

Glyoxal tetramethyl acetal was a mobile, water-clear liquid with the following physical constants: b. p. 158–159° (754 mm.);  $n_D^{20}$  1.4010;  $n_D^{25}$  1.3985;  $d_{25}^{25}$  0.9876. It was readily soluble in the common organic solvents including petroleum ether, and was not easily separated from aqueous or alcoholic solutions by distillation. This separation was possible when ether was the solvent. Ether was also capable of extracting the acetal from water although the partition coefficient was heavily in favor of the latter. The tetramethyl acetal did not reduce hot Fehling's solution. It gave the Ariyama<sup>8</sup> color test for glyoxal only after previous hydrolysis with dilute mineral acid.

**Estimation of Glyoxal Tetramethyl Acetal.**—The stock solution used was prepared by dissolving 0.3913 g. in 1 liter of distilled water. It was kept in a stoppered flask at 0°.

(a) **With 2,4-Dinitrophenylhydrazine.**<sup>7</sup>—Aliquots (50 cc.) of the stock solution were heated with an equal volume of 2 *N* hydrochloric acid for fifteen minutes on the steam-bath. The glyoxal formed in the hydrolysis was weighed as the *bis*-hydrazone<sup>10</sup> of the above reagent. Calcd. for 19.57 mg. of tetramethyl acetal or 7.56 mg. of glyoxal, 54.5 mg. Found, 53.4, 53.6 and 54.0, 54.7 mg. six months later. The acetal thus gave the quantitative amount of glyoxal.

(b) **By Ariyama's Method.**—The above stock solution was diluted (1:20) to contain 1.965 mg. of the acetal in 100 cc. and 5-cc. aliquots of this were hydrolyzed as in (a) for varying times. Quick cooling was followed by the successive addition of 2 cc. of Benedict's uric acid reagent,<sup>11</sup> 1 cc. of *N* sodium cyanide and 25 cc. of *N* sodium carbonate. After standing for five minutes, the mixtures were diluted to 100 cc. and the depths of the blue colors compared. The hydrolysis was thus found to be 48, 93, 100 and 100% complete after 2.5, 5, 10 and 60 minutes of heating. No detectable hydrolysis of the acetal occurred during ten minutes when the acid was cold nor in six months when distilled water was the solvent. In carrying out an estimation of glyoxal or of the tetramethyl acetal,

(10) The *bis*-2,4-dinitrophenylhydrazone had the correct m. p. of 318° but accurate analyses were only occasional, owing to the combustion difficulties reported by others.<sup>7a</sup>

(11) Benedict, *J. Biol. Chem.*, **51**, 189 (1922).

5-cc. samples of the unknown and the standard were hydrolyzed as above for fifteen minutes, the other reagents added, and after suitable dilution the final color comparison was made in an Ernst Leitz Wetzler No. 461 colorimeter. With our instrument, the comparison was accurate to within 5% provided the concentration of the unknown lay within the limits indicated in Table I for the standards used. Standards whose concentrations lay outside the 0.05–0.75 mg./100 cc. range were quite unsuitable for comparative purposes.

TABLE I  
PERMISSIBLE DEVIATIONS OF STANDARD AND UNKNOWN SOLUTIONS

Concn. of standard Mg. glyoxal/100 cc.	Concn. of unknown Mg. glyoxal/100 cc.	
	Minimum	Maximum
0.05	0.04	0.06
.25	.13	.48
.40	.20	.76
.60	.30	.76
.75	.37	.76

### Summary

1. Glyoxal sulfate, readily prepared from acetylene tetrachloride and oleum, gave a nearly quantitative yield of glyoxal tetramethyl acetal when heated with calcium chloride dissolved in absolute methyl alcohol. The new acetal had the following physical constants: b. p. 159° (754 mm.); 98–100° (100 mm.);  $n_D^{20}$  1.4010;  $n_D^{25}$  1.3985;  $d_{25}^{25}$  0.9876.

2. The tetramethyl acetal gave on acid hydrolysis a quantitative yield of glyoxal and could be estimated by methods used for the latter.

3. The acetal was an accessible, stable and satisfactory standard in the colorimetric determination of glyoxal.

CAMBRIDGE, MASS.

RECEIVED DECEMBER 21, 1938

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Oxidation of Methyne and Methylene Groups by Ozone

BY JOHN R. DURLAND<sup>1</sup> AND HOMER ADKINS

Recently an attempt was made to determine with ozone the position of unsaturation in a hydrophenanthrene containing one double bond.<sup>2</sup> These experiments were made upon the basis of the naïve assumption that ozone was a rather specific reagent for alkene linkages. The chief product of the ozonization of the unsaturated hydrophen-

anthrene was an unsaturated ketone, produced by the oxidation of a methylene group, the alkene linkage remaining intact. It therefore seemed advisable to ozonize representative saturated cyclic hydrocarbons. As a result of these experiments there have been obtained saturated alcohols, ketones and acids, and even more surprisingly, unsaturated ketones and hydrocarbons. The yields, in several cases, have been from 20 to 35% of the theoretical.

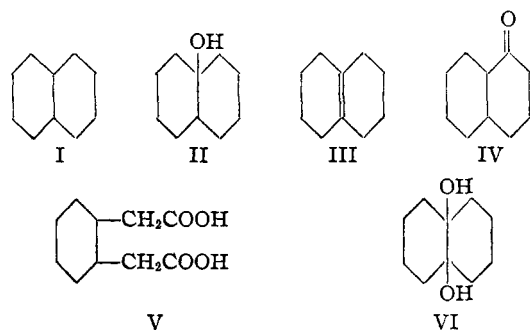
Among the saturated compounds, cyclohexane

(1) At various times during the progress of this work Mr. Durland has been a teaching assistant of the University, a research assistant supported by the Wisconsin Alumni Research Foundation and a Fellow supported by the Monsanto Chemical Company.

(2) Durland and Adkins, *THIS JOURNAL*, **60**, 1501 (1938).

was the most resistant toward ozone, the products identified being cyclohexanone, formic and adipic acids. More interesting results were obtained with decalin, decahydronaphthalene, I. The *cis*-decalin oxidizes more rapidly than the *trans* isomer so that if a mixture of the isomers is ozonized, the products are chiefly from the *cis* compound. Subsequent studies were therefore made with pure *cis* or *trans* isomer.

The fractionation of the products from the ozonization of 26 g. of *cis*-decalin for one hundred forty-seven hours at 0°, gave 7.4 g. of *cis*-decahydronaphthol-9, II, 2 g. of  $\Delta$ -9,10-octahydronaphthalene, III, and small amounts of *cis*- $\alpha$ -decalone, IV. About 10 g. of a mixture of unidentified acids was also obtained.



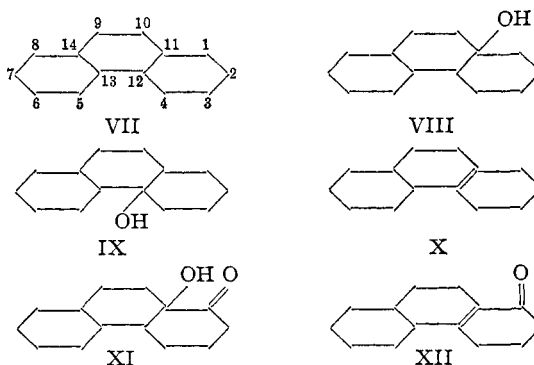
*trans*-Decalin gave in 28% yield the *trans*-decahydronaphthol-9, II, and the *trans*- $\alpha$ -decalone, IV, but unless special precautions were taken the chief product was the octalin, III, in 21% yield. A mixture of acids similar in amount to that from the *cis* isomer was obtained. Among these was identified *trans*-cyclohexane-1,2-diacetic acid, V.

The ozonization of the *cis* isomer of II gave the ditertiary glycol, VI, as well as a mixture of acids. The *cis* and *trans* isomeric alcohols, II, differ from each other considerably with respect to their ease of dehydration to the octalin, III. The *trans* isomer is so easily dehydrated that it could not be obtained except in traces unless care was taken to evaporate solvents under reduced pressure, to remove traces of drying agent and to distill the alcohol at pressures of less than 2 mm.

The ozonization of the saturated tetradecahydrophenanthrene, VII, (39 g.) gave three tertiary alcohols (12 g.), a hydroxy ketone (2 g.), an unsaturated ketone (1 g.), an unsaturated hydrocarbon and acids (21 g.). It is not possible definitely to assign structures to all of these compounds although certain conclusions may safely be drawn. For the sake of convenience in present-

ing the results, the structures will be represented as in formulas VIII to XII, inclusive.

Since only two structural isomeric tertiary alcohols can be derived from tetradecahydrophenanthrene, *i. e.*, VIII and IX, one of the three tertiary alcohols obtained must be a stereoisomer of one of the other two. Any of these three alcohols upon dehydration would presumably give the dodecahydrophenanthrene X, although IX might also give the double bond in the 12-13-position. The unsaturated hydrocarbon obtained by ozonization appears to be the same as that previously obtained,<sup>2</sup> in which the double bond is believed to be located as in X. The ease of dehydration of the hydroxy ketone indicates that the hydroxyl group is on a tertiary carbon atom as indicated in XI. The dehydration product is the same ketone



as that formed by the oxidation of X, hence the double bond in the unsaturated ketone is believed to be as indicated in formula XII. The position of the carbonyl group in the ketones is quite uncertain although for the reasons given below it is probably on the 1-, 4- or 10-carbon. In formulas XI and XII the carbonyl is arbitrarily placed at the 1-carbon. The unsaturated ketone reported here is not the same one as that obtained by Pinkney, Nesty, Wiley and Marvel<sup>3</sup> in which they believe the oxygen to be in the 9-position.

The unsaturated ketone, XII, is produced in good yield (35%) by the ozonization of the unsaturated hydrocarbon, X. The fact that ozone apparently does not add to the alkene linkage in X is, of course, understandable in the light of the resistance of this compound toward the addition of hydrogen.<sup>2</sup> The methylene groups in the 1-, 4- and 10-positions are in the alpha position with respect to the vinyl group and so pre-

(3) Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, 58, 972 (1936). Rapson and Robinson have described a ketone differing from Marvel's in that the double bond is in the 10-11-position [J. Chem. Soc., 1285 (1935)].

sumably would be the ones labilized toward oxidation as are the hydrogens on a carbon atom alpha to a benzenoid, pyrroloid or pyridinoid ring. An even more closely related case is reported by Hüchel<sup>4</sup> and his associates, who obtained  $\Delta$ -9,10-octalone-1 by the oxidation of  $\Delta$ -9,10-octalin. These facts suggest that the carbonyl group is in the 1-, 4- or 10-position.

The course of the oxidation of the saturated hydrocarbons seems fairly clear. That is, ozone reacts primarily at the tertiary carbon atoms. Oxidation subsequently takes place at secondary carbon atoms to give hydroxy ketones. The dehydration of these alcohols gives unsaturated hydrocarbons or unsaturated ketones. Further oxidation gives acids.

The use of ozone as a reagent for the oxidation of steroids is being investigated and the results of this work will be reported later. Cholestanol has been oxidized rapidly in 38% yield to cholestanone. The side chain is in part removed as methyl isohexyl ketone and various cyclic ketones and acids are produced by the ozonization of cholestanol and of dibromocholesteryl acetate.

### Experimental Part

The ozonizations were carried out at 0° in a carbon tetrachloride solution, by passing a stream of oxygen, containing 1 to 2% ozone, at a rate of 2 to 3 liters per hour. The product which separated as a viscous mass on the surface of the solution was removed by filtering through a fritted glass funnel at the end of each ten or twelve hours. The product was then washed from the funnel with acetone. After the completion of an ozonization the acetone and carbon tetrachloride were evaporated, first on a steam-bath and then at 30 mm. at 30°. The solution of products was then stirred with water at 60° for an hour. In some cases 2% hydrogen peroxide was added during hydrolysis.

The solution was extracted with ether and the extract washed with water, then with a sodium carbonate solution, again with water and then dried over anhydrous copper or sodium sulfate. The compounds in the ether solution were then fractionated in a modified Widmer column,<sup>5</sup> having a helix 15 cm. in length with 15 turns. The acids (except formic) were recovered by acidifying the water solutions with phosphoric acid, extracting with ether, drying and evaporating the ether. Formic acid was characterized by Duclaux values and estimated by titration. Acids could sometimes be crystallized from an ether-chloroform mixture. If this failed, they were distilled at 1 to 2 mm. through the modified Widmer and then attempts again made to crystallize the products.

**Cyclohexane.**—Seventy-eight grams of the hydrocarbon ( $n_D^{25}$  1.4229 by hydrogenation of thiophene-free benzene) was ozonized for one hundred hours. About 55 g. reacted.

(4) Hüchel, Daneel, Schwartz and Gercke, *Ann.*, **474**, 121 (1929).

(5) Martha E. Smith and Adkins, *This Journal*, **60**, 662 (1938).

Duclaux values and titration and fractionation indicated that about 3.2 g. of formic acid had been produced. Adipic acid was crystallized out (7.0 g.) and identified by mixed melting point determination. The neutral fraction was treated with Girard's<sup>6</sup> reagent P and 2.8 g. of "ketonic" material separated. The ketone was distilled and identified through its 2,4-dinitrophenylhydrazone, m. p. 157–158°, as cyclohexanone.

**Decalins.**—Naphthalene was hydrogenated over Raney nickel at 190–250° under 200 atm. of hydrogen. The product, b. p. 188–192°,  $n_D^{25}$  1.4745, was then fractionated at 9 mm. through a column containing glass helices. The dimensions of the column were 16 mm. by 1.2 m. (We are indebted to Mr. Howard Waddle for the design and construction of the column.) The properties of the products were as follows: *trans*-decalin, b. p. 61.5–62° (9 mm.), 69–69.5° (15 mm.),  $n_D^{25}$  1.4689; *cis*-decalin, b. p. 66.5–67° (9 mm.),  $n_D^{25}$  1.4800.

*cis*-Decalin (30 g.), in 250 ml. of carbon tetrachloride, was ozonized for one hundred and forty-seven hrs. There were isolated 4 g. of unchanged decalin, 7.4 g. of II (*cis*), 2.2 g. of III and 10 g. of a mixture of acids.

*trans*-Decalin, 34 g., under similar conditions, gave 5.5 g. of III, 8 g. of recovered *trans*-decalin and 10 g. of acids, from which was isolated 0.8 g. of V. In another ozonization 8 g. of *trans*-decalin in 150 ml. of carbon tetrachloride after fifty hours gave 1.9 g. of recovered *trans*-decalin, 1.8 g. of II (*trans*) and 0.1 g. of V from 3 g. of acids separated.

From the ozonization of *cis*-decalin  $\Delta$ -9,10-octahydronaphthalene, b. p. 66–67° (9 mm.),  $n_D^{25}$  1.4953, was separated by fractionation and identified by the preparation of the dibromide, m. p. 163–164°, and the nitrosyl chloride addition product, m. p. 90–91°, as by Hüchel.<sup>4,7</sup> *cis*-Decahydronaphthol-9 was recrystallized from petroleum ether and sublimed in long needles, m. p. 64.5–65°, b. p. 98–99° (9 mm.), 69–70° (1 mm.), which had the characteristic odor.<sup>4</sup>

*cis*- $\alpha$ -Decalone was separated from a fraction, b. p. 100–120° (9 mm.), as a semicarbazone, m. p. 222–223°.<sup>7</sup>

The neutral fraction from *trans*-decalin gave only the  $\Delta$ -9,10-octahydronaphthalene when worked up as above. However, if the solvent was removed at 20° the *trans*-decahydronaphthol-9 (m. p. 50–52° in hexagonal plates after sublimation) could be distilled at 57–59° (1 mm.). The semicarbazone (0.01 g.) of *trans*- $\alpha$ -decalone,<sup>8</sup> m. p. 227–230°, was obtained from a fraction boiling above the alcohol.

*trans*-Cyclohexane-1,2-diacetic acid, m. p. 166–167° (from water), was separated from the mixture of acids produced by ozonization of *trans*-decalin, through the use of a chloroform-ether mixture.

***cis*-Decahydronaphthol-9.**—The alcohol (6.2 g.) m. p. 63–65°, in 200 ml. of carbon tetrachloride was ozonized for twenty-six hours at 0°. There was obtained by the usual procedure 1.74 g. of neutral fraction, 1.8 g. of formic acid and 1.0 g. of a mixture of other acids.  $\Delta$ -9,10-Octalin (0.34 g.) and 0.02 g. of a glycol, decahydronaphthadiol-9,10, m. p. 86–89°,<sup>9</sup> were obtained.

(6) Girard and Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

(7) Hüchel and Naab, *Ann.*, **502**, 149 (1933).

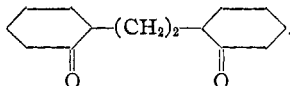
(8) Hüchel, *ibid.*, **441**, 1 (1925).

(9) Crieges, *ibid.*, **522**, 75 (1936).

TABLE I  
 ANALYTICAL DATA

Name	Formula	$n_D^{25}$ or m. p.	°C.	B. p. Mm.	Analyses			
					Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Dodecahydrophenanthrene	C <sub>14</sub> H <sub>22</sub>	1.5135	129	9	88.34	88.04	11.65	11.16
Dodecahydrophenanthrone	C <sub>14</sub> H <sub>20</sub> O	1.5309	150-155	8	82.29	82.36	9.89	10.18
2,4-Dinitrophenylhydrazone of dodecahydrophenanthrone	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub>	82-84° 112-115°	.....	...	62.49	62.15	6.30	6.46
Tetradecahydrophenanthrol "A"	C <sub>14</sub> H <sub>24</sub> O	1.5188	130-132	8	80.70	80.37	11.61	10.58
Tetradecahydrophenanthrol "B"	C <sub>14</sub> H <sub>24</sub> O	1.5183	147-150	7	80.70	80.68	11.61	11.63
Tetradecahydrophenanthrol "C"	C <sub>14</sub> H <sub>24</sub> O	1.5198	114-116	0.4	Z, 1.00 80.70	1.03 80.53	11.61	11.03
Tetradecahydrophenanthradiol "E"	C <sub>14</sub> H <sub>24</sub> O <sub>2</sub>	1.5226	190-198	8	Z, 1.00 74.94 Z, 2.00	0.97 75.07 2.00	10.78	10.60

**Dodecahydrophenanthrene.**—A mixture of isomers (15 g.,  $n_D^{25}$  1.5118) in 150 ml. of carbon tetrachloride was ozonized for thirty-six hours. There was obtained 9.2 g. of the 2,4-dinitrophenylhydrazone of the unsaturated ketone, dodecahydrophenanthrone XII, along with 2.3 g. of the hydrazone of



was formed by the oxidation of  $\Delta$ -12,13-dodecahydrophenanthrene present in the mixture of isomeric dodecahydrophenanthrenes.<sup>2</sup> The dinitrophenylhydrazone of XII can be crystallized from butanol or ethanol but the crystals shrink and "melt" to a dark red tar at room temperatures in contact with the liquid, or vapors of, ether, dioxane, petroleum ether, benzene or chloroform. The hydrazone exists in two forms, one reddish-orange colored, m. p. 82-84°, and the other dark red, m. p. 112-115°. Both show the same analysis but the orange is converted to the red compound upon recrystallization.

**Tetradecahydrophenanthrene.**—Two ozonizations will be described, from the first of which dodecahydrophenanthrene and dodecahydrophenanthrone were the products characterized, while in the second four alcohols were also obtained.

Tetradecahydrophenanthrene (22 g.) in 100 ml. of carbon tetrachloride was ozonized for ninety hours. In working up the products 4 g. of dodecahydrophenanthrene, b. p. 124-128 (8 mm.), 1.3 g. of the ketone, XII, b. p. 115-127° (1.5 mm.), and 8.5 g. of acids were obtained. Upon re-fractionation the dodecahydrophenanthrene was taken at 129° (9 mm.),  $n_D^{25}$  1.5135 and the ketone, 150-155° (8 mm.),  $n_D^{25}$  1.5309. The ketone gave both the orange and red dinitrophenylhydrazones corresponding in m. p. and mixed m. p. to the derivatives obtained in the ozonization of dodecahydrophenanthrene as described in the preceding section. The ketone was obtained in higher yield in materially shorter time from the dodeca- than from the tetradecahydrophenanthrene.

Tetradecahydrophenanthrene in 170 ml. of carbon tetrachloride was ozonized for one hundred and thirty-four hrs. Ten grams of the 50 g. of hydrocarbon submitted to ozonization was recovered unchanged. Four tertiary alcohols were isolated, *i. e.*, 1.9 g. "A," b. p. 130-132° (8 mm.),  $n_D^{25}$  1.5188; 8.0 g. "B," b. p. 147-150° (7 mm.),  $n_D^{25}$  1.5183,  $d_4^{25}$  1.018; and 1.9 g. of "C," b. p. 114-116° (0.4 mm.),  $n_D^{25}$  1.5198. There was also obtained 2 g. of a

ketoalcohol, "D," b. p. 145-148° (0.2 mm.),  $n_D^{25}$  1.5408, 1 g. of the dodecahydrophenanthrone, b. p. 150-155° (8 mm.), and 21 g. of a mixture of acids.

Both alcohols "A" and "B" were hydrogenated over Raney nickel at 200-250° in methylcyclohexane, one mole of hydrogen being absorbed per mole of compound, to give tetradecahydrophenanthrene,  $n_D^{25}$  1.5003 to 1.5009. In the case of "A" the reaction took place within two hours at 200° while with "B" eight hours at 250° was required. "A" was also converted by dehydration, during attempts at purification, to dodecahydrophenanthrene,  $n_D^{25}$  1.5135, which showed the correct analysis for carbon and hydrogen. Alcohol "C" was also dehydrated at its boiling point to give an unsaturated compound, but the quantity available was not sufficient to make it possible to identify the product as dodecahydrophenanthrene. The greater ease of dehydration and hydrogenation of "A" as contrasted with the isomeric alcohols suggests that it is the *trans* isomer.

The results of analysis for carbon and hydrogen and for active hydrogen by the Zerewitinoff method are given in Table I. The analysis for active hydrogen for alcohol "A" was low, apparently because of the insolubility of the addition product in ether. In the case of "C" and "E" the analysis was made in pyridine solution. The analysis could not be repeated on "A" because it was dehydrated during an attempted distillation.

None of the alcohols would form derivatives with benzoyl chloride and all of them reacted with phenyl isocyanate to give diphenylurea as the result of dehydration of the alcohol.

The ketoalcohol fraction, b. p. 145-148° (0.2 mm.), decreased in amount on distillation giving a lower boiling product which gave the dinitrophenylhydrazone of the unsaturated ketone XII. The keto alcohol in methylcyclohexane absorbed one mole of hydrogen over Raney nickel at 125° and gave a glycol, "E."

### Summary

Ozone reacted at 0° at saturated as well as unsaturated linkages oxidizing  $\text{>CH}$  and  $\text{>CH}_2$  groups to tertiary alcohols and ketones, respectively. Ozone in one case reacted with a methylene group in preference to a carbon to carbon double bond, so that an unsaturated ketone was

produced in good yield from an unsaturated hydrocarbon. Several tertiary alcohols have been isolated as the result of the ozonization of alicyclic hydrocarbons. Unsaturated hydrocarbons or ketones may be formed by the dehydration of these alcohols under rather mild conditions.

Rather high yields of acids have been formed as the result of the ozonization of saturated hydrocarbons. These experiments give striking evidence of the mildness of the conditions necessary for oxidation in alicyclic compounds.

MADISON, WISCONSIN RECEIVED DECEMBER 10, 1938

[CONTRIBUTION NO. 147 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

## Symmetrical Dialkoxyacetones

BY HENRY R. HENZE AND BURL G. ROGERS

Although considerable attention has been given to the synthesis of keto ethers, especially of late in this Laboratory,<sup>1</sup> very little study seems to have been made of the preparation of dialkoxy ketones. In fact, the production of but one example of this type, namely, diethoxyacetone, is recorded in the chemical literature.

Apparently the initial synthesis of diethoxyacetone<sup>2</sup> was accomplished through hydrolysis of ethyl ethoxyacetoethoxyacetate. Subsequent investigators,<sup>3</sup> too, with the exception of Gintl,<sup>4</sup> who obtained diethoxyacetone in low yield by the destructive distillation of calcium ethoxyacetate, have used the Claisen condensation in order to prepare this substituted ketone.

Since, in connection with another problem, several dialkoxyacetones were needed, attention has been directed to the development of a general method for their preparation. The utilization of the Claisen condensation for the synthesis of *sym*-dialkoxyacetones has been studied and found to be both tedious and productive of very unsatisfactory over-all yields. Obviously, the interaction of *sym*-dichloroacetone with alcoholates should constitute a direct method of obtaining the desired series of compounds; however, such treatment invariably yielded a brown, resinous mass which could not be distilled.<sup>5</sup> Finally, it was found that good yields of the substituted ketones could be obtained by the oxidation of *sym*-dialkoxypropanols. The efficacy of this method

has been tested by the successful preparation of nine *sym*-dialkoxypropanols, through interaction of *sym*-glycerol dichlorohydrin and appropriate sodium alcoholates, and their subsequent conversion to the corresponding ketones through oxidation by means of sodium dichromate and sulfuric acid.

### Experimental

**Preparation and *sym*-Dialkoxyacetones by the Claisen Condensation.**—Five *n*-alkyl chloroacetates (methyl through amyl) required in this investigation were synthesized in 70% yield according to the method of Conrad<sup>6</sup> and converted in 50% yield into the corresponding *n*-alkyl *n*-alkoxyacetates following a procedure outlined by Schreiner.<sup>7</sup> In turn the alkyl alkoxyacetates were condensed to *n*-alkyl *n*-alkoxyaceto-*n*-alkoxyacetates, by means of the appropriate sodium alcoholate, and hydrolyzed by action of aqueous potassium carbonate solution. The yields of *sym*-di-*n*-alkoxyacetones were low, usually being but 10% of the theoretical. Data concern-

TABLE I  
COMPOUNDS AND PROPERTIES

Compound	<i>n</i> -Amyl chloroacetate	<i>n</i> -Butyl <i>n</i> -butoxyacetate	<i>n</i> -Amyl <i>n</i> -amoxyacetate
Yield, %	68	61	34
B. p. corr. { °C.	198-199	123-123.5	148-149
{ Mm.	744	30	35
$d_{20}^4$	1.0461	0.9214	0.9112
$n_D^{20}$	1.4335	1.4204	1.4284
$\gamma^{20}$ , dynes/cm. <sup>a</sup>	28.03	26.01	26.96
$MR$ {	Calcd.	51.68	60.91
	Found	40.96	51.72
$P$ {	Calcd. <sup>b</sup>	370.2	470.0
	Found	361.9	461.2
Free surface energy, ergs	816.1	914.7	1023.2

<sup>a</sup> Surface tensions were determined at 20° by means of a Cassel precision capillarity meter, *Chem. Ztg.*, **53**, 479 (1929).

<sup>b</sup> Summation values of the atomic parachor values of Sugden, *J. Chem. Soc.*, **125**, 1180 (1924).

(6) Conrad, *Ann.*, **188**, 218 (1877).

(7) Schreiner, *ibid.*, **197**, 8 (1879).

(1) *This Journal*, **56**, 1350 (1934); *ibid.*, **59**, 540 (1937); *J. Org. Chem.*, **2**, 508 (1938).

(2) Grimaux and Lefèvre, *Bull. soc. chim.*, [3] **1**, 11 (1889).

(3) Erlenbach, *Ann.*, **269**, 30 (1892); Darzens and Meyer, *Compt. rend.*, **198**, 478 (1934).

(4) Gintl, *Monatsh.*, **15**, 805 (1894).

(5) It is of interest to note that Grimaux and Lefèvre (ref. 2) reported that they were unable to effect the synthesis of *sym*-diethoxyacetone by interaction of sodium ethylate and *sym*-dichloroacetone. Although reaction occurred, they obtained only resinous material.