*o*-chlorophenyl-1-*p*-chlorophenyl-2-nitropropane was mixed with 80 ml. of methanol and refluxed for 5 hours under a 14 × 2 cm. packed column. The temperature at the top of the column dropped from 64 to 50° during this time. Then 15 ml. was slowly distilled and this distillate was heated to boiling with a solution of 1.5 g. of 2,4-dinitrophenylhydrazine in 100 ml. of ethanol and 2 ml. of concentrated hydrochloric acid. On cooling, 0.7 g. (0.003 mole) of formaldehyde 2,4-dinitrophenylhydrazone crystallized. After recrystallization from ethanol this had a m.p. of 162–164°; a mixed melting point with an authentic sample was also 162–164°.

TERRE HAUTE, IND. RECEIVED OCTOBER 20, 1950

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[6] See J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

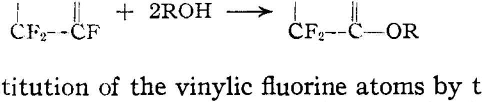
Action of Alcohols on 3,3,4,4-Tetrafluoro-1,2-dichlorocyclobutene-1[1,2]

BY J. D. PARK, C. M. SNOW[3] AND J. R. LACHER

The reaction of alkanols with 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene-1 in the presence of a base under control conditions results in the formation of 1-alkoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene-1, as contrasted to the production of 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutene-1 from the analogous hexafluorocyclobutene reported previously. When an excess of alcoholic alkali solution was used with 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene-1, a cyclic triether having the empirical formula $C_4F_2Cl(OR)_3$ was formed. Various mechanisms are discussed. Some of the physical properties of the ethers including magnetic susceptibilities, along with their ultraviolet and infrared absorption spectra, are presented.

A review of the art on the preparation of fluorinated ethers has been previously covered.[4,5]

It has been shown[5] that the reaction of alcohols with hexafluorocyclobutene in the presence of a base resulted in the unexpected production of a diether as shown by the equation



Substitution of the vinylic fluorine atoms by the -OR groups was postulated, with a mechanism similar to the formation of a substituted anisole from a substituted phenyl halide. The addition

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[1] Presented before the Fluorine Section of the Division of Industrial and Engineering Chemistry, 118th Meeting of the American Chemical Society, Chicago, Illinois, September 3–8, 1950.

[2] This paper represents part of a thesis submitted by C. M. Snow to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950. This work was supported in part by Contract N6-onr-231, Task Order 6, with the Office of Naval Research, United States Navy.

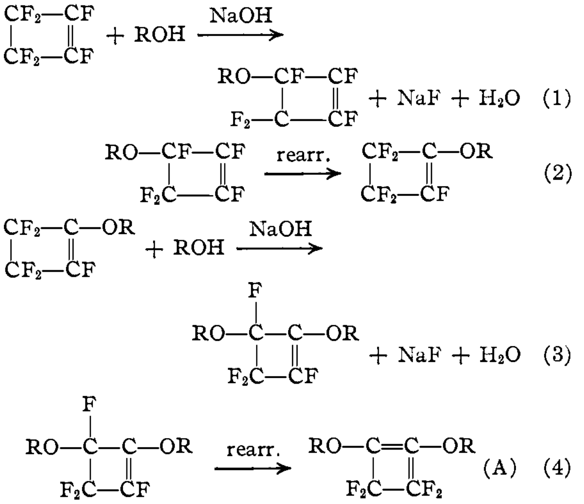
[3] Agricultural Processing Industries, Inc., Denver, Colorado.

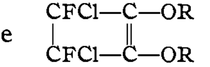
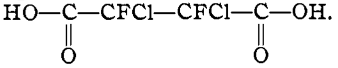
[4] J. D. Park, J. R. Lacher, *et al.*, THIS JOURNAL, **70**, 1550 (1948).

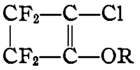
[5] J. D. Park, M. L. Sharrah and J. R. Lacher, *ibid.*, **71**, 2337 (1949).

mechanism proposed by Gibson and co-workers[6] is also applicable here.

However, it is also conceivable that the same diether could be obtained by stepwise substitution of the "allylic" fluorine atoms followed by rearrangement



In order to test this mechanism, the present study was inaugurated with the substitution of CF_2—CCl=CCl—CF_2 for CF_2—CF=CF—CF. If the reaction of CF_2—CCl=CClCF_2 with ROH proceeded according to the above mechanism, the final product should be  $\begin{array}{l}\mathrm{CFCl{-}C{-}OR}\\ \ |\qquad \|\\ \mathrm{CFCl{-}C{-}OR}\end{array}$ (B), which upon oxidation in the usual manner[7] should yield  $\mathrm{HO{-}\underset{O}{\underset{\|}{C}}{-}CFCl{-}CFCl{-}\underset{O}{\underset{\|}{C}}{-}OH}$.

Under the conditions of our experiments neither compound (A) nor compound (B) was obtained. Instead two new series of compounds were obtained, one belonging to the homologous series  $\begin{array}{l}\mathrm{CF_2{-}C{-}Cl}\\ \ |\qquad \|\\ \mathrm{CF_2{-}C{-}OR}\end{array}$ and the other to an homologous series of cyclic triethers having the empirical formula $C_4F_2Cl(OR)_3$.

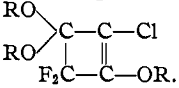
Starting Materials.—The starting intermediate CF_2=CCl_2 was prepared according to a previously described procedure[8] and dimerized according to the procedure of Henne[9] in a stainless steel bomb in the presence of du Pont "Terpene B"[10] polymerization inhibitor. The dimerization product, 3,3,4,4-tetrafluoro-1,1,2,2-tetrachlorocyclobutane, was then dechlorinated with zinc in *n*-butanol to yield quantitatively 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene which boiled at 63–64° at 632 mm. The alkanols used were of technical grade. The reaction with methanol illustrates the procedure used with ethyl and *n*-propyl alcohols.

Procedure.—A solution of 200 g. (1.02 moles) of CF_2—CCl=CCl—CF_2 and 200 ml. of methanol was placed in a 1-l. round-bottomed flask equipped with a stirrer, dropping funnel and upright water-cooled condenser. A solution of 63 g. (1.1 moles) of potassium hydroxide in 200 ml. of methanol was then slowly added through the dropping funnel as fast as the highly exothermic nature of the reaction would permit under slow agitation. Upon completion of the reaction, water was added to the reaction mixture and the ether layer removed. Upon fractionation, a 75% yield of CF_2—C(OCH_3)=CCl—CF_2 was obtained. This material boiled at 117° at 760 mm. pressure. Similar yields of the ethyl and propyl ethers were obtained. With hexafluorocyclobutene[6] both vinylic fluorines were replaced by alkoxy groups whether the reaction was carried out in an excess or deficiency of alkali dissolved in alcohol.

If the above procedure was altered by adding the olefin to the saturated solution of potassium hydroxide in alcohol and allowed to reflux vigorously during the reaction period, along with the monoether (40%) is obtained a cyclic triether (45%) having the empirical formula $C_4F_2Cl(OR)_3$ and some unidentified tarry substances (15%). Similar products were obtained by retreatment of CF_2—C(OCH_3)=CCl—CF_2 with an alcoholic solution of alkali under reflux conditions. No diethers were isolated.

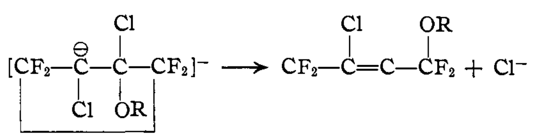
Proof of Structure.—All of the monoethers showed unsaturation with potassium permanganate and gave no test for the presence of the hydroxyl group when treated with metallic sodium. The infrared spectra displayed absorption bands near 1750 cm.$^{-1}$ (in the vicinity of the carbon-to-carbon double bond stretching band in hydrocarbons).

The structure of the unsaturated ethers CF_2—CCl=C(OR)CF_2 was proved by oxidation with potassium permanganate followed by hydrolysis to give tetrafluorosuccinic acid, m.p. 86° (lit. 86.4–87.4°).

The structure of the triethers has not as yet been definitely established. Based on preliminary data, the structure is probably  $\begin{array}{l}\mathrm{(RO)_2C{-}C{-}Cl}\\ \qquad |\quad\ \|\\ \quad \mathrm{F_2C{-}C{-}OR}\end{array}$.

On the basis of this work, the alternative mechanism of stepwise substitution of the "allylic" fluorine atoms followed by rearrangement is untenable. To explain the base-catalyzed formation of CF_2—C(OR)=CCl—CF_2 the mechanism is proposed

CF_2—CCl=CCl—CF_2 + $(OR)^-$ ⟶


$$[\mathrm{CF_2{-}\overset{\ominus}{\underset{Cl}{C}}{-}\overset{Cl}{\underset{OR}{C}}{-}CF_2}]^- \longrightarrow \mathrm{CF_2{-}\overset{Cl}{C}{=}C{-}\overset{OR}{C}F_2} + Cl^-$$

The course of the reaction is complicated by the presence of the allylic fluorine atoms in the resulting unsaturated cyclic monoether which further react to form the triethers.

Physical Properties.—Some physical properties of the ethers are listed in Table I. The boiling points, densities and refractive indices are in line with what one might expect for an homologous series.

The diamagnetic susceptibilities were measured by means of the Quincke method[11a] previously described.[11b] The molar susceptibilities are given in Table I.

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[6] Presented at Chicago, Ill., Sept. 3–8, 1950, in the Fluorine Symposium, Am. Chem. Soc., 21-L Paper 38 by J. D. Gibson, J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner and R. H. Lafferty, Jr.

[7] A. L. Henne and W. J. Zimmerschied, THIS JOURNAL, **69**, 283 (1947).

[8] J. D. Park, C. M. Snow and J. R. Lacher, *ibid.*, **73**, 861 (1951).

[9] A. L. Henne and R. P. Ruhn, *ibid.*, **69**, 279 (1947).

[10] A terpene fraction consisting principally of dipentene and terpenolene boiling at 176–196° and having refractivity and density values of $n^{20}D$ 1.470–1.478 and $d^{1.58}_4$ 0.855–0.870.

[11] (a) G. Quincke, *Ann. Physik*, **24**, 347 (1885); **34**, 401 (1888).

[11] (b) J. E. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **72**, 333 (1950).

TABLE I

PHYSICAL PROPERTIES

	B.p., °C. 760 mm.	n^{20}_D	MRD Found	MRD Calcd.[a]	d^{20}_4	Mol. wt. Calcd.	Mol. wt. Found	ARF	$\chi_M \times 10^6$ Add.[b]	$\chi_M \times 10^6$ Exptl.	Analyses, Cl, % Calcd.	Analyses, Cl, % Found
$CF_2—CCl=C(OCH_3)CF_2$	117	1.3799	29.33	30.20	1.4614	190.54	188.1	1.25	−104.00	− 87.65	18.61	19.21
$CF_2—CCl=C(OC_2H_5)CF_2$	129.5	1.3843	33.95	35.09	1.3642	204.57	200.9	1.31	−115.86	− 99.22	17.33	17.33
$CF_2—CCl=C(OC_7H_7)CF_2$	141	1.3900	38.57	40.55	1.2777	218.60	208.4	1.52	−127.72	−111.27	16.22	16.30
Methyl triether	205.5	1.4300	43.02	42.03	1.3188	214.62	222.6	0.53	−110.58	−109.46	16.52	16.34
Ethyl triether	238.5	1.4332	56.88	56.16	1.1883	256.66	260.3	0.67	−146.16	−142.96	13.81	13.94

[a] Calculated from the Lorenz–Lorentz formula. [b] Based on the addition of Pascal's constants. Benzene used as a standard $\chi(g) = -0.701 \times 10^{-6}$.

The ultraviolet absorption spectra of the ethers were measured with a Beckman quartz spectrophotometer in a 10-mm. quartz cell. The extinction coefficient, E, defined by $\log I/I_0 = El$ was measured; l is the length of the cell in cm. which is unity in the present case. Readings were made at approximately 10 Å. in the regions where absorption took place. The results are given in Fig. 1 and Fig. 1a.

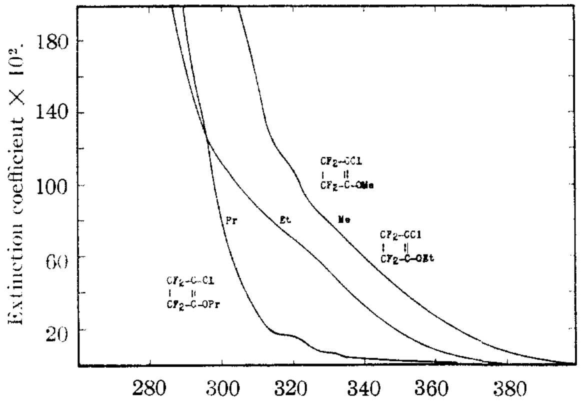

Fig. 1.—Ultraviolet absorption spectra.

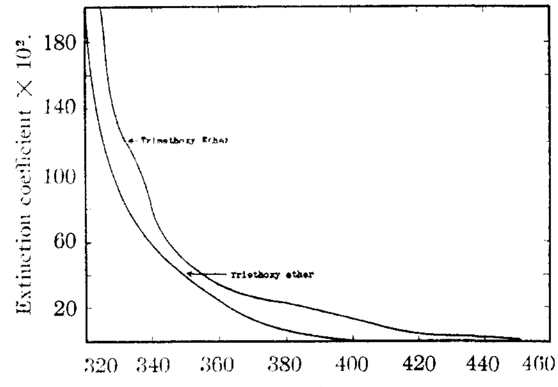

Fig. 1a.—Ultraviolet absorption spectra.

The infrared absorption spectra of the mono- and triethers were measured using an automatic recording Perkin–Elmer Infrared spectrometer, model 12B. The results obtained are given in Figs. 2 and 3. The spectra of the monoethers are strikingly similar and confirm their homologous nature. It is possible to refer certain regions of absorption back to functional group in the molecule.[12] The strong absorption at 3.27–3.47 μ which appears in all compounds is due to the C–H stretching vibration in the alkyl groups. The band at 5.80–5.94 μ is in the re-

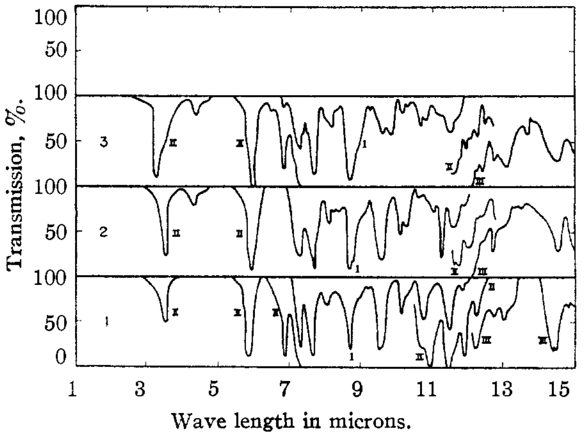

Fig. 2.—The infrared absorption spectrograms at room temperature: I, in a 10-cm. gas cell at ind. press.; II, in a 0.025-mm. liquid cell; and III, in a 0.1-mm. liquid cell of (1) $CF_2—CCl=C(OMe)CF_2$, (2) $CF_2—CCl=C(OEt)CF_2$ and (3) $CF_2—CCl=C(OPr)CF_2$.

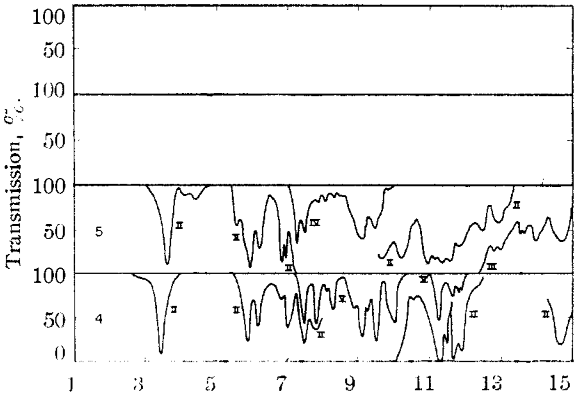

Fig. 3.—The infrared spectrograms at room temperature: II, in a 0.025-mm. liquid cell; III, in a 0.1-mm. liquid cell; IV a 1% soln. of the ether in heptane in a 0.025-mm. liquid cell; and V, a 2% soln. of the ether in a 0.025-mm. liquid cell of (4) $C_4F_2Cl(OMe)_3$ and (5) $C_4F_2Cl(OEt)_3$.

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[12] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

gion of the double bond stretching vibration. These absorption spectra confirm the chemical evidence for the presence of a double bond in these compounds. In the triethers, the strong absorption at 3.47–3.57 μ is characteristic of the C–H stretching vibration in the alkyl groups and the double bond stretching vibration bands at 6.13–6.18 μ.

BOULDER, COLORADO RECEIVED NOVEMBER 20, 1950

[CONTRIBUTION FROM RESEARCH CENTER, B. F. GOODRICH COMPANY]

β-Propiolactone. X.[1] Reactions with Compounds Containing Active Methylenic Hydrogen

BY T. L. GRESHAM, J. E. JANSEN, F. W. SHAVER, M. R. FREDERICK AND W. L. BEEARS

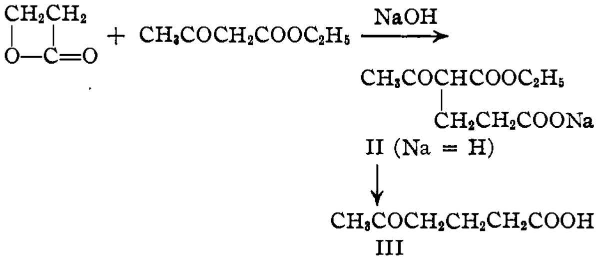
Reactions of β-propiolactone in water or alcohol with ethyl acetoacetate, acetylacetone, benzoylactone, cyanoacetamide and diethyl malonate are described. The products isolated in all cases were the result of C-alkylation. Some evidence was obtained for the presence of unstable O-alkylates in certain cases.

The reactions of β-propiolactone (I) with salts of inorganic and organic acids are described in previous papers.[2,3] It was of interest to investigate the reactions of I with the sodio derivatives of compounds containing active methylenic hydrogen. In general these reactions were found to be rapid and could be conducted either in water or alcohol. The only products isolated and identified were those resulting from carbon alkylation.

Since the O-alkylated derivatives would be expected to pyrolyze readily and the formation of acrylic acid and the original active methylene compound during redistillation of the crude products was evidence for their presence, none was isolated.

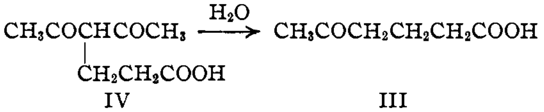
Competing reactions were the hydrolysis of I and the reaction of I at the carboxylate ion in the primary product. No appreciable improvement in the yields of C-alkylation products, which were usually in the range of 40%, was obtained by variation of the reaction conditions. The reactions are unique, however, in that they provide a direct synthesis of the free β-carboxyethyl alkylates. Some of these compounds have not been prepared previously or are difficult to prepare by other means.

The salt of 4-carbethoxy-5-oxohexanoic acid (II) is formed rapidly from ethyl acetoacetate and I in aqueous or alcoholic sodium hydroxide. It was difficult to obtain the pure product by distillation because it was contaminated with certain by-products, principally 5-oxohexanoic acid (III) and in the case of the alcohol reactions, the ester of II. Slow decomposition to acrylic acid and ethyl acetoacetate was observed during the distillation but pure II was stable. This mixture was extracted with two portions of water and redistilled after each washing. Since the compound still was not pure attempts were made to crystallize it at sub-zero temperatures. No crystallization occurred except at the surfaces where the material was exposed to atmospheric moisture. This was shown to be the hydrate and the whole product was recrystallized as the hydrate. Dehydration yielded pure 4-carbethoxy-5-oxohexanoic acid. The product was readily hydrolyzed to III with dilute base or acid.



$$\begin{array}{c}CH_2CH_2\\ |\quad\ \ |\\ O{-}C{=}O\end{array} + CH_3COCH_2COOC_2H_5 \xrightarrow{NaOH} \underset{\text{II (Na = H)}}{\begin{array}{l}CH_3COCHCOOC_2H_5\\ \qquad\quad\ |\\ \qquad\quad CH_2CH_2COONa\end{array}} \downarrow \underset{\text{III}}{CH_3COCH_2CH_2CH_2COOH}$$

Acetylacetone and I in aqueous or alcoholic sodium hydroxide give the salt of 4-acetyl-5-oxohexanoic acid (IV). Slow decomposition to acrylic acid and acetylacetone occurred during distillation, again indicating the presence of unstable O-alkylate in the crude product. Hydrolysis of IV with base gave III. The competing hydrolysis of I and reaction with the carboxylate ion of II and of IV probably obscured any difference in yield of C-alkylate which might have been expected from the great difference in enol content of ethyl acetoacetate and acetylacetone.



$$\underset{\text{IV}}{\begin{array}{l}CH_3COCHCOCH_3\\ \quad\ |\\ CH_2CH_2COOH\end{array}} \xrightarrow{H_2O} \underset{\text{III}}{CH_3COCH_2CH_2CH_2COOH}$$

With benzoylacetone the C-alkylate was more readily hydrolyzed with base and thus the only product isolated from the basic reaction solution was γ-benzoylbutyric acid (V).

$$\underset{\text{V}}{C_6H_5COCH_2CH_2CH_2COOH}$$

Cyanoacetamide and I in aqueous sodium hydroxide gave the salt of 4-cyanoglutaramic acid (VI), a new compound. In absolute alcohol with sodium ethylate the product was a mixture of VI and 3-cyanoglutarimide[4] (VII) which was readily separated by crystallization from alcohol. It was not possible to form VII from VI under the conditions of the reaction, or with other dehydrating methods, thus it is not likely that VI is the intermediate in the formation of the cyclic imide, VII. Strong hydrolysis of VII with acid gave glutaric acid. With milder conditions and base the hydrolysis of VII gave a new compound which is

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[1] For Paper IX of this series see THIS JOURNAL, **72**, 4867 (1950).

[2] Gresham, Jansen, Shaver and Gregory, *ibid.*, **70**, 999 (1948).

[3] Gresham, Jansen and Shaver, *ibid.*, **70**, 1003 (1948).

[4] C. Barat, *J. Indian Chem. Soc.*, **8**, 37–44 (1931).