

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

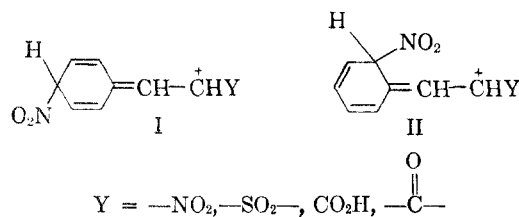
**Orientation in the Nitration of  $\omega$ -Styryltrimethylammonium Picrate<sup>1</sup>**WILLIAM E. TRUCE AND JOHN A. SIMMS<sup>2</sup>

Received December 17, 1956

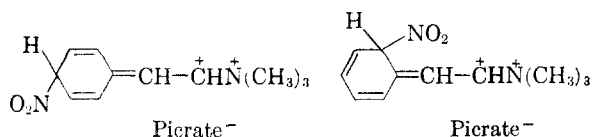
The preparation and characterization of  $\omega$ -styryltrimethylammonium picrate is described. This compound is nitrated almost exclusively in the *ortho* and *para* positions with about 2% of the *meta* isomer being formed.

A number of  $\omega$ -substituted styrenes have been nitrated, and in all instances, *ortho-para* orientation has been observed.<sup>3,4,5</sup> Nitration of  $\omega$ -nitrostyrene<sup>3</sup> or of  $\omega$ -styrenesulfonyl chloride,<sup>6</sup> for example, yields less than 2% of the *meta* isomer.

Bordwell and Rohde<sup>6</sup> concluded from competitive nitration experiments that cinnamic acid and  $\omega$ -styrenesulfonyl chloride are less reactive than benzene and compare to chlorobenzene in reactivity. One explanation<sup>5,6</sup> for the observed *ortho-para* orientation by the deactivating and negatively-substituted vinyl group is that the transition state is stabilized because of contributions from resonance forms such as I and II. Analogous forms for the attack at the *meta* position are not possible. The cor-



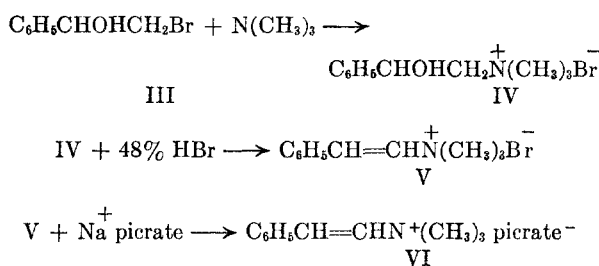
responding resonance forms for  $\omega$ -styryltrimethylammonium picrate are:



On the assumption that resonance forms involving adjacent like charges are often unimportant<sup>7,8</sup> it was hoped that this idea on orientation could be tested by nitrating  $\omega$ -styryltrimethylammonium

picrate (VI), and determining the quantity of *meta* isomer formed.<sup>9</sup> It should be noted that resonance forms I and II, also, would have adjacent like charges. However, in the case of the ammonium compound this would be more pronounced. Formation of an appreciable amount of *meta* isomer should indicate that the contribution of the side chain to the stabilization of the transition state is decreased by the violation of the adjacent charge rule.

$\omega$ -Styryltrimethylammonium picrate (VI) was prepared in 35% yield by the following sequence of reactions:



The preparation of  $\beta$ -hydroxy- $\beta$ -phenylethyltrimethylammonium bromide (IV) required the use of a sealed tube since the reaction was very slow at the reflux temperature of trimethylamine. The dehydration with 48% hydrobromic acid produced  $\omega$ -styryltrimethylammonium bromide (V) in good yield, but also caused some cleavage to trimethylamine hydrobromide. A simple metathesis of V with sodium picrate produced VI quantitatively.

Compound V was characterized as  $\omega$ -styryltrimethylammonium bromide on the basis of three facts. First, it was synthesized from a known compound,  $\beta$ -hydroxy- $\beta$ -phenylethyl bromide through a known intermediate,  $\beta$ -hydroxy- $\beta$ -phenylethyltrimethylammonium bromide.<sup>9</sup> Second, although all the hydrogenation catalysts investigated caused some hydrogenolysis, and a pure reduction product could not be obtained, the impure reduction product (m.p. 218.5–220.50°) gave a mixed melting point of 228–230° with  $\beta$ -phenylethyltrimethylammonium bromide (VII, m.p. 237°). Third, the infrared spectrum has absorption maxima at 13.25  $\mu$  and at 14.5  $\mu$ , which also occur in the spectra of styrene,  $\alpha$ -methylstyrene, and  $\beta$ -methylstyrene.<sup>10</sup> Also, a band,

(1) Taken from Mr. Simms' Ph. D. Thesis, Purdue University, 1956.

(2) Dow Chemical Co. Fellow, 1954–1955.

(3) J. W. Baker and I. W. Wilson, *J. Chem. Soc.*, 842 (1927).

(4) H. W. Underwood and E. L. Kuchmann, *J. Am. Chem. Soc.*, 48, 254 (1926).

(5) L. N. Ferguson, *J. Chem. Ed.* 32, 42 (1955); this paper also gives reference to a number of papers pertaining to transition state resonance.

(6) F. G. Bordwell and K. Rohde, *J. Am. Chem. Soc.* 70, 1191 (1948); see also F. G. Bordwell and H. Stange, *J. Am. Chem. Soc.*, 77, 5941 (1955).

(7) L. Pauling, *The Nature of the Chemical Bond*, p. 199, Cornell University Press, Ithaca, New York, 1948.

(8) W. G. Wheland, *Advanced Organic Chemistry*, p. 424, John Wiley and Sons, Inc., New York, N. Y., 1950.

(9) H. J. Nienburg and G. Klein, Ger. Patent 633,983, *Chem. Abstr.*, 31, 7012 (1937).

(10) American Petroleum Institute, Research Project No. 44; Spectra 170, 329, 330, respectively.

which occurs at 10.40  $\mu$ , is probably indicative of *trans* olefinic hydrogens.<sup>11</sup>

The isomer distribution in the nitration of  $\omega$ -styryltrimethylammonium picrate (VI) was determined by oxidizing the mixture of crude nitro picrates to a mixture of nitrobenzoic acids with potassium permanganate and then determining the nitrobenzoic acids by the method of Flurschein and Holmes.<sup>12</sup> The assumption was made that unequal loss (because of destructive oxidation) of the isomeric nitro  $\omega$ -styryltrimethylammonium picrates and the nitrobenzoic acids did not occur to an appreciable extent. This had been shown experimentally in determining the isomer distribution for the nitration of benzyltrimethylammonium picrate<sup>13</sup> and of  $\beta$ -phenylethyltrimethylammonium picrate.<sup>14</sup> It has also been shown that none of the three nitrobenzoic acids is selectively oxidized by alkaline potassium permanganate.<sup>12</sup> Analysis of mixtures of nitrobenzoic acids with known compositions showed that the presence of 2% of *m*-nitrobenzoic acid could be determined within  $\pm 0.5\%$ .

The nitration of  $\omega$ -styryltrimethylammonium picrate with concentrated nitric acid proceeded rapidly at 0°. The temperature was held below 5° during the addition of the picrate to the nitric acid and the solution was then allowed to warm to room temperature and stand for a few minutes. The yield of the nitro product varied between 75% and 96%. Some loss of the *ortho* isomer may have occurred during the isolation of the mixture of nitro- $\omega$ -styryltrimethylammonium picrates. The low *ortho* value shown in Table 1, analysis B, is probably due to this factor. The oxidation of the nitration product with alkaline potassium permanganate proceeded cleanly and rapidly.

The results from three nitrations of  $\omega$ -styryltrimethylammonium picrate are tabulated in Table I. The percentage of *meta* isomer is consistently small and corresponds to  $1.8 \pm 0.5\%$  of the starting  $\omega$ -styryltrimethylammonium picrate.

It can be concluded from the above results that the  $-\text{CH}=\overset{+}{\text{C}}\text{HN}(\text{CH}_3)_3$  grouping orientates *ortho-para* in much the same way as does the side chain in cinnamic acid,  $\omega$ -nitrostyrene, and  $\omega$ -styrenesulfonyl chloride. Hence, the increased positive charge adjacent to the  $\beta$ -carbon of the vinyl group, in this work as compared to the above, does not seem to alter the orientation appreciably. A possible explanation may be that the positive charge of the quaternary nitrogen is dissipated by the nega-

(11) F. A. Miller, in H. Gilman, *Organic Chemistry*, Vol. III, Chap. 2, p. 144, John Wiley and Sons, Inc., New York, N. Y., 1953.

(12) B. Flurschein and E. L. Holmes, *J. Chem. Soc.*, **133**, 451 (1928). For a recent application of this method see: (b) W. Davey and J. R. Gwilt, *J. Soc. Chem. Ind.*, **69**, 330 (1950).

(13) F. R. Gross, C. K. Ingold, *et al.*, *J. Chem. Soc.*, **2440** (1926).

(14) C. K. Ingold, *et al.*, *J. Chem. Soc.*, **257** (1927).

TABLE I  
ISOMER DISTRIBUTION IN NITRATION OF  
 $\omega$ -STYRYLTRIMETHYLAMMONIUM PICRATE

Experiment	<i>o/p</i>				Reagent	Temperature
	<i>o</i> , %	<i>m</i> , %	<i>p</i> , %	Ratio		
A	12.8	1.6	64.1	0.2	HNO <sub>3</sub> , 1.5 sp. gr.	3.5° during addition, 5–25° for 0.5 hr.
B	6.6	1.2	53.0	0.1	HNO <sub>3</sub> , 1.5	0–3° during addition, 0–25° for 1 hr.
C	23.8	2.3	48.0	0.5	HNO <sub>3</sub> , 1.5 sp. gr.	0–5° during addition, 5° for 0.5 hr.

\* Determined by oxidizing the nitro picrates to a mixture of nitrobenzoic acids and analyzing the acid mixture. The values are based on the starting picrate, and are not normalized to 100% because of the wide variation in the *ortho* percentages.

tively charged picrate anion. In any case the adjacent charge rule is not an important factor in this reaction.

#### EXPERIMENTAL<sup>15</sup>

$\beta$ -Hydroxy- $\beta$ -phenylethyl bromide (III). This compound, b.p. 102–104° (2 mm.), was prepared from styrene in 72% yield by method of Read and Reid.<sup>16</sup>

$\beta$ -Hydroxy- $\beta$ -phenylethyltrimethylammonium bromide (IV). Trimethyl (60 ml., 0.677 mole) was charged into a cooled Carius tube containing 25 g. (0.13 mole) of  $\beta$ -hydroxy- $\beta$ -phenylethyl bromide; the tube was sealed, and then heated at 95° for 98 hr. The white solid product was washed from the tube with methanol. Most of the methanol was evaporated and the product, wt. 25.3 g. (77%) m.p. 200–210°, was precipitated by the addition of ethyl ether. It was recrystallized from methanol: (1) wt. 17.4 g. m.p. 225–226; (2) wt. 3.0 g., m.p. 213–216° (lit.<sup>9</sup> m.p. 228°).

*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>NOBr: Br, 30.72. Found: Br, 30.60. Similar results were obtained when the reaction mixture was allowed to stand at room temperature for 19 days.

$\omega$ -Styryltrimethylammonium bromide (V).  $\beta$ -Hydroxy- $\beta$ -phenylethyltrimethylammonium bromide (15 g.) was dissolved in 100 ml. of 47% hydrobromic acid; the solution was refluxed for 45 min., and then allowed to stand at room temperature for 5 hr. The hydrobromic acid was stripped off at reduced pressure and the light pink solid residue was dissolved in hot methanol. Addition of a mixture of acetone and ether to the concentrated solution, and subsequent cooling yielded 12.6 g. (90%) of white solid, m.p. 173–178°. Two recrystallizations from 1-propanol yielded 7.0 g. of pure white crystals, m.p. 190–191°. This material decolorized dilute potassium permanganate immediately. It also decolorized bromine water (yielding a sticky yellow precipitate).

*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>NBr: C, 54.65; H, 6.62; N, 5.79; Br, 32.95. Found: C, 54.38; H, 6.82; N, 5.84; Br, 32.89.

The infrared spectrum was determined, using the Nujol mull method, with the Perkin-Elmer model 21 double-beam spectrophotometer. The absorption peaks and their intensities are: 3.45 (s), 6.80 (s), 7.15 (w), 7.50 (v.w.), 8.20 (w), 9.30 (v.w.), 10.05 (m), 10.40 (s), 10.85 (m), 11.80 (w), 12.95 (m), 13.25 (s), 14.30  $\mu$  (s). The peak at 10.40 may indicate a *trans* arrangement of hydrogens at the double bond.

(15) All melting points are uncorrected.

(16) J. Read and W. G. Reid, *J. Chem. Soc.*, **1489** (1928).

The ultraviolet spectrum of  $\omega$ -styryltrimethylammonium bromide was determined on the Cary recording spectrophotometer, model 10-11M. The curve was very simple, with a single absorption maximum at 247  $m\mu$ ,  $\epsilon_{\max}$  15,350.

**Reduction of  $\omega$ -styryltrimethylammonium bromide.** The olefin (2.00 g.) was dissolved in 120 ml. of absolute ethanol and shaken with hydrogen at 39 p.s.i. in a Parr hydrogenator with 1 g. of 5% palladium chloride on charcoal<sup>17</sup> for 14 hr. at room temperature. The residue obtained by evaporating the solution under an air jet was recrystallized from 1-propanol to yield 1.14 g. of product, m.p. 184-200°. This material did not decolorize potassium permanganate and was evidently a mixture of trimethylamine hydrobromide and  $\beta$ -phenylethyltrimethylammonium bromide. It was purified by treating a water solution with silver oxide, filtering, and then acidifying the filtrate with hydrobromic acid. The residue obtained by evaporation of the solution weighed 0.54 g. (m.p. 218-220°), after one recrystallization from a mixture of 1-propanol and acetone. Two more recrystallizations raised the melting point to 224-226°.

This compound was also prepared using as catalyst: 10% palladium on charcoal.

**$\beta$ -Phenylethyltrimethylammonium bromide (VII).** To 20 ml. of trimethylamine in a Carius tube cooled in a dry ice bath was added 12.3 g. of  $\beta$ -phenylethyl bromide<sup>18</sup> and the tube was sealed. After standing at room temperature for 3 days the tube appeared to contain only white solid. It was cooled, opened, and the product washed out with methanol. The mixture was concentrated and acetone was added in order to precipitate the product as a white crystalline solid, wt. 9.3 g. (m.p. 235-237°). A sample for analysis, after recrystallization from 1-propanol, melted at 237.5-238.0° (lit.<sup>19</sup> 220°). Chloroplatinate, m.p. 249-250° (lit.<sup>20</sup> 250°); picrate, m.p. 130-131° (lit.<sup>21</sup> 131°).

*Anal.* Calcd. for  $C_{11}H_{13}NBr$ : B, 32.74. Found: Br, 32.62.

**Analysis of the mixture formed by nitrating  $\omega$ -styryltrimethylammonium picrate.** The method of Flurschein and Holmes<sup>12</sup> was used to determine the composition of the mixture of nitrobenzoic acids formed by oxidizing the crude nitration product with alkaline potassium permanganate. The *ortho* and *meta* acids are readily soluble in dilute alcohol (50% by volume), whereas *p*-nitrobenzoic acid has been found to be only 0.16% (w/v) soluble at 20°. The *para* isomer can therefore be separated and weighed as such. An empirically-determined correction of 0.2 g./100 ml. of solvent must be added to the weight found.<sup>22</sup> The soluble acids are then reduced with titanous chloride under strongly acidic conditions, and the mixture brominated with a slight excess of bromine water. The *o*- and *p*-aminobenzoic acids (the *para* acid was produced from the portion of the *p*-nitrobenzoic acid that dissolved in the extracting solvent) were simultaneously brominated and decarboxylated to yield 2,4,6-tribromoaniline. *m*-Aminobenzoic acid yields 2,4,6-tribromo-3-aminobenzoic acid. The two products are extracted from the aqueous mixture with ether and then separated by washing the ether with potassium bicarbonate solution. After correcting for the solubility of the *p*-nitrobenzoic acid, the amount of 2,4,6-tribromoaniline obtained is proportional to the *o*-nitrobenzoic acid in the original mixture. Similarly, the amount of 2,4,6-tribromo-3-aminobenzoic acid is proportional to the *m*-nitrobenzoic acid originally present.

The analytical method was checked with mixtures made from purified *o*-, *m*-, and *p*-nitrobenzoic acids (Eastman Organic Chemicals). The *p*-nitrobenzoic acid (m.p. 239.5-

240°) was recrystallized twice from 95% ethanol and the *meta* (m.p. 141-142°) and *ortho* isomers (m.p. 146.5-147°) were recrystallized twice from 1% hydrochloric acid. The mixtures were analyzed as such or were heated for a few minutes with dilute alkaline potassium permanganate. The precipitate of manganese dioxide was filtered off, and the nitrobenzoic acid mixture recovered by ether extraction of the acidified solution. This preliminary treatment duplicated the potassium permanganate oxidation step in the nitration product analysis.

Table II shows the results of such a check and shows that this method can be used to determine small amounts of *m*-nitrobenzoic acid in the presence of much higher percentages of the *ortho* and *para* isomers.

TABLE II  
ANALYSIS OF SYNTHETIC MIXTURE OF NITROBENZOIC ACIDS

Iso-mer	Starting Weight, G.	Starting Weight, %	Weight Found, G.	Recovery, %	% of Re-covered	Total Starting Weight
<i>o</i>	0.810	33.3	0.830	102.5	34.5	34.1
<i>m</i>	0.0797	3.20	0.070	88.4	2.93	2.89
<i>p</i>	1.5482	63.5	1.5005	97.3	62.6	61.7
						98.7

**Nitration of  $\omega$ -styryltrimethylammonium picrate.** In three nitrations of  $\omega$ -styryltrimethylammonium picrate the above analytical method gave *meta* values which were fairly constant ( $1.8 \pm 0.5\%$  based on starting picrate), although the *o/p* ratio varied considerably from nitration to nitration. The following typical nitration is given in detail.

A.  $\omega$ -Styryltrimethylammonium picrate (m.p. 183-184°, wt. 5.825 g.) was added to 50 ml. (sp. gr. 1.5) of nitric acid cooled in an ice bath. The temperature was maintained at 3-5° by the rate of addition of the picrate. After the light yellow solution was removed from the ice bath the temperature rose to 25° over a period of 0.5 hr. It was allowed to stand at 25° for 10 min. and was then poured into cracked ice. The picric acid that precipitated went back into solution as the mixture was neutralized with concentrated sodium hydroxide. After a slight excess of base had been added a yellow solid formed. The mixture was cooled, filtered, and after drying the product in a vacuum desiccator over phosphorous pentoxide, it weighed 5.14 g., and had m.p. 150-159° (1). Concentration of the filtrate under an air jet and extraction with 400 ml. of ethyl acetate in two portions yielded 0.615 g. of yellow solid, m.p. 135-155° (2). The water layer was evaporated to dryness, and the pulverized residue of salts extracted with ethyl acetate. Evaporation of the extract yielded 0.454 g. of brown solid, m.p. 120-125° (3).

*Anal.* Calcd. for  $C_{17}H_{17}N_3O_5$ : C, 46.90; H, 3.94. Found: (1) C, 46.79; H, 3.91; (2 and 3) C, 40.07; H, 2.63.

Fractions 1, 2, and 3 were combined and mixed with 200 ml. of 1N sodium hydroxide. The mixture was heated on the steam plate and an excess of 5% potassium permanganate (700 ml.) was slowly added until the color persisted. The residual permanganate was destroyed by the addition of sodium bisulfite and the precipitated manganese dioxide filtered off. After the filtrate had been acidified with dilute sulfuric acid, it was concentrated to 100 ml., cooled, and extracted with three 200 ml. portions of ethyl ether. The dried extract yielded 2.44 g. (96%) of mixed nitrobenzoic acids. This mixture was pulverized, placed in a tared Gouch crucible, and extracted as in the analytical example with 69 ml. of dilute (50% by volume) ethanol. The weight of the *p*-nitrobenzoic acid, after drying at 80° for 3 hr. and after correcting for solubility, was found to be 1.636 g., m.p. 237-240° (lit.<sup>23</sup> 238°).

(23) S. M. McElvain, *Org. Syntheses, Coll. Vol. I*, 385 (1941).

(17) R. Monzingo, *Org. Syntheses, Coll. Vol. III*, 686 (1955).

(18) A. W. Dox, *J. Am. Chem. Soc.* 2844 (1924).

(19) V. Braun, *Ann.*, 382, 45 (1911).

(20) H. Decker, P. Becker, *Ber.*, 45, 2404 (1912).

(21) J. Reilly and P. J. Drumm, *J. Chem. Soc.*, 871 (1935).

(22) G. M. Bennett, *Analyst*, 73, 191 (1948).

TABLE III  
ISOMER DISTRIBUTION IN NITRATION OF  
 $\omega$ -STYRYLTRIMETHYLAMMONIUM PICRATE AS  
DETERMINED BY OXIDATION TO NITROBENZOIC ACIDS

Exp.	Isomer	Wt. Acid Found, G.	Based on	Based on
			Mixed Acids from $\text{KMnO}_4$ Oxidation, %	Starting Picrate, %
A	<i>o</i>	0.328	13.50	12.80
	<i>m</i>	0.0432	1.78	1.64
	<i>p</i>	1.6367	67.20	64.10
			82.48	78.54
	<i>o/p</i> ratio	0.201		
B	<i>o</i>	0.139	9.15	6.60
	<i>m</i>	0.0254	1.66	1.20
	<i>p</i>	1.1139	73.50	53.00
			84.31	60.80
	<i>o/p</i> ratio	0.125		
C	<i>o</i>	0.528	27.90	23.80
	<i>m</i>	0.051	2.70	2.30
	<i>p</i>	1.063	56.40	48.00
			87.00	74.10
	<i>o/p</i> 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.<sup>24</sup> 120°), representing 0.328 g.

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

of *o*-nitrobenzoic acid, and 2,4,5-tribromo-4-aminobenzoic acid, wt. 0.0966 g., m.p. 164–167° (lit.<sup>26</sup> 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  $\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_9$ : 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  $\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_8$ : 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.

(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 $\alpha$ -Enol- $\gamma$ -butyrolactones Derived from Condensations of Ketones with Diethyl Oxalacetate<sup>1</sup>

GARDNER W. STACY, JAMES WM. CLEARY, AND MELVIN J. GORTATOWSKI<sup>2</sup>

Received January 2, 1957

Alkylations of  $\alpha$ -enol- $\gamma$ -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  $\alpha$ -enol- $\gamma$ -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*  $\alpha$ -enol- $\gamma$ -butyrolactones has been reported recently from this laboratory.<sup>3</sup> In continuation of the investigation of

(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).

these substances, the authors desired to study some alkylation reactions and the nature of the products derived therefrom. Schinz and Hinder<sup>4</sup> had observed methylation of an aldehyde-derived  $\alpha$ -enol- $\gamma$ -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

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