TABLE VI

DESCRIPTION OF THE VAPOR PHASE CHROMATOGRAPHIC COLUMNS

Column	Packing				Column	
	Liquid phase	Wt %	Solid support	Mesh size	Length, m	O.d., in.
A	Gum rubber phenyl Methyl GE-SE-552	15	GAS-Pack WAB	60–80	1.5	$^1/_4$
B	Versamid 900	10	GAS-Pack WAB	60–80	1.5	$^1/_4$
C	Dimethyl sulfolane	33	Firebrick	100–120	3.0	$^1/_4$
D	Reoplex 400	15	GAS-Pack WAB	60–80	2.3	$^3/_8$
E	Versamid 900	15	GAS-Pack WAB	60–80	2.3	$^3/_8$

pure isomers were separated by vpc and analyzed spectroscopically.

Analyses.—The infrared spectra of the pyridines purified by gas chromatography were taken with a Baird infrared spectrophotometer, Model 4-55. Samples of 8-10 μl were placed between two sodium chloride plates using air as a reference.

Nmr spectra were obtained on a Varian A-60 spectrometer at room temperature. Samples varying from 20 to 50 μl in carbon tetrachloride, total volume 400 μl, with an addition of 1–2 drops of tetramethylsilicon (TMS) as reference were used (Table V).

Refractive indices were measured on a Zeiss Opton refractometer with a thermostat at 20 ± 0.1°. All samples used for analysis were of purity higher than 95%.

Analyses and separations were performed with an F & M Model 720 dual-column gas chromatograph with a thermal conductivity detector, using helium as a carrier gas. The columns used are listed in Table VI.

The yields of alkenylated pyridines were determined by calculating the peak areas in relation to the internal standard *n*-butylcyclohexane added in known amount before alkenylation. The peak areas were determined from their heights and standard deviations[20] using the Bartlett and Smith method[21] in case of overlapped peaks.

The composition, purity, and consumption of piperylene was analyzed on column C at a column temperature of 30° and an injection port temperature of 70°, helium flow 100 ml/min, inlet pressure 35 psi; 20-μl samples were injected.

The composition of the product obtained from the reaction of γ-picoline with either *cis*- or *trans*-piperylene was analyzed on column A at 170° with a helium flow of 100 ml/min and an inlet pressure of 35 psi. The composition of the reaction products of 4-ethylpyridine was analyzed on column B at 160° with the same helium flow and inlet pressure; 40-μl samples were injected.

For preparative separation and purification of the various alkenylpyridines, the following conditions were used (compound, column, temperature, helium flow in ml/min): **2**, **3**, **4**, **7**, and **8**, D, 160°, 100; **5** and **6**, D, 140°, 125; **9a**, **9b**, **10**, and **11**, E, 190–200°, 100; **13**, **14**, **15**, **16**, **17**, and **18**, E, 170°, 100. The product obtained from each separation was analyzed again on vpc and when necessary the compound was repurified. The relative retention times of the alkyl- and alkenylpyridines are described separately.[22]

Registry No.—**1**, 108-89-4; **2**, 34993-35-6; **3**, 34993-36-7; **4**, 34993-37-8; **5**, 34993-38-9; **6**, 34993-39-0; **7**, 34993-40-3; **8**, 27876-24-0; **9a**, 34993-42-5; **10**, 34993-43-6; **11**, 34993-44-7; **12**, 536-75-4; **13**, 34993-45-8; **14**, 34993-46-9; **15**, 34993-47-0; **16**, 34993-48-1; **17**, 34993-49-2; **18**, 34993-50-5; *cis*-piperylene, 1574-41-0; *trans*-piperylene, 2004-70-8.

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Alkylation of Disodioacetylacetone with Halo Ketals

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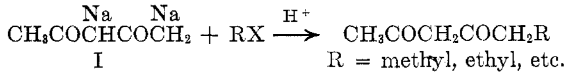
The reaction of bromo and chloro ketals (II) with disodioacetylacetone (I) were investigated. For II, $n = 1$; X = Br or Cl; R = CH_3—no reaction occurred. For II, $n = 2$; X = Br; R = CH_3—alkylation occurred in low yield. For II, $n = 3$, 4, or 5; X = Br or Cl; R = CH_3 or CH_3CH_2—alkylation occurred in fair to good yields to form the terminal alkylation products. These ketal β-diketones were hydrolized to the corresponding triketones. Copper chelates of the triketones were prepared.

In an effort to extend the versatility and usefulness of alkylations of dicarbanions of β-diketones, we have observed that 2-(chloromethyl)-2-methyl-1,3-dioxolane or 2-(bromomethyl)-2-methyl-1,3-dioxolane did not alkylate disodioacetylacetone (I) under the conditions in which simple alkyl halides (methyl iodide, butyl bromide, etc.[2]) alkylate I (see eq 1). That this lack of reactivity is a characteristic of these two compounds rather than a characteristic of ketal halides in general is discussed in the present paper.



$$\underset{\text{I}}{\mathrm{CH_3CO\overset{Na}{C}HCO\overset{Na}{C}H_2}} + \mathrm{RX} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3COCH_2COCH_2R} \qquad (1)$$

R = methyl, ethyl, etc.

The procedure involved conversion of acetylacetone to I by means of 2 molar equiv of sodium amide in liquid ammonia and treatment of this with 1 equiv of ketal halide (Scheme I). The results are summarized in Table I. It can be seen from Table I that, for $n = 1$, alkylation does not occur, but for II, $n = 2$, X = Br, alkylation does occur in poor yield. For $n = 3$, 4, and 5, X = Cl or Br, the reaction proceeds in much better yield. This indicates that, if the carbon bonded to the halogen is bonded to or near the ketal group, little or no alkylation reaction occurs because of the steric hindrance (II, $n = 1$, X = Cl or Br, similar to neopentyl halides), but, when the carbon bonded to halogen is further away from the ketal group, the steric hindrance decreases and allows the alkylation to proceed

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[2] C. R. Hauser and T. M. Harris, *J. Amer. Chem. Soc.*, **80**, 6360 (1958); K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 61 (1965).

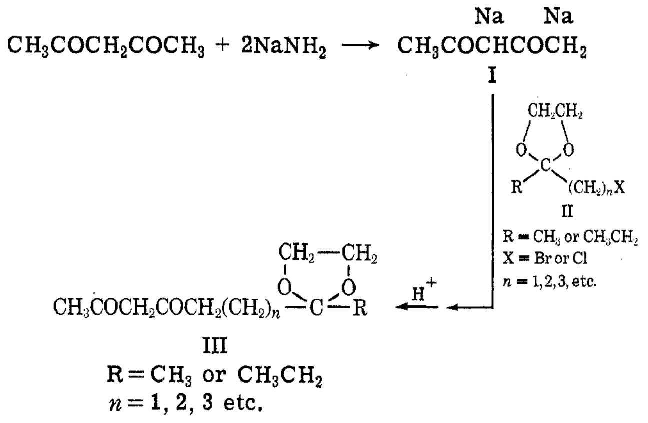
TABLE I

ALKYLATIONS OF DISODIOACETYLACETONE WITH HALO DIOXOLANES

Reaction	Halo dioxolane	Product	Reaction time, hr	Bp, °C (mm)	Yield, %
1	2-(Chloromethyl)-2-methyl-1,3-dioxolane	None	0.5		0
2	2-(Chloromethyl)-2-methyl-1,3-dioxolane	None	4		0
3	2-(Bromomethyl)-2-methyl-1,3-dioxolane	None	2		0
4	2-(2-Bromoethyl)-2-methyl-1,3-dioxolane	8-Ethylenedioxy-2,4-nonanedione	2	68–71 (0.10)	19
5	2-(3-Chloropropyl)-2-methyl-1,3-dioxolane	9-Ethylenedioxy-2,4-decanedione	2	97–98 (0.05)	47
6	2-(3-Chloropropyl)-2-methyl-1,3-dioxolane	9-Ethylenedioxy-2,4-decanedione	16	101–104 (0.15)	68[a]
7	2-(3-Chloropropyl)-2-methyl-1,3-dioxolane	9-Ethylenedioxy-2,4-decanedione	24	87–110 (0.09–0.10)	35
8	2-(3-Bromopropyl)-2-methyl-1,3-dioxolane	9-Ethylenedioxy-2,4-decanedione	2	96–100 (0.01)	54
9	2-(3 Chloropropyl)-2-ethyl-1,3-dioxolane	9-Ethylenedioxy-2,4-undecanedione	5	104–114 (0.15–0.25)	12
10	2-(3-Chloropropyl)-2-ethyl-1,3-dioxolane	9-Ethylenedioxy-2,4-undecanedione	24	103–109 (0.05)	45
11	2-(3-Chloropropyl)-2-ethyl-1,3-dioxolane	9-Ethylenedioxy-2,4-undecanedione	72	109–120 (0.15)	58[b]
12	2-(4-Bromobutyl)-2-methyl-1,3-dioxolane	10-Ethylenedioxy-2,4-undecanedione	24	119–123 (0.07–0.08)	52
13	2-(4-Bromobutyl)-2-ethyl-1,3-dioxolane	10-Ethylenedioxy-2,4-dodecanedione	2	115–122 (0.08)	64
14	2-(4-Bromobutyl)-2-ethyl-1,3-dioxolane	10-Ethylenedioxy-2,4-dodecanedione	24	111–121 (0.12)	47
15	2-(5-Chloropentyl)-2-methyl-1,3-dioxolane	11-Ethylenedioxy-2,4-dodecanedione	2	132–138 (0.07)	28
16	2-(5-Bromopentyl)-2-methyl-1,3-dioxolane	11-Ethylenedioxy-2,4-dodecanedione	24	115–121 (0.08–0.10)	47
17	2-(5-Chloropentyl)-2-ethyl-1,3-dioxolane	11-Ethylenedioxy-2,4-tridecanedione	2	129–132 (0.08)	30
18	2-(5-Bromopentyl)-2-ethyl-1,3-dioxolane	11-Ethylenedioxy-2,4-tridecanedione	2	127–132 (0.07)	66
19	2-(5-Bromopentyl)-2-ethyl-1,3-dioxolane	11-Ethylenedioxy-2,4-tridecanedione	24	131–134 (0.10)	55

[a] This reaction was run on a 0.25-mol scale; all others were run on a 0.05-mol scale. [b] 2,4,9-Undecanetrione (2.21 g) was filtered from this sample. The remaining 4.38 g was redistilled at 102–106° (0.10 mm) and was shown to be 9-ethylenedioxy-2,4-undecanedione. The combined yield of diketodioxolane and triketone was 58%.

SCHEME I



by an SN2 mechanism.[3] Except for $n = 1$ and $n = 2$ *vs.* the reactions $n = 3$, 4, and 5, there does not appear to be a definite trend in yields with changing n.

It was necessary to distill these liquid β-diketone dioxolanes at low pressures (Table I) to avoid decomposition, which could occur even below 140°. In general it was found that reactions stopped after 2 hr had a greater yield than those allowed to react for 24 hr. This may have been caused, in part, by a slow hydrolysis (see footnote *b*, Table I). In those cases where all the other variables were the same except for a different halogen, the yields were better when X = Br than when X = Cl. This does not mean that the bromo compound is always preferable to the chloro compound. Although 9-ethylenedioxy-2,4-decanedione was formed in better yield with a 2-hr reaction time when X = Br rather than Cl, the ease and yield in preparation of 5-chloro-2-pentanone was much better than that of 5-bromo-2-pentanone and, therefore, more than compensates for the difference in yield of the dianion reaction. The difference in yield of 11-ethylenedioxy-2,4-tridecanedione when X = Cl *vs.* X = Br would indicate that in this case the bromo compound is preferable. Comparison of reactions 7 *vs.* 10, 12 *vs.* 14, 15 *vs.* 17, and 16 *vs.* 19 shows no consistent trend when changing R from methyl to ethyl, although in three of the four

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(3) The low yield when $n = 2$ may not only be caused by steric hindrance but also may be caused by a competing elimination reaction.

comparisons the yield of R = ethyl is 2 to 10% better than when R = methyl.

The structures of the diketodioxolanes were supported by analogy with previous alkylations of dianions of β-diketones,[2] by elemental analysis (see Table II), by conversion into derivatives which will be discussed below, and by infrared and nmr spectra. For example, the ^{1}H nmr spectrum of 9-ethylenedioxy-2,4-decanedione shows sharp singlets at τ 8.75, 7.96, 6.25, and 4.34 with relative areas of 3:3:4:1. Similarly, the ^{1}H nmr spectrum of 9-ethylenedioxy-2,4-undecanedione shows sharp singlets at τ 8.03, 6.20, and 4.50 with relative areas of 3:4:1. In addition there is a triplet (relative area 3) at τ 9.03. The spectra also show the hydroxylic absorption of the enol forms of these β-diketones at very low field (-6 to -5τ). It is apparent from the ir and nmr data that the carbonyl groups and the dioxolane are both present in the products. In addition it should be noted that the sharp singlet being used as a reference (τ 7.86) has a relative area of three in each of the spectra. This indicates that alkylation has taken place at the methyl group of acetylacetone rather than at the more acidic methylene group. For the latter to be true it would be necessary for this singlet to have a relative area of six, indicating the presence of two equivalent methyl groups adjacent to the β-diketone.

TABLE II

ANALYSES OF β-DIKETONE DIOXOLANES

Registry no.	Compd		C, %	H, %
34956-71-3	8-Ethylenedioxy-2,4-nonanedione ($C_{11}H_{18}O_4$)	Calcd	61.68	8.41
		Found	61.92	8.46
34956-72-4	9-Ethylenedioxy-2,4-decanedione ($C_{12}H_{20}O_4$)	Calcd	63.13	8.83
		Found	63.36	9.08
34956-73-5	9-Ethylenedioxy-2,4-undecanedione ($C_{13}H_{22}O_4$)	Calcd	64.44	9.15
		Found	64.68	9.15
34956-74-6	10-Ethylenedioxy-2,4-undecanedione ($C_{13}H_{22}O_4$)	Calcd	64.44	9.15
		Found	64.25	9.11
34956-75-7	10-Ethylenedioxy-2,4-dodecanedione ($C_{14}H_{24}O_4$)	Calcd	65.60	9.44
		Found	65.38	9.53
34982-06-4	11-Ethylenedioxy-2,4-dodecanedione ($C_{14}H_{24}O_4$)	Calcd	65.60	9.44
		Found	65.71	9.53
34956-76-8	11-Ethylenedioxy-2,4-tridecanedione ($C_{15}H_{26}O_4$)	Calcd	66.64	9.69
		Found	66.49	9.78

Another procedure which is generally used in showing where alkylation occurred on a β-diketone is the formation of copper chelates of the β-diketone.[2] The β-diketone dioxolanes formed a solid copper chelate very slowly if at all. Of the several attempts that were made only two chelated β-diketone dioxolanes (8-ethylenedioxy-2,4-nonanedione and 9-ethylenedioxy-2,4-undecanedione) were isolated. The structure of these was supported by elemental analysis and infrared spectra (see Experimental Section).

Each of the β-diketone dioxolanes was hydrolzyed to its corresponding triketone in an ethanol–water mixture using a drop of concentrated hydrochloric acid to catalyze the reaction. These triketones are low-melting solids with the exception of 2,4,8-nonanetrione, which was observed to freeze slightly below room temperature. This compound was extremely difficult to isolate, since it appears to be much more soluble in ethanol than the other triketones listed in Table III. The structure of each of these triketones was supported by analysis (Table III) and conversion to copper chelates. Unlike the β-diketone dioxolanes the triketones readily formed copper chelates. The melting point, elemental analysis, and infrared spectra data of these are given in Table IV. The two absorption bands in the 6.10–6.60 μ region are consistent with the unsubstituted methylene group of the β-diketone.[4] It should also be noted that there is an absorption band in the 5.8–5.9 μ region, an absorption band attributed to a free carbonyl group. This is what one would expect from such triketones, since only the β-diketone portion of each molecule should be involved in the formation of the copper chelate, thus leaving two free carbonyl groups in each of the chelates. A further study of the chemistry of these β-diketone dioxolanes and triketones is in progress as well as a study of the reactions of acetal halides with dicarbanions of β-diketones.

Experimental Section[5]

Halo Ketones and Halo Ketals.—2-(Chloromethyl)-2-methyl-1,3-dioxolane was formed from chloracetone and ethylene glycol by the procedure of Salmi.[6] 2-(Bromomethyl)-2-methyl-1,3-dioxolane was formed from 2,2-dimethyl-1,3-dioxolane[7] and bromine by the procedure of Field.[8]

2-(2-Hydroxyethyl)-2-methyl-1,3-dioxolane was produced by a modification of the Bouveault–Blanc reaction to the reduction of ethyl acetoacetate ethylene acetal[9] and by the method of Willimann and Schninz.[10] 2-(2 Bromoethyl)-2-methyl-1,3-dioxolane was prepared from 2-(2-hydroxyethyl)-2-methyl-1,3-dioxolane (29 g, 0.22 mol) and phosphorus tribromide (20.8 g, 0.075 mol) in 55% yield, bp 76–77° (11 mm) [lit.[10] bp 76° (11 mm)].

Purchased 5-chloro-2-pentanone decomposed after a short period of time even after being freshly distilled. 5-Chloro-2-pentanone was prepared in 65% yield[11] and 5-bromo-2-pentanone was prepared in 25% yield[11] from 2-acetyl-γ-butyrolactone. 2-(3-Chloropropyl)-2-methyl-1,3-dioxolane and 2-(3-bromopropyl)-2-methyl-1,3-dioxolane were prepared from the corresponding halo ketone by the procedure of Salmi.[6]

II (n = 4 or 5; X = Br or Cl; R = CH_3 or CH_3CH_2) was prepared by the same procedure starting with cyclopentanone or cyclohexanone. A typical sequence of reactions is given. A 1-l. three-necked flask was equipped with an inlet tube and a pressure-compensating addition funnel. In this flask 24 g (1.0 mol) of magnesium turnings, 111.2 g (1.02 mol) of ethyl bromide, a small crystal of iodine, and 400 ml of anhydrous ether were cooled to $-40°$ in a Dry Ice–acetone bath. Cyclohexanone (98 g, 0.98 mol) was allowed to drip in slowly over a period of about 24 hr while the temperature was maintained between -40 and $-20°$.[12] When the addition of ketone was complete the reaction mixture

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[4] R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

[5] Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Chemalytics, Inc., Tempe, Ariz. The infrared spectra were recorded on a Beckman infrared spectrophotometer Model IR-8 and Perkin-Elmer grating infrared spectrophotometer Model 237B using potassium bromide pellets for solids and sodium chloride plates for liquids. The ^{1}H nmr spectra were obtained on a Varian Model A-60 spectrometer. The samples were either neat or dissolved in carbon tetrachloride with tetramethylsilane as the standard.

[6] E. J. Salmi, *Ber.*, **71B**, 1803 (1938).

[7] A. F. Isbell and D. W. Hodd, *J. Chem. Eng. Data*, **7**, 575 (1962).

[8] N. D. Field, *J. Amer. Chem. Soc.*, **83**, 3504 (1961).

[9] L. Palfray and P. Angluret, *C. R. Acad. Sci.*, **244**, 404 (1947).

[10] L. Willimann and H. Schninz, *Helv. Chim. Acta*, **32**, 2152 (1949).

[11] G. W. Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 597.

[12] D. G. M. Diaper, *Can. J. Chem.*, **33**, 1720 (1955).

TABLE III

TRIKETONES FROM HYDROLYSIS OF β-DIKETONE DIOXOLANES

Registry no.	Hydrolysis Product	Mp, °C		C, %	H, %
34956-77-9	2,4,8-Nonanetrione ($C_9H_{14}O_3$)	*a*			
34956-78-0	2,4,9-Decanetrione ($C_{10}H_{16}O_3$)	35–36	Calcd	65.19	8.75
			Found	65.13	8.90
34956-79-1	2,4,9-Undecanetrione ($C_{11}H_{18}O_3$)	45–46	Calcd	66.64	9.15
			Found	66.85	9.34
34956-80-4	2,4,10-Undecanetrione ($C_{11}H_{18}O_3$)	42–43.5	Calcd	66.64	9.15
			Found	66.46	9.36
34956-81-5	2,4,10-Dodecanetrione ($C_{12}H_{20}O_3$)	51–52	Calcd	67.89	9.50
			Found	67.62	9.49
34956-82-6	2,4,11-Dodecanetrione ($C_{12}H_{20}O_3$)	48–49	Calcd	67.89	9.50
			Found	67.88	9.74
34956-83-7	2,4,11-Tridecanetrione ($C_{13}H_{22}O_3$)	57–58	Calcd	68.99	9.80
			Found	68.79	9.87

[a] The compound was liquid at room temperature. No boiling point or melting point was recorded for this compound, nor was an analysis received.

TABLE IV

COPPER CHELATES OF TRIKETONES. MELTING POINT, ANALYSES, AND INFRARED DATA

Registry no.	Copper chelate of	Mp, °C		C, %	H, %	Cu, %	Absorption bands (microns)		
34952-73-3	2,4,8-Nonanetrione ($C_{18}H_{26}CuO_6$)	141–142		*a*			5.86	6.34	6.56
34952-74-4	2,4,9-Decanetrione ($C_{20}H_{30}CuO_6$)	143.5–144 dec	Calcd	55.86	7.03	14.78	5.86	6.35	6.56
			Found	55.64	6.96	14.52			
34952-75-5	2,4,9-Undecanetrione ($C_{22}H_{34}CuO_6$)	146.5–148 dec	Calcd	57.69	7.48	13.87	5.85	6.37	6.59
			Found	58.01	7.49	13.70			
34952-76-6	2,4,10-Undecanetrione ($C_{22}H_{34}CuO_6$)	128.5–129 dec	Calcd	57.69	7.48	13.87	5.86	6.40	6.55
			Found	57.77	7.71	13.88			
34952-77-7	2,4,10-Dodecanetrione ($C_{24}H_{38}CuO_6$)	139.5–140.5 dec	Calcd	59.30	7.88	13.07	5.84	6.40	6.56
			Found	58.99	7.98	13.19	5.90		
34952-78-8	2,4,11-Dodecanetrione ($C_{24}H_{38}CuO_6$)	139–140 dec	Calcd	59.30	7.88	13.07	5.86	6.36	6.56
			Found	59.39	7.94	13.15			
34952-79-9	2,4,11-Tridecanetrione ($C_{26}H_{42}CuO_6$)	141.5–142 dec	Calcd	60.74	8.23	12.36	5.86	6.36	6.57
			Found	60.78	8.23	12.20			

[a] No analysis. Copper chelate of diketodioxolane was also prepared. See Experimental Section.

was allowed to warm to room temperature and stirring was continued for an additional 8 hr. The grey slurry of the magnesium salt in ether was slowly poured into a mixture of 300 g of ice and 130 ml of concentrated HCl in an ice bath. The flask was rinsed with water and ether. The aqueous layer was separated from the ether layer and extracted once with 40 ml of ether. The combined ethereal solutions were extracted with 40 ml of water once, 40 ml of saturated sodium bisulfite solution three times, and 40 ml of saturated potassium carbonate solution once. The ether solution was dried over anhydrous Na_2SO_4 and filtered, and the ether was removed under vacuum. The residue was distilled to afford 82.4 g (66%), bp 60–61° (7 mm) [lit.[13] bp 61–63° (7 mm)].

To a 1-l. three-necked flask equipped with a sealed stirrer, addition funnel, and condenser were added 700 ml of water, 30 g (0.75 mol) of sodium hydroxide pellets, and 48 g (0.375 mol) of 1-ethylcyclohexanol. The two layers were stirred vigorously for about 5 min before the mixture was cooled in an ice bath. Bromine (80 g) was added to the cold reaction mixture over a 2-hr period. The ice bath was removed and 75 ml of methylene chloride was added to the flask. The two layers were separated and the aqueous layer was extracted twice with 75 ml of methylene chloride. The methylene chloride solution was extracted with 75 ml of saturated $NaHCO_3$ and 75 ml of water. The methylene chloride solution was dried in the dark over anhydrous $MgSO_4$. The solution was filtered and the methylene chloride was removed under reduced pressure. The remaining liquid was allowed to stand at 50–60° for 2 hr in the sunlight. The solution was distilled at reduced pressure. It was necessary to collect the product in a flask which was submerged in a Dry Ice–acetone bath in order to prevent the halo ketone from turning black before it could be used in the next step. This is a modification of the procedure of Englund.[14] This reaction gave 27.4–32.3 g (35–42%) of 8-bromo-3 octanone, bp 74–80° (0.22 mm).

By a modification of the method of Salmi[6] the halo ketal was formed. The halo ketone was removed from the Dry Ice–acetone bath and was allowed to melt directly into dry benzene. The reaction flask was wrapped in order to keep out light. The reaction afforded a 76–89% yield of 2-(5-bromopentyl)-2-ethyl-1,3-dioxolane, bp 78–82° (0.07 mm). This appears to be a new compound.

Anal. Calcd for $C_{10}H_{19}BrO_2$: C, 47.82; H, 7.62; Br, 31.82. Found: C, 47.74; H, 7.72; Br, 31.60.

2-(4-Bromobutyl)-2-ethyl-1,3-dioxolane, which was made by the same procedure, appears to be a new compound.

Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.58; H, 7.22; Br, 33.70. Found: C, 45.26; H, 7.43; Br, 33.82.

The other compounds prepared by this procedure have been made before. The physical properties we observed are consistent with those published earlier.

Alkylation of I with Halo Ketals.—To a solution of I prepared as described previously[2] was added 1 equiv of ketal halide II (see Table I for quantities) in 20 ml of ether over 5 min. After the reaction mixture was allowed to stir (see Table I for reaction times), anhydrous ether was added and the ammonia was allowed to evaporate by warming the reaction mixture with a warm water bath. The ethereal suspension was cooled in ice and a mixture of 50 g of ice and 10 ml of hydrochloric acid was added and stirred for about 0.5 min. Immediately, the two layers were separated and the aqueous layer was extracted with three 25-ml portions of ether. The water layer was checked prior to extraction to be sure that it was slightly acidic. The combined ethereal solution was dried over anhydrous $MgSO_4$ for several hours and filtered. The ether was removed at reduced pressure. The residue was

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(13) F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933).

(14) B. E. Englund, U. S. Patent 2,675,402 (1954); T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956).

distilled under vacuum. See Table I for boiling points and yields.

Hydrolysis of Diketodioxolanes. Preparation of Triketones.—A solution of 5 ml of ethanol and 3 ml of water was used to dissolve approximately 1 g of the desired diketodioxolane. One drop of concentrated hydrochloric acid was added to this solution. The acidic solution was heated to near reflux temperature for 2 hr. At the end of this time the acidic solution was cooled in an ice bath and scratched occasionally with a stirring rod. The solid triketone precipitated within a few minutes in most cases. A few cases required a greater period of scratching. In a few cases it was necessary to remove some of the solvent at reduced pressure and then repeat the above precedure. The solid, flaky white triketone was filtered and then recrystallized from a small amount of ethanol. The resulting triketones were dried overnight at room temperature at about 0.1–0.2 mm.

Preparation of Copper Chelates.—A small amount of the *β*-diketodioxolane was dissolved in a small amount of methanol. A saturated solution of cupric acetate was then added two drops at a time. The glass container was scratched with a stirring rod after each addition of cupric acetate. Once the solid chelate was observed the cupric acetate was added more rapidly with continuous stirring. The chelate was filtered and recrystallized from methanol. It was then dried overnight under vacuum at about 0.1–0.2 mm. In the event that the dry blue chelate contained green spots on the surface, it was shaken vigorously with water for several minutes, filtered, and then redried in the vacuum. In only two cases was a solid precipitate formed from a *β*-diketodioxolane, and then only after a long period of scratching. The others that were attempted gave oils.

The copper chelate of 9-ethylenedioxy-2,4-undecanedione showed the following results.

Anal. Calcd for $C_{26}H_{42}CuO_8$: C, 57.18; H, 7.75 Cu, 11.63. Found: C, 56.99; H, 7.66 Cu, 11.89.

Elemental analysis of the copper chelate of 8-ethylenedioxy-2,4-nonanedione showed the following results.

Anal. Calcd for $C_{22}H_{34}CuO_8$: C, 53.92; H, 6.99; Cu, 12.97. Found: C, 53.71; H, 6.94; Cu, 12.80.

The above procedure was repeated for the triketones which readily formed the copper chelates. See Table IV.

Registry No.—I, 34956-84-8; II (R = Et, X = Br, $n = 5$), 34956-85-9; II (R = Et, X = Br, $n = 4$), 34956-86-0; 8-bromo-3-octanone, 2146-62-5; 9-ethylenedioxy-2,4-undecanedione copper chelate, 34952-80-2; 8-ethylenedioxy-2,4-nonanedione copper chelate, 34952-81-3.

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Nitration Studies. XVIII. Conversion of Lower Nitroalkanes to Higher Members of the Series

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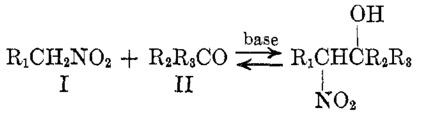
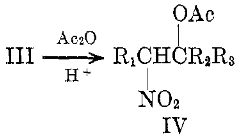
The lower primary nitroalkanes may be converted to higher nitroalkanes by a one pot synthesis involving successive reactions with aldehydes, acylating agents, and sodium borohydride. Overall conversions are in the 75–80% range. Lower aldehydes also give dialkylated products, *e.g.*, 3-nitropentane from nitromethane and acetaldehyde. With ketones isolation of the intermediate nitro alcohol is desirable. The mechanism of the reduction step in particular is discussed.

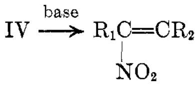
An attractive route for the preparation of higher primary and secondary nitroalkanes involves the condensation of an aldehyde or a ketone with a lower primary nitroalkane followed by acylation, elimination, and reduction of the product (eq 1–4). This process



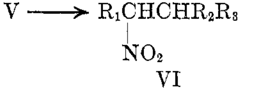
$$\underset{\text{I}}{R_1CH_2NO_2} + \underset{\text{II}}{R_2R_3CO} \overset{\text{base}}{\rightleftarrows} \underset{\text{III}}{R_1\underset{NO_2}{C}H\overset{OH}{C}R_2R_3} \quad (1)$$



$$\text{III} \xrightarrow[H^+]{Ac_2O} \underset{\text{IV}}{R_1\underset{NO_2}{C}H\overset{OAc}{C}R_2R_3} \quad (2)$$

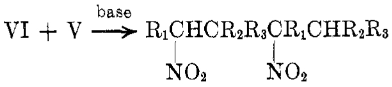


$$\text{IV} \xrightarrow{\text{base}} \underset{\text{V}}{R_1\underset{NO_2}{C}{=}CR_2R_3} \quad (3)$$



$$\text{V} \xrightarrow{NaBH_4} \underset{\text{VI}}{R_1\underset{NO_2}{C}HCHR_2R_3} \quad (4)$$

has not proved to be very useful, since published procedures[3] involve isolation of intermediates (III, IV, V), are time consuming (4–5 days) and lead to poor overall yields (14–33%). The low yields result in part from isolation steps and in part from the occurrence of side reactions (eq 5) in the reduction of V leading to 1,3-dinitroalkanes (VII).



$$\text{VI} + \text{V} \xrightarrow{\text{base}} \underset{\text{VII}}{R_1\underset{NO_2}{C}HCR_2R_3\underset{NO_2}{C}R_1CHR_2R_3} \quad (5)$$

We wish to report an improved procedure for the processes shown in eq 1–4 which involves no isolation of intermediates. The synthesis is generally performed in one reaction vessel over a 24-hr period and provides VI in high yields (*cf.* Table I) based on I or II. In some cases (ketones) much better results are obtained if the intermediate nitro alcohol is isolated.

Various methods[4a] for the preparation of the higher

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