X-ray diffraction pattern. Significantly, the alpha or lowest melting polymorph of tristearin, and similar triglycerides, is characterized by a single strong line corresponding to about 4.15 Å. There is no such correlation between the beta or highest melting form of tristearin and the highest melting form of the distearin compounds. The β-form of tristearin is characterized by a strong line corresponding to approximately 4.6 Å. The short spacings for the highest melting form of the distearin compounds correspond more nearly to those of the β'-form of tristearin, which is characterized by two strong lines corresponding to approximately 4.2 and 3.8 Å.

The long spacings for the α- and β-forms of tristearin are approximately 50.6 and 45.2 Å., respectively. These spacings are recognized as being associated with a double-chain-length structure; that is, the repeating units in the crystals have a length equal to about that of two stearic acid chains. The long spacings listed in Table II for the distearin fumarate, succinate and adipate range from 49.8 to 58.3 Å. It can be concluded that in the polymorphic forms represented in Table II the distearin compounds are crystallized in a double-chain-length structure.

When crystallized from solvents like *n*-hexane, the distearin compounds tend to form long, needle-like crystals. This tendency to form needle-like crystals appears to be enhanced by the presence of impurities. In the course of the experimental work some masses of crystals were obtained which resembled asbestos in appearance.

Insofar as infrared absorption spectra are concerned, each of the diolein and distearin esters of fumaric, succinic and adipic acids behaved like tristearin and other ordinary triglycerides containing no *trans* isomers. All of the characteristic absorption bands found for tristearin occur in the spectra of the dibasic acid-containing compounds; and the latter possess no unique bands.

One of the characteristics which differentiates the diglyceride esters of the dibasic acids from practically all of the ordinary triglycerides is their relatively high viscosity, a characteristic which should prove to be of practical value in several areas of utilization. In Table III are recorded the kinematic viscosities of the diglyceride esters of the dibasic acids at two temperatures, together with the viscosities of diolein and several common oils. At 38.8 and 98.8° the diolein esters of the dibasic acids are approximately twice as viscous as are cottonseed oil and coconut oil, though not as viscous as is castor oil. In conformance with the nature of the usual viscosity–temperature relationship for oils, the viscosity of the diolein esters increases quite rapidly as the temperature is decreased below 38.8°. At 28.2° the diolein adipate possesses a viscosity of 148.8 centistokes and the diolein succinate a viscosity of 128.0 centistokes.

TABLE III

VISCOSITY OF SOME NATURAL OILS, 1,3-DIOLEIN AND THE FUMARATES, SUCCINATES AND ADIPATES OF 1,3-DIOLEIN AND 1,3-DISTEARIN

Compound	Kinematic viscosity, centistokes, at 38.8°	98.8°
Diolein fumarate	86.50	13.60
Diolein succinate	77.00	13.00
Diolein adipate	116.70	21.27
Distearin fumarate	Solid	20.64
Distearin succinate	Solid	17.87
Distearin adipate	Solid	18.93
1,3-Diolein	48.50	8.50
Coconut oil	29.79	6.06
Cottonseed oil	38.88	8.39
Castor oil	293.4	20.08

Acknowledgment.—The authors wish to express their appreciation to Mildred Murray, Elsie F. DuPré and R. T. O'Connor for the X-ray and infrared data and to Alva F. Cucullu for some of the chemical analyses reported.

NEW ORLEANS 19, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Studies on the Synthesis of a Spiroepoxy Ketal[1]

BY K. R. HUFFMAN[2] AND D. S. TARBELL

RECEIVED JULY 1, 1958

Treatment of 2-benzhydrylidenetetrahydrofuran with perbenzoic or perphthalic acid does not yield the expected spiroepoxy ketal. Action of *t*-butyl hypochlorite or N-bromosuccininimide on the benzhydrylidenetetrahydrofuran does not give the corresponding halohydrin, but leads to 2,2-diphenyl-3-ketotetrahydropyran by a rearrangement involving ring enlargement. Treatment of ethyl α-propionylpropionate with ethylene chlorohydrin and sodium hydride yielded, by ester interchange and alkylation on the carbonyl oxygen, a cyclic ketene acetal XVI whose structure was proved by degradation. α-Chloroacetyl-α-methyl-γ-butyrolactone has been synthesized; hydrolysis with mineral acid yields 2,3-dihydroxy-2,3-dimethyltetrahydrofuran by a rearrangement reaction. The structure of this compound was proved by periodate oxidation.

During studies on the structure of fumagillin,[3] we have considered at various times the possibility that two of the non-carbonyl oxygens in alcohol-I, derived from fumagillin, were combined in a spiroketal system. One such structure is the 1,4-dioxaspiro[2.4]heptane system (I), for whose presence in fumagillin some interesting arguments could be adduced. We have not found examples of structures analogous to I in the literature[4]; the present

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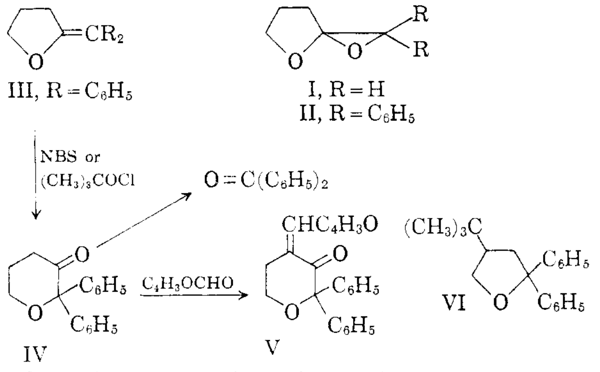
[1] Aided by a grant from the National Institutes of Health.

[2] Abbott Laboratories Fellow, 1957–1958.

[3] J. M. Ross, D. S. Tarbell, W. E. Lovett and A. D. Cross, THIS JOURNAL, **78**, 4675 (1956), for example.

[4] A derivative containing a spiroepoxy ketal group is postulated as an intermediate in the formation of anhydro sugars by E. Zissis, L. C. Stewart and N. K. Richtmyer, *ibid.*, **79**, 2593 (1957).

paper describes a number of synthetic approaches to this structure, which, while so far unsuccessful, have led to a number of interesting rearrangements and alkylation reactions in the general field of oxygen heterocycles.


III, R = C_6H_5

I, R = H

II, R = C_6H_5

IV

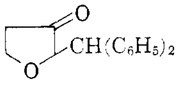
V

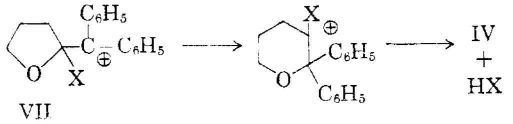
VI

For the preparation of the ring system I, the epoxidation of 2-benzhydrylidenetetrahydrofuran[5] (III) by peracids was first examined. Reaction of III with perbenzoic acid under a variety of conditions yielded a viscous oil, which could not be distilled, and which showed bands in the infrared at 3400 (hydroxyl), 1767 (γ-lactone) and 1704 cm.$^{-1}$ (carbonyl), among others.[5a] Treatment of the crude product with dinitrophenylhydrazine reagent gave a good yield of benzophenone 2,4-dinitrophenylhydrazone. The use of perphthalic acid, which is known in some cases to give better epoxide formation than perbenzoic acid,[6] gave results similar to those above.[7] Hydrogen peroxide in methanolic sodium hydroxide yielded 93% of starting material after 13 hours at room temperature.

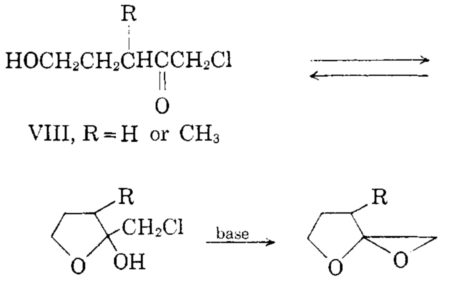
From these results, and from Stevens' studies on epoxy ethers showing that in some cases they react readily with benzoic acid at room temperature,[8] it seemed advisable to attempt to add the elements of hypohalous acid to the double bond in III and then to close the epoxide ring under basic conditions. However, the action of *t*-butyl hypochlorite in aqueous dioxane containing acetic acid, or of N-bromosuccinimide in aqueous dioxane containing perchloric acid, on III yielded as sole product a crystalline ketone, $C_{17}H_{16}O_2$.

That this ketone had the structure IV was shown by the following facts. It showed a band at 1715 cm.$^{-1}$ in the infrared[8a] indicating a non-conjugated carbonyl group, and it formed crystalline carbonyl derivatives. It was oxidized by chromic acid to benzophenone; it yielded a crystalline monofurfurylidene derivative V, with furfural and base, indicating *one* free methylene group adjacent to the carbonyl group; and its ultraviolet spectrum was very similar to that of 2,2-diphenyl-4-*t*-butyltetrahydrofuran[9] (VI). The formation of IV from III presumably involves addition of a positive halogen to III forming VII, followed by migration of the ring oxygen as


IVa


VII

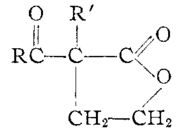
In addition to the epoxyethers which have been prepared by epoxidation of vinyl ethers,[7] Stevens and his collaborators[8,10] have prepared numerous examples by the action of an alkoxide on an α-halogen ketone. The preparation of structure I by this method would require a chloromethyl γ-hydroxypropyl ketone VIII, which might be expected to react with base in the tautomeric hemiketal form IX to form the spiroepoxy ketal I.


$$HOCH_2CH_2\overset{\displaystyle R}{\overset{|}{C}}H\underset{\displaystyle O}{\underset{\|}{C}}CH_2Cl$$

VIII, R = H or CH_3

IX. R = H or CH_3

An isomer of VIII, methyl α-chloro-γ-hydroxypropyl ketone, is an intermediate in the synthesis of the thiazole portion of thiamine, and is prepared by chlorination of α-acetobutyrolactone and then hydrolysis.[11] The preparation of VIII by this procedure would require an α-alkyl-α-acylbutyrolactone such as X, which presumably could be chlorinated to yield the chloroacetyl compound XI; hydrolysis and decarboxylation of this should give VIII, or a suitable homolog.


XIa, R = $C_6H_5SO_2CH_2$, R′ = CH_3
XII, R = CH_3, R′ = H
XIII, R = C_2H_5, R′ = H
XIV, R = C_2H_5, R′ = CH_3

X, R = R′ = CH_3
XI, R = $ClCH_2$, R′ = CH_3

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[5] A. L. Dounce, R. H. Wardlow and R. Connor, This Journal, **57**, 2556 (1935).

[5a] The carbonyl band of benzophenone (1656 cm.$^{-1}$) was also present.

[6] C. K. Bradsher and L. Rapoport, This Journal, **65**, 1646 (1943).

[7] Peracids have been used in numerous cases to prepare epoxides from vinyl ether types; for example, (a) M. Bergmann and A. Miekeley, *Ann.*, **432**, 319 (1923); (b) D. Badran, *Bull. soc. chim.*, **49**, 1551 (1931); (c) R. A. Raphael and C. M. Roxburgh, *J. Chem. Soc.*, 3405 (1955); C. L. Stevens and J. Tazuma, This Journal, **76**, 715 (1954). The epoxidation of steroid enol acetates by peracids is an important synthetic method; T. H. Kritchevsky and T. F. Gallagher, *J. Biol. Chem.*, **179**, 507 (1949); This Journal, **73**, 184 (1951); A. H. Soloway, W. J. Considine, D. K. Fukushima and T. F. Gallagher, *ibid.*, **76**, 2941 (1954).

[8] C. L. Stevens, W. Malik and R. Pratt, *ibid.*, **72**, 4758 (1950); C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

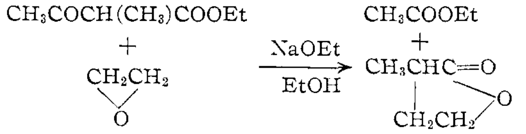
[8a] An alternative structure, IVa, suggested as a possibility by the referee, seems unlikely on the basis of the infrared spectrum. A tetrahydrofuranone such as IVa would be expected to have a carbonyl frequency near 1750 cm.$^{-1}$ (C. Sandris and G. Ourisson, *Bull. soc. chim.*, [5], **23**, 958 (1956).

[9] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, fig. 118.

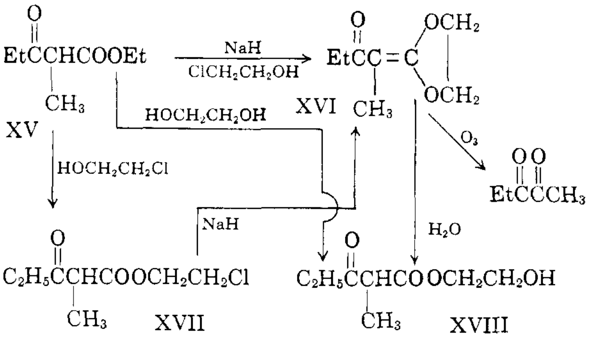
[10] C. L. Stevens, M. L. Weiner and R. C. Freeman, This Journal, **75**, 3977 (1953); C. L. Stevens and S. J. Dykstra, *ibid.*, **75**, 5975 (1953); C. L. Stevens and J. J. DeYoung, *ibid.*, **76**, 718 (1954).

[11] E. R. Buchman, *ibid.*, **58**, 1803 (1936); J. R. Stevens and G. A. Stein, *ibid.*, **62**, 1045 (1940).

The attempted preparation of the α-propionyl-α-methylbutyrolactone (XIV) by the action of ethylene oxide in the presence of sodium hydride or sodium ethoxide on the β-keto ester XV yielded only starting material.[12] Treatment of XV with ethylene chlorohydrin and sodium hydride yielded, instead of the expected lactone XIV, two products; one was a crystalline solid, m.p. 121–122.5°, whose analysis corresponded to the composition $C_8H_{12}O_3$. It showed bands in the infrared at 1650 and 1600 cm.$^{-1}$, and had a single maximum in the ultraviolet at 266 (4.21).[13] It gave positive tests for unsaturation, and was converted by acid hydrolysis to diethyl ketone, isolated as the dinitrophenylhydrazone. Ozonization yielded 2,3-pentanedione, characterized as the bis-dinitrophenylhydrazone. Contact with atmospheric moisture converted the solid into a liquid which was identical with the second product obtained along with the crystalline material in the original alkylation. When water was excluded in the work-up of the reaction mixture, none of the liquid product was obtained.



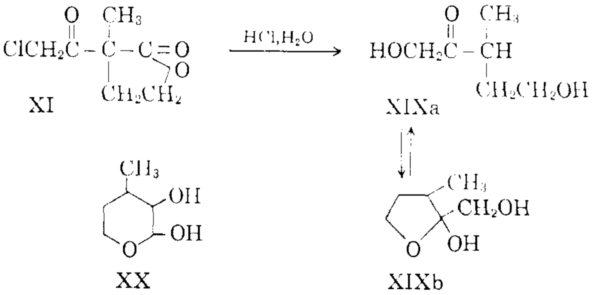
The chemical properties of the crystalline material indicated that it possessed the cyclic ketene acetal structure XVI, apparently formed through ester interchange followed by intramolecular O-alkylation. The spectral properties agreed with those of similar compounds obtained by Parker[14] by the action of sodium hydride on β-bromoethyl esters of various β-keto or β-cyano acids. In later experiments, XVI was obtained in good yield by preparation of the β-chloroethyl ester XVII, through interchange of ethylene chlorohydrin with the ethyl ester XV, followed by sodium hydride treatment in a separate stage.



The liquid product formed by the addition of water to XVI was shown to be β-hydroxyethyl α-propionylpropionate (XVIII), by synthesis of the latter through an ester interchange of XV with ethylene glycol. The product formed in this manner showed the same physical properties as the liquid obtained in the original alkylation. Cyclic ketene acetals such as XVI are known to have a great affinity for water.[15]

The preparation of α-propionylbutyrolactone (XIII) by condensation of ethyl propionate and butyrolactone was carried out, but in poor yield, although methylation of this acyllactone to give XIV was satisfactory. In view of the poor yield in the first step, compound XIV was not chlorinated; instead, the more accessible α-acetylbutyrolactone[16] was methylated with sodium hydride in dimethylformamide and benzene with methyl iodide[17] to give α-acetyl-α-methylbutyrolactone (X). This was chlorinated readily with sulfuryl chloride to give a crystalline chloro compound which must have structure XI; the chloro compound XI was further characterized by conversion to the crystalline phenyl sulfone XIa by treatment with sodium benzenesulfinate.

Hydrolysis of the chloroacetyl lactone XI with acid proceeded with decarboxylation, but it did not yield the expected chloromethyl ketone VIII (R = CH_3). Instead, a crystalline product, m.p. 63.5–65°, $C_6H_{12}O_3$, was produced, which showed no carbonyl band in the infrared, and which consumed exactly one mole of periodate upon titration. The most probable structure for this product would be XIXb, the hemiketal form of the hydroxyketone derived from XI by hydrolysis, decarboxylation and replacement of the chlorine by hydroxyl. Another possible structure would be XX



which would be obtained from XIXa by isomerization to the hydroxyaldehyde $HOCH_2CH_2CH(CH_3)$-$CHOHCHO$, followed by cyclization.[18]

The incorrectness of both structures XIXb and XX for the crystalline product was shown by periodate oxidation experiments. Structure XIXb should yield formaldehyde and α-methyl-γ-butyrolactone, and XX should yield 4-hydroxy-2-methylbutyraldehyde.[19] None of these products was formed; instead the periodate results show that the correct structure for the compound is 2,3-dihydroxy-2,3-dimethyltetrahydrofuran (XXIa) because periodate oxidation yielded acetic acid, 4-hydroxy-2-butanone and 4-acetoxy-2-butanone. These products would be expected by cleavage of XXIa and of its open-chain tautomer XXIb,

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[12] F. N. Stepanov, *Zhur. Obshchei Khim.*, **25**, 2480 (1955) (*C. A.*, **50**, 9291 (1956)) has recently found that cleavage of the acyl group attends efforts to form acyllactones of the type of XIV, by alkylation of the substituted β-ketoesters with ethylene oxide, as

[13] Ultraviolet spectra are reported with the λ_{max} in mμ, and log *E* in parentheses.

[14] C. O. Parker, This Journal, **78**, 4944 (1956).

[15] S. M. McElvain and M. J. Curry, *ibid.*, **70**, 3781 (1948).

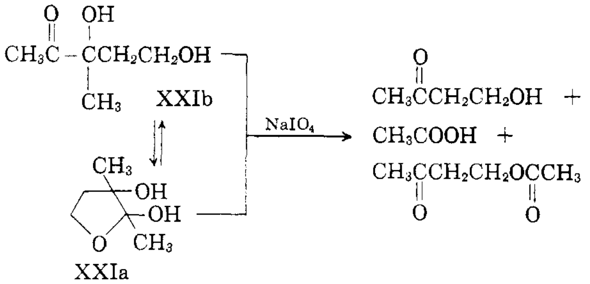
[16] We are indebted to Mr. R. D. Babson, Stonewall Process Development, Merck and Co., Elkton, Va., for supplying this material.

[17] General method of F. J. Marshall and W. N. Cannon, *J. Org. Chem.*, **21**, 245 (1956).

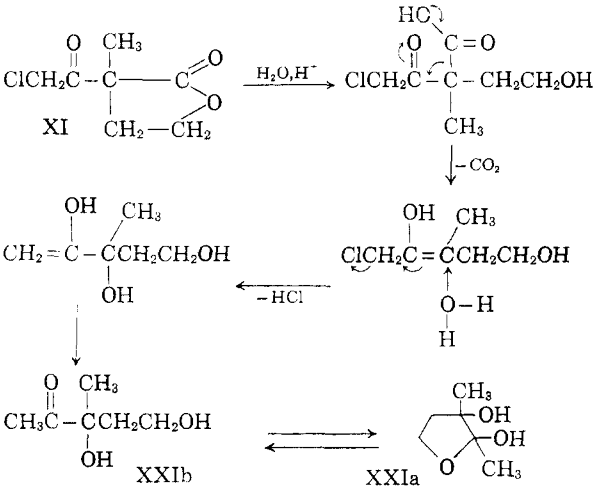
[18] K. Heyns and W. Stumme, *Ber.*, **89**, 2833 (1956), report the isomerization by mild acid of $HO(CH_2)_3COCH_2OH$ to $HO(CH_2)_3$ $CHOHCHO$, which exists in the hemiacetal form.

[19] C. M. Hill, G. W. Senter, L. Haynes and M. E. Hill, This Journal, **76**, 4538 (1954).

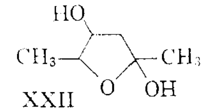
which apparently exists to some extent in aqueous solution. The 4-hydroxy-2-butanone and its acetate could not be separated by distillation, but their presence in the mixture was established by elementary analysis, infrared properties and preparation of solid derivatives.



Stevens and Lenk[20] have observed a similar case of hydrolysis of an α-halogen ketone accompanied by rearrangement, and have suggested an allylic shift as the mechanism. A similar mechanism for the rearrangement observed in the present work would be

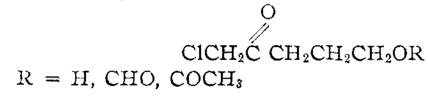


It may be pointed out that compound XXIa is isomeric with a desoxyfuranohexose XXII which occurs as a structural unit in the antibiotic amicetin.[21]



XXII

The preparation of the chloromethyl ketone VIII was attempted by free radical addition[22] of chloroacetaldehyde to allyl alcohol or its esters



$$ClCH_2CHO + CH_2{=}CHCH_2OR \longrightarrow ClCH_2\overset{O}{C}CH_2CH_2CH_2OR$$

$$R = H, CHO, COCH_3$$

None of the desired product appeared to be formed under the conditions tried, with benzoyl peroxide as catalyst.

Experimental[23]

2-Benzhydrylidenetetrahydrofuran (III), m.p. 108–109°, was prepared in 79% yield by a slight modification of the published procedure.[5] Its ultraviolet spectrum showed a broad maximum in the region 268–274 (4.24).

Reaction with Perbenzoic Acid.—In a typical experiment, 1.0 g. of III in 100 ml. of dry chloroform was treated with 11.5 ml. of 0.36 *M* perbenzoic acid[24] solution in chloroform and the resulting mixture was allowed to stand at room temperature for 30 min. Titration at this point showed the absence of active oxygen. The solution was washed with bicarbonate three times, then with water, was dried and the solvent was removed *in vacuo*. The viscous yellow oil which resulted did not crystallize; it showed the infrared properties described earlier, decomposed on attempted vacuum distillation and even upon heating on the steam-bath. Treatment of the crude product with dinitrophenylhydrazine reagent gave a derivative, m.p. 236–238° after recrystallization from ethanol–ethyl acetate, which was shown to be identical with benzophenone 2,4-dinitrophenylhydrazone, by a mixed m.p. with an authentic sample.

Conversion of 2-Benzhydrylidenetetrahydrofuran (III) to 2,2-Diphenyl-3-ketotetrahydropyran (IV). A. By *t*-Butyl Hypochlorite.—*t*-Butyl hypochlorite[25] was prepared in 69% yield. To a solution composed of 5.0 g. of III, 200 ml. of dioxane, 40 ml. of glacial acetic acid and 100 ml. of water was added 2.50 g. (1.1 mole equiv.) of *t*-butyl hypochlorite dropwise with stirring. The solution was allowed to stand at room temperature for 12 hr., was extracted twice with chloroform, the chloroform extract was washed four times with 5% bicarbonate solution, twice with water and was dried. Removal of solvent *in vacuo* gave a pale yellow oil, which was taken up in alcohol; after ten days in the refrigerator, 0.80 g. of pale yellow crystals had been deposited, m.p. 86–89°. One crystallization from alcohol gave 0.75 g. (14%) of white needles, m.p. 88–90°. Two more recrystallizations on the analytical sample raised the m.p. to 91–92.5°, unchanged by further recrystallization. The ultraviolet spectrum showed the maxima: 225 (4.15), 252 (2.85), 259 (2.88).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.71; H, 6.43.

The 2,4-dinitrophenylhydrazone, after two recrystallizations from ethanol, melted at 173.5–175.5°.

Anal. Calcd. for $C_{23}H_{20}N_4O_5$: C, 63.88; H, 4.66. Found: C, 64.06; H, 4.96.

The oxime, after three crystallizations from alcohol, melted at 201–203° with darkening.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41. Found: C, 76.65; H, 6.60.

The monofurfurylidene derivative (V) was prepared according to Alexander.[26]

After one crystallization from alcohol, the yellow needles had a m.p. of 107.5–108.5°, unchanged by further recrystallization.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.67; H, 5.60.

B. By N-Bromosuccinimide.[27]—To a solution of 1.0 g. of III in 45 ml. of dioxane was added a solution composed of 0.80 g. of N-bromosuccinimide, 15 ml. of water, 1.0 ml. of 60% perchloric acid and 10 ml. of dioxane. The resulting solution was allowed to stand at room temperature for 3 hr.; most of the solvent was removed under reduced pressure, and the remaining liquid was then diluted with 200 ml. of water and cooled. The white solid was collected by filtration and was washed several times with water. Three recrystallizations from ethanol gave 0.20 g. (19%) of white needles, m.p. 90–92°. A mixed m.p. with a sample of the ketone obtained in the experiments with *t*-butyl hypochlorite was undepressed. It was necessary to recrystallize

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[20] C. L. Stevens and C. T. Lenk, *J. Org. Chem.*, **19**, 538 (1954); *cf.* A. I. Oumnoff, *Bull. soc. chim.*, **43**, 568 (1928).

[21] C. L. Stevens, R. J. Gasser, T. K. Mukherjee and T. H. Haskell, THIS JOURNAL, **78**, 6212 (1956).

[22] E. C. Ladd, U. S. Patent 2,560,770 (*C. A.*, **46**, 9584 (1952)); R. L. Huang, *J. Chem. Soc.*, 2528 (1957); T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1009, 1269 (1952).

[23] All m.p.'s are corrected. Microanalyses are by Miss Annette Smith. Ultraviolet spectra were taken in 95% alcohol.

[24] Prepared according to the procedure of G. Braun, in "Organic Syntheses," Coll. Vol. I, 2nd Ed., p. 431, and D. Swern in "Organic Reactions," Vol. 7, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 393.

[25] H. M. Teeter, *et al.*, *Ind. Eng. Chem.*, **41**, 849 (1949).

[26] K. Alexander, *et al.*, THIS JOURNAL, **72**, 5506 (1950).

[27] *Cf.* H. L. Slates and N. L. Wendler, *ibid.*, **78**, 3749 (1956).

the product to rather high purity, else it turned deep purple on standing.

Oxidation of IV to Benzophenone.—A solution of 10 ml. of acetic acid and 8 ml. 2 *N* sulfuric acid, containing 100 mg. of IV, was heated on the steam-bath for 6 hr. while powdered sodium dichromate was added in small portions until the red color was permanent. The solution was then cooled, diluted with 100 ml. of water, and the aqueous solution was extracted three times with ether. The ether extracts were combined, washed three tines with 5% sodium bicarbonate, and dried over sodium sulfate. Removal of the ether at the steam-bath gave a colorless, semi-solid material which was treated directly with a solution of 2,4-dinitrophenylhydrazine. One recrystallization of the derivative from ethanol–ethyl acetate gave orange crystals, m.p. 235.5–237.5°. A mixed m.p. with an authentic sample of the 2,4-dinitrophenylhydrazone of benzophenone (m.p. 236–238°) gave no depression.

Ethyl α-propionylpropionate (XV) was prepared in 54% yield by the condensation of ethyl propionate with diisopropylaminomagnesium bromide as catalyst.[28] In one run, diisobutylaminomagnesium bromide was used as catalyst, following the same procedure. From 96.5 g. of diisobutylamine there was obtained 21.2 g. of the **N,N-diisobutylamide of XV**, $C_2H_5COCH(CH_3)CON(C_4H_9)_2$, b.p. 154–157° (28 mm.), which crystallized on standing to give large transparent prisms, m.p. 36–40°. The material could not be recrystallized, and was purified by distillation.

Anal. Calcd. for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.28. Found: C, 69.91; H, 11.59.

The infrared spectrum showed bands at 1721 (ketone carbonyl) and 1626 (cm.$^{-1}$) (amide). All attempts at forming ketone derivatives were unsuccessful.

Formation of the Ketene Acetal XVI from Ethyl α-Propionylpropionate (XV) and Ethylene Chlorohydrin.—To a stirred suspension of 2.28 g. of sodium hydride in 300 ml. of dry ether was added dropwise a solution of 15.0 g. of ethyl propionylpropionate in 25 ml. of ether. Stirring was continued for 0.5 hr. at which point the mixture had almost completely solidified. Ethylene chlorohydrin (12.7 g.) was then added dropwise, and the mixture was refluxed with stirring for 7 hr. with continual distillation of the ether and addition of dry benzene, in order to reach a higher temperature. The benzene solution then was decanted from the precipitated sodium chloride, washed twice with water, and was dried. The solvent was removed at the steam-bath, leaving a colorless liquid which deposited soft white needles on standing overnight. A second crop was collected by cooling at 5° for several hours. The total yield of crude ketene acetal XVI was 2.50 g. (17%), m.p. 97–113°. Three recrystallizations from hexane on an analytical sample raised the m.p. to 121–122.5°. The spectral properties of this compound have been mentioned above.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.33; H, 7.89.

Distillation of the filtrate gave 4.0 g. (27%) of starting material, b.p. 40–42° (0.5 mm.), and 5.5 g. (33%) of **β-hydroxyethyl α-propionylpropionate (XVIII)**, b.p. 106–108° (0.5 mm.), n^{28}_{D} 1.4400. When the reaction was repeated, eliminating the water wash, none of this product was obtained. The compound gave a deep blue color with ferric chloride, and showed hydroxyl, ester and ketone bands at 3413, 1742 and 1712 cm.$^{-1}$, respectively. The infrared spectrum and other properties agreed with those of the product obtained by an ester interchange reaction as follows.

A solution of 10.0 g. of ethyl α-propionylpropionate and 5.9 g. of ethylene glycol was heated at 160° for 30 hr. during which time over 70% of the theoretical amount of ethanol was collected by continuous distillation. The resulting solution was distilled directly giving 4.2 g. (38%) of the hydroxyethyl ester, b.p. 103–109° (0.4 mm.). A redistilled sample had b.p. 96–98° (0.1 mm.), $n^{20.5}_{\mathrm{D}}$ 1.4463.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.89; H, 8.29.

β-Chloroethyl α-Propionylpropionate (XVII).—A solution of 12.4 g. of ethyl α-propionylpropionate and 6.7 g. of ethylene chlorohydrin was heated in an oil-bath at 165° for 18 hr., with continuous removal by distillation of the ethanol formed. Distillation gave 3.2 g. (26%) of starting material, b.p. 36–40° (0.2 mm.), and 8.7 g. (58%) of the β-chloroethyl ester XVII, b.p. 69–71° (0.2 mm.), n^{20}_{D} 1.4478.

Anal. Calcd. for $C_8H_{13}ClO_3$: C, 49.89; H, 6.80. Found: C, 49.94; H, 6.89.

The Ketene Acetal XVI from β-Chloroethyl α-Propionylpropionate.—To a stirred suspension of 0.67 g. of sodium hydride in 50 ml. of dry ether, was added slowly, dropwise, 5.40 g. of β-chloroethyl α-propionylpropionate. After addition was complete, 50 ml. of dry benzene was added and the mixture refluxed with stirring for 4.5 hr. After an additional 100 ml. of benzene was added, the sodium chloride was removed by filtration and the solvent was removed at reduced pressure, leaving a white crystalline mass. One recrystallization from hexane gave 2.90 g. (67%) of the ketene acetal XVI, m.p. 118–123°. The product prepared in this way gave no depression on mixed m.p. with the material obtained above.

Properties of the Ketene Acetal XVI. A. Hydrolysis to Diethyl Ketone.—A solution of 200 mg. of the ketene acetal XVI in 20 ml. of 1% sulfuric acid was warmed on the steam-bath for 1 hr. After neutralization with potassium carbonate, the solution was extracted three times with ether. The ethereal solution was dried and the solvent removed to give a colorless liquid, which was treated directly with a solution of 2,4-dinitrophenylhydrazine. The derivative which precipitated melted at 133–141°. Two recrystallizations from ethanol–ethyl acetate gave orange needles, m.p. 152–154°. A mixed m.p. with an authentic sample of the 2,4-dinitrophenylhydrazone of diethyl ketone, m.p. 152.5–154°, was undepressed.

B. Ozonization to 2,3-Pentanedione.—Ozone was bubbled through a solution of 500 mg. of XVI in 50 ml. of ethyl acetate at −25° for 25 min. until a blue color was observed. The excess ozone was removed by passing nitrogen through the solution, then 50 ml. of water was added and the mixture was allowed to stand overnight. After heating on the steam-bath for 15 min., the organic layer was separated, the water layer was extracted once with ethyl acetate and the combined ethyl acetate solutions were dried. The solvent was removed at the steam-bath and the yellow oily residue treated with a solution of 2,4-dinitrophenylhydrazine. The derivative which formed slowly had m.p. 267–268° with dec. Two recrystallizations from aqueous dioxane gave small orange-red needles of the same m.p. Reported values for the bis-2,4-dinitrophenylhydrazone of 2,3-pentanedione are[29] 274–276° and 280–281° with dec.

C. Hydrolysis to β-Hydroxyethyl α-Propionylpropionate (XVIII).—Upon exposure to atmospheric moisture for a period of 10 days, XVI was transformed into a colorless liquid, n^{20}_{D} 1.4472. The infrared spectrum was identical with that of the hydroxyethyl ester XVIII.

α-Propionyl-γ-butyrolactone (XIII).—The general procedure of Ebel and Weissbarth[30] to prepare α-aceto-γ-butyrolactone was followed. From 87.5 g. of γ-butyrolactone, 115 g. ethyl propionate and 12.1 g. of sodium was obtained 6.8 g. (9%) of α-propio-γ-butyrolactone as a colorless liquid, b.p. 125–129° (8 mm.). A redistilled sample had b.p. 74–75° (0.06 mm.), n^{25}_{D} 1.4550.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.18; H, 7.24.

The infrared spectrum showed carbonyl bands at 1754 and 1715 cm.$^{-1}$ This material gave a deep purple color with ferric chloride.

α-Methyl-α-propionyl-γ-butyrolactone (XIV).—The alkylation of α-propionyl-γ-butyrolactone was accomplished in 73% yield using sodium hydride and methyl iodide in benzene–dimethylformamide according to the general method of Marshall and Cannon.[17] The pale yellow product, b.p. 53–55° (0.08 mm.), n^{20}_{D} 1.4530, turned colorless on standing for 24 hr.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.03; H, 7.80.

α-Acetyl-α-methyl-γ-butyrolactone (X).—The alkylation of α-aceto-γ-butyrolactone was carried out in a similar manner. Thus, a 1-mole run yielded 96 g. (67.5%) of colorless product, b.p. 104–105° (8 mm.), n^{20}_{D} 1.4553; the

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[28] F. C. Frostick, Jr., and C. R. Hauser, THIS JOURNAL, **71**, 1350 (1949).

[29] P. F. Wiley, *et al.*, *ibid.*, **79**, 6062 (1957); I. M. Heilbron, *et al.*, *J. Chem. Soc.*, 54 (1946).

[30] F. Ebel and O. Weissbarth, German Patent 801,276 (*C. A.*, **45**, 2972 (1951)).

semicarbazone, after three crystallizations from water, melted[31] at 184–185.5°.

α-Chloroacetyl-α-methyl-γ-butyrolactone (XI).—To a solution of 10.0 g. of α-acetyl-α-methyl-γ-butyrolactone (X) in 20 ml. of dry benzene was added 9.6 g. of sulfuryl chloride, and the resulting solution was allowed to stand at room temperature until gas evolution had ceased. After gently warming on the steam-bath for 15 min., the solvent was removed at reduced pressure, leaving a pale yellow oil which crystallized on standing overnight in the refrigerator. The yield of crude product was 12.4 g. (100%), m.p. 34–38°. One recrystallization from chloroform–petroleum ether at −50° gave 9.9 g. (80%) of white crystals, m.p. 37–42°. Three further recrystallizations from chloroform–petroleum ether raised the m.p. of an analytical sample to 45.5–47°.

Anal. Calcd. for $C_7H_9ClO_3$: C, 47.60; H, 5.14. Found: C, 47.82; H, 5.26.

Conversion to the **phenyl sulfone XIa** was effected by refluxing for 1 hr. a solution of 0.9 g. of the chloro compound and 1.0 g. of sodium benzenesulfinate in 10 ml. of 50% ethanol. Two recrystallizations from ethanol gave white prisms, m.p. 90.5–91.5°.

Anal. Calcd. for $C_{13}H_{14}O_5S$: C, 55.32; H, 5.00. Found: C, 55.16; H, 5.17.

Acid Hydrolysis of α-Chloroacetyl-α-methyl-γ-butyrolactone (XI) to 2,3-Dihydroxy-2,3-dimethyltetrahydrofuran (XXIa).—A mixture of 31.0 g. of the crude chlorolactone XI and 100 ml. of 1% hydrochloric acid was heated on the steam-bath for 2.5 hr. until carbon dioxide was no longer evolved. The resulting dark brown solution was neutralized with solid sodium bicarbonate and then extracted three times with ether to remove all of the deeply colored material, which was discarded. The remaining clear aqueous solution was continuously extracted with ether for 96 hr., the ether extract was dried over sodium sulfate and the ether was removed at the steam-bath, leaving a colorless oil which crystallized on cooling in the refrigerator for several hours. One recrystallization from ether gave 9.3 g. (40%) of white crystals of compound XXIa, m.p. 62.5–67.5°. Two further recrystallizations from ether gave an analytical sample, m.p. 63.5–65°. The infrared spectrum in a potassium bromide pellet showed a double hydroxyl band at 3356 and 3226 cm.$^{-1}$ with no absorption in the carbonyl region. In chloroform solution, however, the spectrum was radically different, a single hydroxyl band at 3401 and a strong carbonyl band at 1706 cm.$^{-1}$ being observed.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.23; H, 9.16.

Preparation of the following derivatives was attempted without success: phenylhydrazone, 2,4-dinitrophenylhydrazone, semicarbazone, 3,5-dinitrobenzoate, phenylurethan, benzilidene acetal and trityl ether.

In a periodate titration by the method of Jackson,[32] a 253-mg. sample of XI consumed 409 mg. (1.00 equiv.) of sodium metaperiodate, after a reaction time of two hours. The calculated value, based on a molecular weight of 132, is 410 mg.

Reaction of 2,3-Dihydroxy-2,3-dimethyltetrahydrofuran (XXIa) with Sodium Metaperiodate.—A solution of 4.6 g. of the diol XXIa and 7.5 g. of sodium metaperiodate in 150 ml. of water was allowed to stand at room temperature for 4 hr. and then continuously extracted with ether for 24 hr. The ether extract was dried and the solvent was removed leaving a colorless liquid, which was distilled. Two fractions were collected.

Fraction 1 (0.4 g.) was collected at 52–55° (80 mm.). It was identified as acetic acid by preparation of the *p*-bromophenacyl ester, m.p. and mixed m.p. 84.5–85.5°.

Fraction 2, 1.6 g., b.p. 72–73° (9 mm.), was identified as a mixture of 4-hydroxy-2-butanone and 4-acetoxy-2-butanone by comparison of the properties shown in Table I with synthetic samples and by mixed m.p.'s of derivatives.

TABLE I

	4-Hydroxy-butanone[a]	4-Acetoxy-butanone[b]	Product
Compn., %	C, 54.53	C, 55.37	C, 54.67
	H, 9.15	H, 7.75	H, 8.26
B.p., °C. (mm.)	61–62.5 (8)	69–70 (9)	72–73 (9)
n^tD	1.4280	1.4143[c]	1.4211
t, °C.	26	25	20
Main infrared bands, cm.$^{-1}$	3356, 1709	1733, 1715, 1236	3390, 1733 1715–1709, 1236

[a] J. T. Hays, G. F. Hager, H. M. Engelmann and H. M. Spurlin, THIS JOURNAL, **73**, 5369 (1951). The reported values are: b.p. 73–76° (12 mm.), n^{20}D 1.4290. [b] E. R. Buchman and H. Sargent, *ibid.*, **67**, 400 (1945), report b.p. 76–78° (8 mm.). [c] C. H. Hoffman, *et al.*, *ibid.*, **79**, 2316 (1957), give n^{25}D 1.4148.

Treatment of the mixture with 2,4-dinitrophenylhydrazine gave the derivative of methyl vinyl ketone, m.p. 212–213° dec., after four recrystallizations from aqueous pyridine. A mixed m.p. with the same derivative prepared either from authentic 4-hydroxy-1-butanone or methyl vinyl ketone was undepressed. The reported m.p. is 217°.[33]

Fraction 2 gave a **3,5-dinitrobenzoate**, which after three recrystallizations from ethanol–water had m.p. 101–102°. It did not depress the m.p. of the same derivative prepared from authentic 4-hydroxy-2-butanone.

Anal. Calcd. for $C_{11}H_{10}N_2O_7$: C, 46.81; H, 3.57. Found: C, 47.00; H, 3.67.

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[31] While the present work was in progress, F. N. Stepanov and O. K. Smirnov, *Zhur. Obshchei Khim.*, **27**, 1042 (1957) (*C. A.*, **52**, 2747 (1958)), reported the following properties: for the lactone X, b.p. 125–126° (18 mm.), n^{20}D 1.4561; for the semicarbazone, m.p. 190°.

[32] E. L. Jackson, in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 361.

[33] I. N. Nazarov, L. A. Kazitsyna and I. I. Zaretskaya, *Zhur. Obshchei Khim.*, **27**, 606 (1957) (*C. A.*, **51**, 16383 (1957)).

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

The Curtius Rearrangement. II. The Decomposition of *o*-Substituted Benzazides in Toluene

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RECEIVED MAY 26, 1958

The rates of decomposition of six *o*-substituted benzazides were determined volumetrically by collecting the nitrogen evolved. The rates of *o*-substituted derivatives were much higher than those of *m*- and *p*-derivatives. The relative reactivities followed the order of the bulkiness of *o*-substituents, although the changes were relatively small compared to the divergence between *o*-isomers and *m*-, *p*-isomers. These results are attributed to the increase in the steric requirement of the migrating group, and discussed in terms of the steric restriction of resonance of the benzene ring with the azidocarbonyl residue, and the steric compression of migrating group.

In an earlier paper,[1] the effect of *m*- and *p*-substituents on the rate of the Curtius rearrangement of benzazides was reported and discussed. The kinetic study of this rearrangement has now been extended to *o*-substituted benzazides.

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[1] Y. Yukawa and Y. Tsuno, THIS JOURNAL, **79**, 5530 (1957).