TABLE III

ISOMER DISTRIBUTION IN NITRATION OF ω-STYRYLTRIMETHYLAMMONIUM PICRATE AS DETERMINED BY OXIDATION TO NITROBENZOIC ACIDS

Exp.	Isomer	Wt. Acid Found, G.	Based on Mixed Acids from $KMnO_4$ Oxidation, %	Based on Starting Picrate, %
A	*o*	0.328	13.50	12.80
	m	0.0432	1.78	1.64
	p	1.6367	67.20	64.10
			82.48	78.54
	o/p ratio 0.201			
B	*o*	0.139	9.15	6.60
	m	0.0254	1.66	1.20
	p	1.1139	73.50	53.00
			84.31	60.80
	o/p ratio 0.125			
C	*o*	0.528	27.90	23.80
	m	0.051	2.70	2.30
	p	1.063	56.40	48.00
			87.00	74.10
	o/p ratio 0.495			

The filtrate was reduced as usual and then brominated with 275 ml. of bromine water. 2,4,6-Tribromoaniline, wt. 0.9111 g., m.p. 114–118° (lit.[24] 120°), representing 0.328 g. of *o*-nitrobenzoic acid, and 2,4,5-tribromo-4-aminobenzoic acid, wt. 0.0966 g., m.p. 164–167° (lit.[25] 169°), representing 0.0432 g. of *m*-nitrobenzoic acid were recovered as indicated earlier. The results of this experiment are summarized in Table III, A.

B. The picrate (4.9340 g., m.p. 183–184°) was added over a period of 15 min. to 50 ml. of nitric acid (sp. gr. 1.5) cooled in an ice bath. The light yellow solution was then removed from the bath and allowed to stand for 1 hr. The usual workup yielded 4.133 g. (75%, m.p. 145–155°) of the mono nitration product.

Anal. Calcd. for $C_{17}H_{17}N_5O_9$: C, 46.90; H, 3.94. Found: C, 46.36; H, 3.88.

The filtrate was evaporated to dryness and the residue of salts extracted with ethyl acetate. The black tarry material recovered from the extract was discarded.

Oxidation as directed in experiment A yielded 1.521 g. of mixed acids. Analysis of this mixture gave the results shown in Table III, B.

C. The picrate (5.168 g.) was added to 50 ml. of nitric acid (sp. gr. 1.5) cooled in an ice bath. The yellow solution was allowed to stand at 5° for 30 min. The usual workup yielded (1) 5.26 g. (m.p. 138–160°, 90% yield) of yellow solid. Extraction of the concentrated filtrate with ethyl acetate offered (2) 0.303 g. (m.p. 130–160°) of brown solid.

Anal. Calcd. for $C_{17}H_{17}N_5O_9$: C, 46.90; H, 3.94; N, 16.09. Found: (1) C, 41.60; H, 4.40; N, 16.31. (2) C, 34.25; H, 3.27; N, 15.78.

Although both fractions were very impure, they were combined and oxidized as usual to yield 1.891 g. (89%) of mixed acids. Analysis of this mixture gave the results shown in Table III, C.

LAFAYETTE, IND.

(24) F. Asinger, *J. Prakt. Chem.*, **142**, 299 (1935).

(25) J. J. Sudborough, L. L. Lloyd, *J. Chem. Soc.*, **75**, 589 (1899).

[CONTRIBUTION FROM THE FULMER CHEMICAL LABORATORY, THE STATE COLLEGE OF WASHINGTON]

Alkylation of α-Enol-γ-butyrolactones Derived from Condensations of Ketones with Diethyl Oxalacetate[1]

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Alkylations of α-enol-γ-butyrolactones, derived from condensations of diethyl oxalacetate with cyclohexanone and acetone, respectively, are described. *p*-Nitrobenzyl chloride and 1-chloromethylnaphthalene are employed as alkylating agents with the sodium salts of the α-enol-γ-lactones dissolved in dimethylformamide. The structure of the resulting alkylation products has been shown to be that of an enol ether (II), as based on evidence relating to alkaline and acidic decomposition reactions and infrared absorption spectra.

The formation of *ketone-derived* α-enol-γ-butyrolactones has been reported recently from this laboratory.[3] In continuation of the investigation of these substances, the authors desired to study some alkylation reactions and the nature of the products derived therefrom. Schinz and Hinder[4] had observed methylation of an aldehyde-derived α-enol-γ-lactone either by reaction of the lactone with diazomethane or by reaction of the sodium salt of the lactone with methyl iodide in absolute ethanol. The structure was inferred to be that of an enol ether from the ultraviolet absorption spectrum and from its apparent nonidentity with a

(1) Presented in part before the Division of Organic Chemistry at the 121st Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y., March 24, 1952, and in part before a Northwest Regional Meeting of the AMERICAN CHEMICAL SOCIETY, Eugene, Ore., June 10, 1955.

(2) Abstracted in part from theses submitted by James Wm. Cleary and Melvin J. Gortatowski in partial fulfillment of the requirements for the degrees of Doctor of Philosophy and Master of Science, respectively, the State College of Washington, February 1956 and June 1952.

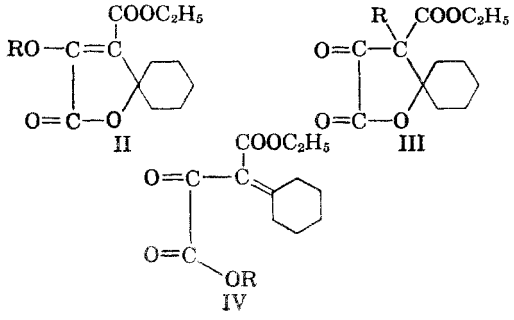
(3) G. W. Stacy, J. W. Cleary, and M. J. Gortatowski, *J. Am. Chem. Soc.*, **79**, 1451 (1957).

(4) H. Schinz and M. Hinder, *Helv. Chim. Acta*, **30**, 1349 (1947).

C-alkylation product (no direct comparison with this substance was made, however).

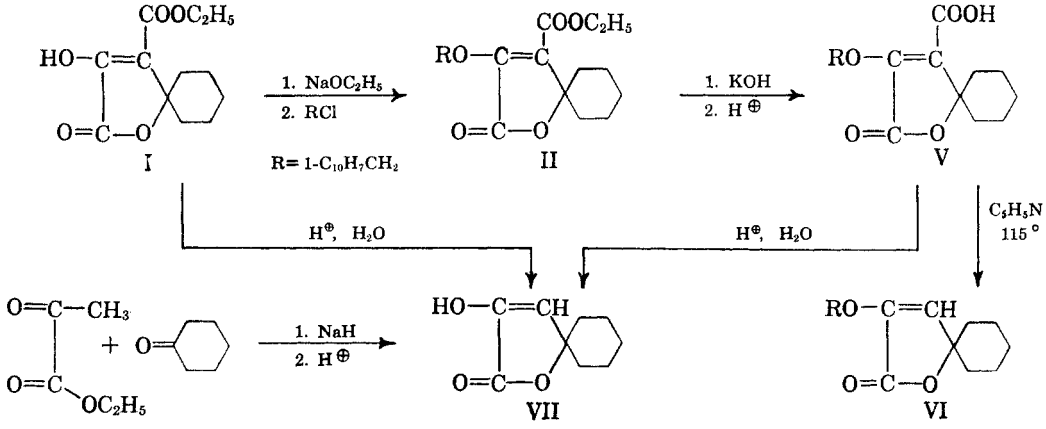
In an initial attempt to prepare an alkylation product, the sodium salt of the authors' cyclohexanone-derived α-enol-γ-lactone I[3] was heated under reflux in absolute ethanol with *p*-nitrobenzyl chloride in accord with the procedure described by Schinz and Hinder.[4] Under these conditions, it was not possible to obtain an alkylation product. However, when the same reactants were heated in dimethylformamide,[5] an excellent yield of an alkylation product was obtained. In like manner, the corresponding acetone-derived α-enol-γ-lactone[6] and an aldehyde-derived (isovaleraldehyde) α-enol-γ-lactone[7] were alkylated by *p*-nitrobenzyl chloride; the yield for the latter substance was not as good as those for the two ketone-derived α-enol-γ-lactones. As the presence of a nitro group was deemed disadvantageous in connection with some of the structure studies contemplated, the corresponding 1-naphthylmethyl derivative (II, R = 1-$C_{10}H_7CH_2$) was prepared in a similar manner by the reaction of I with 1-chloromethylnaphthalene. In later preparative runs, it was found that the crude sodium salt of I could be used just as well as the purified salt in obtaining the 1-naphthylmethyl derivative.

In respect to the structure of these alkylation products, it appeared desirable to consider several possibilities. In addition to the enol ether structure II, other logical possibilities were the *C*-alkylation structure III and the enoic ester structure IV.



C-Alkylation products, of course, are encountered frequently in the alkylation of β-keto esters.[8] The enoic ester structure IV would correspond to the type of product obtained in the Stobbe condensation.[9] Stecher and Clements have studied similar structures, which were β-bromobenzylidenepyruvic esters.[10]

In the structure proof of the authors' alkylation products, an initial observation, which argued against structures III and IV, was the lack of reactivity of the alkylation product with 2,4-dinitrophenylhydrazine. The next point of evidence involved the reaction of the alkylation product with alkali.



It has been observed that the α-enol-γ-lactone I, on being heated in alkaline solution, undergoes lactone ring opening followed by a reverse aldol condensation to yield cyclohexanone.[3] It might be anticipated that alkaline treatment of a structure such as III would result in a similar decomposition, while a structure such as IV would undergo a dual saponification with removal of both 1-naphthylmethyl and ethyl groups; on the other hand, structure II would be expected to undergo merely saponification of the carbethoxy group. By appropriate alkaline treatment of the alkylation product, therefore, it appeared that a choice among structures II–IV might be made. Accordingly, the alkylation product was heated with 20% potassium hydroxide solution, and an acid V was obtained. The acid V was decarboxylated by heating in pyridine to give a product VI, which did not react with ferric chloride solution or 2,4-dinitrophenylhydrazine.

(5) (a) J. C. Sheehan and W. A. Bolhofer, *J. Am. Chem. Soc.*, 72, 2786 (1950); (b) H. L. Rice and G. R. Pettit, *J. Am. Chem. Soc.*, 76, 302 (1954); (c) F. J. Marshall and W. N. Cannon, *J. Org. Chem.*, 21, 245 (1956).

(6) Minimal studies were carried out on the acetone-derived α-enol-γ-lactone because of the limited amount of this substance that was available (ref. 3).

(7) G. W. Stacy and G. D. Wagner, *J. Am. Chem. Soc.*, 74, 909 (1952).

(8) P. Karrer, *Organic Chemistry*, 4th English ed., Elsevier Publishing Company, Inc., New York, N. Y., 1950, p. 269.

(9) W. S. Johnson and G. H. Daub, *Org. Reactions*, VI, 1 (1951).

(10) E. D. Stecher and A. Clements, *J. Am. Chem. Soc.*, 76, 503 (1954).

These facts together with the infrared absorption spectra of these compounds strongly support an enol ether structure for II, V, and VI. Although the normal absorption for a γ-lactone carbonyl is about 1770 cm.$^{-1}$, it would be lowered by conjugation with the enol ether C=C.[11] This proved to be the case, for a strong absorption band was to be found at 1740–1750 cm.$^{-1}$. The conjugated double bond of the γ-lactone ring also was borne out in respect to the carbethoxy group of II and the carboxyl group of V. The carbonyl frequencies for these groups again were lowered in agreement with the fact that the carbonyl groups are part of a conjugated system. Davison and Bates[12] reported a doubling of the absorption for the C=C stretching frequency at about 1610 cm.$^{-1}$ and 1635 cm.$^{-1}$ for a number of vinyl ethers. For the authors' enol ethers, similar absorptions were observed at about 1600 cm.$^{-1}$ and 1640–1650 cm.$^{-1}$, respectively. Finally, a strong absorption band corresponding to the carbon-oxygen single bond stretching frequency of an enol ether was found at about 1190–1215 cm.$^{-1}$.

Although decarboxylation of the acid V had been accomplished in low yield by heating in pyridine, it occurred more readily when V was heated in aqueous acid. At the same time hydrolytic removal of the 1-naphthylmethyl group occurred, so that the product was the α-enol-γ-lactone VII. The hydrolytic removal of the 1-naphthylmethyl group constituted further evidence for the enol ether structure of V and, therefore, of the alkylation product II because the facile acid hydrolysis of vinyl and enol ethers is, of course, well known.[13]

The α-enol-γ-lactone VII gave a blood-red color with ferric chloride solution and failed to react with 2,4-dinitrophenylhydrazine. The infrared absorption spectrum of VII was found to be similar to those of the α-enol-β-carbethoxy-γ-lactones previously reported,[3] except for the absorption band corresponding to the conjugated β-carbethoxy group, which, of course, was missing in the present case. The α-enol-γ-lactone VII also was converted to a *p*-nitrobenzoate (enol ester), and again the infrared absorption spectrum of this derivative was in good agreement with the assigned structure.[3] Further, VII could be prepared by an alternate and more direct approach. Preparation of α-enol-γ-lactones similar to VII has been accomplished by condensation of aldehydes with pyruvic acid under alkaline conditions.[4] When such a procedure was applied in the present case, however, formation of VII was not observed. On the other hand, condensation of ethyl pyruvate with cyclohexanone in the presence of sodium hydride did succeed. This constitutes a new example of the Stobbe-type condensation.[9] The product obtained in this manner was proved to be identical with that produced from V by a mixed melting point determination and by identity of the infrared absorption spectra.

It had been noted by Schinz and Hinder that aldehyde-derived α-enol-β-carbethoxy-γ-lactones suffered loss of the carbethoxy group when heated under acidic conditions.[4] Excellent yields were obtained by heating with aqueous acids in the presence of a trace of hydroquinone over a period of several hours. Particularly since V could be readily converted to VII, it seemed that our cyclohexanone-derived α-enol-β-carbethoxy-γ-lactone I could also be converted to VII in parallel with the results reported[4] for the aldehyde-derived products. This was realized, but only after the heating period was extended to 15 hr. and a larger quantity of hydroquinone was used. When a 2-hr. period was employed, only starting material was isolated from the reaction mixture. When long heating periods were employed, but only a trace of hydroquinone was added to the reaction mixture, only very small amounts of the product VII were obtained.

EXPERIMENTAL[14]

Alkylation of α-enol-γ-butyrolactones. Ethyl β-(1-hydroxycyclohexyl)-α-(1-naphtylmethoxy)fumarate γ-lactone (II). To 50 ml. of absolute ethanol was added 1.73 g. (0.075 gram atom) of sodium; 18.0 g. (0.075 mole) of I was dissolved in 50 ml. of hot absolute ethanol and added slowly with swirling to the sodium ethoxide solution. A white precipitate formed immediately, and the mixture was heated under reflux for 0.5 hr., after which the ethanol was removed by evaporation under reduced pressure leaving the sodium salt of I. To this was added 100 ml. of dry dimethylformamide, and the mixture was heated at 90° to expel any remaining ethanol and to effect the complete solution of the sodium salt. 1-Chloromethylnaphthalene, 13.2 g. (0.075 mole), was added to the mixture, which then was heated on a steam bath for 4.5 hr. During the course of the reaction the solution turned red and sodium chloride precipitated. The mixture was poured slowly with stirring and cooling into 300 ml. of water, and the resulting mixture was allowed to stand in an ice bath overnight. The precipitate was collected by filtration and dried to yield 24.9 g. (87%) of crude II, m.p. 104–107°. Recrystallization from dilute ethanol accompanied by treatment with Norit gave 18.1 g. (63% yield) of fine, colorless needles, m.p. 117.5–118.5°. Further purification for preparation of an analytical sample was accomplished by sublimation, m.p. 119–120°.

Anal. Calcd. for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.35; H, 6.51.

The sodium salt of I, as obtained directly from the reaction mixture involving the condensation of cyclohexanone with sodium diethyl oxalacetate,[3] could be used in the preparation of alkylation products. In this way, 1.31 g. (5.0 mmoles) of the sodium salt of I and 0.88 g. (5.0 mmoles) of 1-chloromethylnaphthalene in dimethylformamide re-

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, N.Y., 1956, pp. 171–6.

(12) W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

(13) A. W. Johnson, *et al.*, in E. H. Rodd, ed., *Chemistry of Carbon Compounds*, Vol. I (A), Elsevier Publishing Company, Inc., New York, N.Y., 1951, p. 324.

(14) All melting points are corrected, and boiling points are uncorrected. The microanalytical work was performed by Galbraith Laboratories, Knoxville, Tenn. For details on determination of the infrared absorption spectra see ref. 3.

acted to form 0.88 g. (46% yield) of II, m.p. 118.5–119.5°.

The infrared absorption spectrum of II showed bands that were assignable to conjugated γ-lactone (1750 cm.$^{-1}$, s), conjugated ester (1690 cm.$^{-1}$, s), C=C (1640 cm.$^{-1}$, m; 1598 cm.$^{-1}$, w), and enol ether (1190 cm.$^{-1}$, s).

Ethyl β-(1-hydroxycyclohexyl)-α-(p-nitrobenzoxy)fumarate γ-lactone. The procedure for this and following alkylations was essentially the same as that described for II above. From reaction of 1.55 g. (5.9 mmoles) of the sodium salt of I and 0.51 g. (3.0 mmoles) of *p*-nitrobenzyl chloride in 50 ml. of dimethylformamide was obtained 0.94 g. (84% yield) of the crude alkylation product, m.p. 128.0–128.5°. Recrystallization from 95% ethanol afforded colorless, flat plates, m.p. 131–132°.

Anal. Calcd. for $C_{19}H_{21}NO_7$: C, 60.79; H, 5.63; N, 3.73. Found: C, 60.79; H, 5.66; N, 3.78.

The infrared absorption spectrum of this alkylation product showed bands that were assignable to conjugated γ-lactone (1757 cm.$^{-1}$, s), conjugated ester (1708 cm.$^{-1}$, s), C=C (1650 cm.$^{-1}$, m; 1600 cm.$^{-1}$, w), and enol ether (1193 cm.$^{-1}$, s).

Ethyl β-(2-hydroxyisopropyl)-α-(p-nitrobenzoxy)fumarate γ-lactone. From 0.50 g. (2.5 mmoles) of the α-enol-γ-lactone,[3] from which the sodium salt was prepared by reaction with 0.059 g. of sodium, and 0.43 g. (2.5 mmoles) of *p*-nitrobenzyl chloride in 10 ml. of dimethylformamide, there was obtained 0.59 g. (71% yield) of light yellow crystals, m.p. 108–110°. This was recrystallized from benzene-ligroin with charcoal treatment to yield 0.37 g. (45%) of alkylation product as colorless crystals, m.p. 113–114.5°.

Anal. Calcd. for $C_{16}H_{17}NO_7$: C, 57.31; H, 5.11; N, 4.18. Found: C, 57.56; H, 5.03; N, 4.23.

The infrared absorption spectrum showed bands that were assignable to conjugated γ-lactone (1756 cm.$^{-1}$, s), conjugated ester (1690 cm.$^{-1}$, s), C=C (1647 cm.$^{-1}$, m; 1600 cm.$^{-1}$, m), and enol ether (1212 cm.$^{-1}$, s).

Ethyl β-(1-hydroxyisoamyl)-α-(p-nitrobenzoxy)fumarate γ-lactone. From reaction of 1.48 g. (5.9 mmoles) of the sodium salt of the α-enol-γ-lactone[7] and 0.51 g. (2.9 mmoles) of *p*-nitrobenzyl chloride in 50 ml. of dimethylformamide was obtained 0.32 g. (36% yield) of an alkylation product, m.p. 95–96°. An analytical sample was prepared by repeated recrystallization from 95% ethanol, m.p. 97–98°.

Anal. Calcd. for $C_{18}H_{21}NO_7$: C, 59.49; H, 5.82; N, 3.85. Found: C, 59.39; H, 5.87; N, 3.68.

STRUCTURE PROOF

β-(1-Hydroxycyclohexyl)-α-(1-naphthylmethoxy)fumaric acid γ-lactone (V). A mixture of 0.28 g. (0.75 mmole) of II and 10 ml. of 20% potassium hydroxide solution was heated under reflux for 2.5 hr. With cooling the resulting reaction mixture was acidified slowly with concentrated hydrochloric acid. To insure complete precipitation, the acidified mixture was allowed to stand for 8 hr. in an ice bath, after which the precipitate was collected by filtration to yield 0.24 g. (91%). Recrystallization from dilute ethanol accompanied by Norit treatment gave 0.17 g. (64% yield) of a colorless, microcrystalline product, m.p. 149° (dec.).

Anal. Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.77; H, 5.79.

The infrared absorption spectrum revealed bands that were assignable to conjugated γ-lactone (1752 cm.$^{-1}$, s), conjugated carboxyl group (1672 cm.$^{-1}$, s), C=C (1640 cm.$^{-1}$, w; 1598 cm.$^{-1}$, w), and enol ether (1188 cm.$^{-1}$, s).

β-(1-Hydroxycyclohexyl)-α-(1-naphthylmethoxy)acrylic acid γ-lactone (VI). In a decarboxylation procedure quite similar to a number that have been reported,[15] 5.63 g. (0.016 mole) of V (with a trace of hydroquinone) in 50 ml. of anhydrous pyridine was heated under reflux for 0.5 hr. The pyridine was removed by distillation under reduced pressure leaving a viscous, brown residue, which then was stirred for 0.5 hr. with 20 ml. of 3*N* hydrochloric acid. The supernatant acid was removed, and the residue was taken up in ether, which then was washed with 5% sodium hydroxide solution and saturated sodium chloride solution, respectively. (The sodium hydroxide extract was later acidified to give 1.35 g of the starting material V.) The ether was removed leaving 2.54 g. of a brown, semisolid residue. This was crystallized from ethanol to yield 0.52 g. (10%) of coarse, round crystals, m.p. 114–116°. A sample for analysis was recrystallized several times from dilute ethanol to give fine, colorless platelets, m.p. 119–120°.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.80; H, 6.32.

The infrared absorption spectrum showed bands that were assignable to conjugated γ-lactone (1742 cm.$^{-1}$, s), C=C (1638 cm.$^{-1}$, m; 1599 cm.$^{-1}$, w), and enol ether (1181 cm.$^{-1}$, s).

α-Hydroxy-β-(1-hydroxycyclohexyl)acrylic acid γ-lactone (VII). *A. By heating the acid* V *under acidic conditions.* A mixture of 2.18 g. (6.2 mmoles) of V, 50 ml. of ethanol, and 35 ml. of 20% sulfuric acid, to which a trace of hydroquinone had been added, was heated under reflux for 5.5 hr. This was poured into 300 ml. of ice water and allowed to stand overnight; a small amount of heavy, red oil separated and was discarded. The aqueous phase was extracted with portions of ether until the extracts were colorless. The ether was evaporated to give 0.90 g. of a viscous, brown residue which contained a few crystals. This was taken up in hot benzene and filtered; the benzene was removed leaving 0.85 g. of a glassy solid. This crude product was extracted with hot, olefin-free ligroin, and the extract was filtered and allowed to stand at room temperature for a day. The resulting precipitate was collected by filtration to yield 0.36 g. (34%) of colorless crystals, which melted partially at 118–120° and completely at 127°. A sample of this was recrystallized several times from a mixture of benzene and ligroin to give pure VII, m.p. 134.4–135.0°.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.24.

The infrared absorption spectrum revealed bands that were assignable to enolic hydroxyl (3150 cm.$^{-1}$, s), conjugated γ-lactone (1730 cm.$^{-1}$, s), and C=C (1640 cm.$^{-1}$, m; 1610 cm.$^{-1}$, w).

B. By condensation of cyclohexanone with ethyl pyruvate. A 200-ml three-necked flask, equipped with a reflux condenser and stirrer, was flushed with a stream of dry nitrogen. A mixture of 3.60 g. (0.15 mole) of sodium hydride in 25 ml. of benzene was placed in the flask, and with stirring a mixture of 17.4 g. (0.15 mole) of ethyl pyruvate[16] and 4.91 g. (0.05 mole) of cyclohexanone was added in portions of 0.5 ml. at intervals of about 1 min. After the addition of several milliliters of this mixture, 0.5 ml. of absolute ethanol was added. The exothermic reaction which ensued was moderated by cooling the flask in a pan of cold water, which was removed near the end of the addition. When the addition had been completed, another 25-ml. quantity of anhydrous benzene was added, and the stirring was continued. The mixture soon soldified and had to be broken into small lumps. After a total of 2 hr. of stirring, 15 ml. of concentrated hydrochloric acid in 60 ml. of water was added slowly. The mixture was extracted with ether, and the combined ether extracts in turn were extracted with 5% sodium bicarbonate solution and washed with saturated sodium sulfate solution. After removal of the ether, an orange semisolid weighing 4.28 g. (51% yield) was obtained. Recrystallization accompanied by Norit treatment afforded 1.16 g. (14% yield) of VII as colorless crystals, m.p. 135.5–136.5°.

C. By heating the ester I under acidic conditions. A mixture of 2.40 g. (0.01 mole) of I, 5 ml. of water, 20 ml. of glacial acetic acid, and 20 ml. of concentrated hydrochloric acid, to

(15) H. R. Snyder and E. L. Eliel, *J. Am. Chem. Soc.*, 71, 663 (1949).

(16) C. L. Stevens and A. E. Sherr, *J. Org. Chem.*, 17, 1228 (1952).

which 0.10 g. of hydroquinone had been added, was heated under reflux for 15 hr. The reaction mixture was poured into 100 ml. of water and allowed to stand overnight. The precipitate was separated by filtration, washed with several portions of hot water, and discarded. The filtrate and washings were extracted with ether, and the ether was in turn extracted with 5% sodium bicarbonate solution. Removal of the ether resulted in a residue of 1.23 g. (65% yield) of crude product VII. Recrystallization from benzene accompanied by charcoal treatment yielded 0.34 g. (20%) of colorless crystals, m.p. 136–137°.

The identity of VII, as obtained by these three different methods, was established by the identity of the infrared spectra and mixed melting point determinations.

When I was treated under acidic conditions for short periods of time, only starting material was obtained from the reaction mixture. A sample of 1.00 g. (4.2 mmoles) of I with a trace of hydroquinone was dissolved in a mixture of 10 ml. of glacial acetic acid, 2 ml. of concentrated hydrochloric acid, and 5 ml. of water. The solution was heated under reflux for 1.5 hr. and then was cooled in an ice bath. There was obtained 0.65 g. (65%) of I (Identity with the starting material was established by a mixed melting point determination). None of the expected product VII could be isolated from the reaction mixture.

Longer heating (12 hr.) in the absence of hydroquinone resulted in intractable reaction mixtures from which only traces of product and no starting material could be isolated. The necessity of having hydroquinone present to prevent resinification of some of the substances involved was clearly demonstrated.

p-Nitrobenzoate of VII. In a procedure similar to those previously described,[3] 1.00 g. (5.4 mmoles) of *p*-nitrobenzoyl chloride and 0.42 g. (2.5 mmoles) of VII in 10 ml. of pyridine reacted to yield 0.90 g. of crude enol ester. Recrystallization from a benzene-ligroin mixture accompanied by charcoal treatment gave 0.39 g. (39% yield). An analytical sample was prepared by recrystallizing twice from benzene to give clear, colorless platelets, m.p. 174–176°.

Anal. Calcd. for $C_{16}H_{15}NO_6$: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.60; H, 4.98; N, 4.46.

The infrared absorption spectrum revealed bands that were assignable to enol ester (1760 cm.$^{-1}$, s), conjugated γ-lactone (1737 cm.$^{-1}$, s), and C=C (1646 cm.$^{-1}$, m; 1607 cm.$^{-1}$, m).

Acknowledgments. This investigation was supported by a Frederick Gardner Cottrel grant from the Research Corporation and in part by research funds of the State College of Washington. We are indebted to Mr. George D. Wagner of the Division of Industrial Research of the State College of Washington for determination of infrared absorption spectra and aid in their interpretation.

PULLMAN, WASH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF RHODE ISLAND]

Hunsdiecker Reaction of Silver Salts of *Cis*- and *Trans*-1,2-Cyclohexanedicarboxylic Acid[1]

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The Hunsdiecker reaction was carried out on the silver salts of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid. The same product, *trans*-1,2-dibromocyclohexane, was obtained from both salts. The isomerization appears to take place at an intermediate stage in the reaction. The mechanistic implications are discussed briefly.

The Hunsdiecker reaction, by which metal salts of carboxylic acids, usually the silver salts, are decarboxylated to the organic halide by the action of halogen, has attracted considerable attention in the past few years both as a method of synthesis of halogen compounds and mechanistically.[2] The present study was initiated from the former point of view in connection with a study of routes to the synthesis of alicyclic vicinal dihalides. The synthesis of the *cis* isomers of 1,2-dihalocycloalkanes was the principal interest, and accordingly it was decided to determine whether the Hunsdiecker reaction was capable of yielding *cis* dibromides from *cis* dicarboxylic acids.

The problem of isomerization was immediately apparent. A review of the literature disclosed that isomerization is not uncommon in the Hunsdiecker reaction. It was obvious from an examination of the literature that racemization of optically active compounds is to be expected when the carboxylic acid salt group is attached to the asymmetric carbon.[3] Little or no optical activity is preserved in the alkyl halides resulting from Hunsdiecker reactions of this type. However, the work in this laboratory was to be undertaken using geometrical isomers rather than optical isomers, the materials chosen being the silver salts of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid. It was not so evident from the literature that isomerization would take

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(2) For an extensive review see: R. G. Johnson and R. K. Ingham, *Chem. Revs.*, 56, 219 (1956).

(3) (a) C. L. Arcus, A. Campbell, and J. Kenyon, *J. Chem. Soc.*, 1510 (1949). (b) R. T. Arnold and R. Morgan, *J. Am. Chem. Soc.*, 70, 4248 (1948). (c) J. Cason, M. J. Kalm, and R. H. Mills, *J. Org. Chem.*, 18, 1670 (1953). (d) Heintzeler, *Ann.*, 569, 102 (1950). (e) R. G. Johnson and R. K. Ingham, Ref. (2), cite also: C. E. Berr, Doctoral Dissertation, University of California, Los Angeles (1952).