

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

A Novel Synthesis of Substituted Phenylglyoxylic Acids<sup>1</sup>By I. MOYER HUNSBERGER<sup>2</sup> AND E. D. AMSTUTZ

Up to the present time there has not been available a general and convenient method for the synthesis of hydroxy-substituted phenylglyoxylic acids. Of the methods which have been used for the preparation of phenylglyoxylic acids only one<sup>3</sup> appears to be suited to the use of mono- and polyhydroxybenzenes. This procedure uses cyanogen and yields by-products formed by reaction of both nitrile groups.

applied to resorcinol and orcinol, 2,4-dihydroxyphenylglyoxylic acid and 2,4-dihydroxy-6-methylphenylglyoxylic acid lactone (IV), respectively, being obtained in agreement with Karrer and Ferla's<sup>3</sup> results using cyanogen. The general procedure then was extended to 4-ethyl-, 4-*n*-butyl-, 4-*n*-hexyl-, 4-*n*-octyl-, 4-*n*-nonyl-, 4-*n*-dodecyl- and 2-ethyl-4-methyl-resorcinol, the results of which are recorded in Table I. In all cases

TABLE I

## PREPARATION OF HYDROXYPHENYLGLYOXYLIC ACIDS

Substituted 2,4-dihydroxyphenylglyoxylic acids	Crystallization solvent	Yield, %	M. p., °C.	Color	Analyses, %			
					Calcd. C	Calcd. H	Found C	Found H
Lactone of 6-methyl-(IV) <sup>a</sup>	None	53	213.1-215 <sup>b</sup>	Yellow				
5-Ethyl-	Water	60	148.5-149.4	Golden yellow	57.14	4.80	57.22	5.66
5- <i>n</i> -Butyl-	Water	70	152-154	Light yellow	60.50	5.92	60.75	6.09
5- <i>n</i> -Hexyl-	5% ethanol	50	151-153.2	Bright	63.23	6.77	62.84	7.03
5- <i>n</i> -Octyl- <sup>c</sup>	20% ethanol	..	144.2-145	yellow	65.29	7.54	65.01	7.82
5- <i>n</i> -Nonyl- <sup>d</sup>	40% ethanol	30	143.5-146 <sup>e</sup>	Bright	66.21	7.84	66.58	8.18
5- <i>n</i> -Dodecyl-	65% ethanol	62	150.5-152 <sup>e</sup>	yellow	68.55	8.62	68.74	8.70
3-Ethyl-5-methyl-(II) <sup>f</sup>	Bz. pet. ether (b. p. 35-60°)	15	128-129.5	Light orange	58.92	5.39	58.70	5.46

<sup>a</sup> The insoluble reaction product was removed by filtration, washed with fresh ether and hydrolyzed directly to produce the lactone by thirty minutes heating in water near the boiling point. Extraction of the aqueous filtrate with ether followed by removal of the acid with sodium bicarbonate yielded additional (IV). <sup>b</sup> Karrer and Ferla (ref. 3) listed 212°. <sup>c</sup> Anhydrous zinc chloride was added. A suck-back of the concentrated sulfuric acid traps necessitated pouring contents of reaction flask and acid traps separately into ice. The solidified material thus obtained was saponified under nitrogen to the crude acid. <sup>d</sup> Since no crystallization had occurred, water and ice were added to the reaction mixture. After removing the ether the ethyl ester separated as a red oil which was extracted with ether and the ether with sodium bicarbonate. Upon heating the latter a cream-colored precipitate settled out and was filtered off. Its solubility in water indicated it to be the sodium salt, and acidification produced the crude acid. Evaporation of the ether produced the ethyl ester as a red oil, from which more crude acid was obtained as above. Fractionation was effected by successive dilutions with water. <sup>e</sup> Uncorrected. <sup>f</sup> The ethyl ester was obtained as brown-orange crystals, m. p. 74-77°, saponification of which produced crude II.

In this paper is reported the synthesis of a series of new 2,4-dihydroxy-5-*n*-alkylphenylglyoxylic acids (I) and of 2,4-dihydroxy-3-ethyl-5-methylphenylglyoxylic acid (II) by condensation of alkylresorcinols with ethyl cyanofornate in the presence of anhydrous hydrogen chloride. These glyoxylic acids were desired in order to compare their antibacterial activity with that of the alkylresorcinols from which they are derived. Especial interest was taken in compound II because of the striking structural similarity of one of its quinonoid forms (such as IIa and b) with that deduced<sup>4</sup> for the antibiotic citrinin (III). Further, it was felt that the cyanofornate condensation might have some value in synthetical work on citrinin.

The ethyl cyanofornate condensation first was

(1) Taken in part from a thesis submitted by I. Moyer Hunsberger in partial fulfillment of the requirements for the M.S. degree.

(2) The Wm. S. Merrell Co. Fellow, 1945-1946; American Chemical Society Predoctoral Fellow, 1946-.

(3) Karrer and Ferla, *Helv. Chim. Acta*, **4**, 203 (1921).

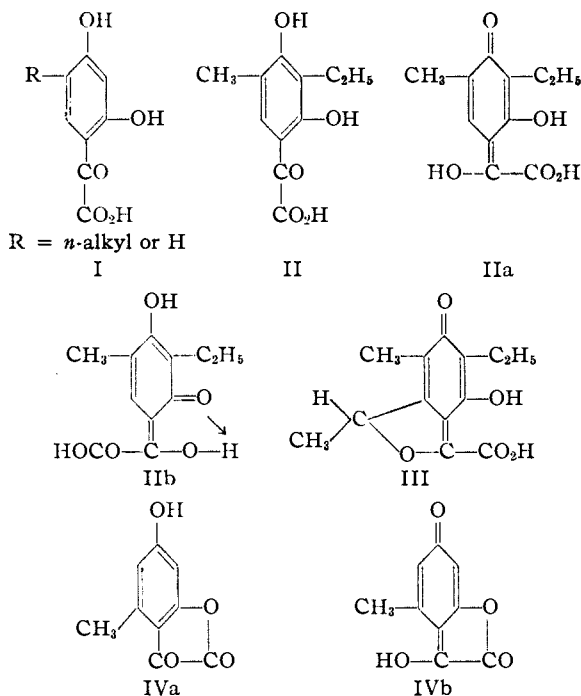
(4) Coyne, Raistrick and Robinson, *Phil. Trans. Roy. Soc.*, **220**, 297 (1931); Hetherington and Raistrick, *ibid.*, **220**, 269 (1931). Very recent evidence [cf. Sprenger and Ruoff, *J. Org. Chem.*, **11**, 189 (1946); Gore, Panse and Venkataraman, *Nature*, **157**, 333 (1946)] has cast doubt on the correctness of structure III.

dry hydrogen chloride was introduced into a dry ethereal solution of ethyl cyanofornate and alkylresorcinol. After a length of time depending on the individual reaction the ketimine ethyl ester hydrochloride precipitated as highly-colored crystals which were hydrolyzed by hot water to the glyoxylic acid ethyl ester and thence by water or dilute alkali to the free glyoxylic acid (I).<sup>5</sup> In no case did the esters crystallize well so that purification was effected after saponification. Purification of the acids increased in difficulty with increase in weight of the 5-*n*-alkyl group.

Although the position of the entering keto-carboxyl (COCO<sub>2</sub>H) group as *ortho* to one and *para* to the other phenolic hydroxyl group of the resorcinol nucleus was not proved rigorously in this investigation,<sup>6</sup> the general behavior of resor-

(5) Only in the case of compounds derived from 4-*n*-octyl- and 4-*n*-nonyl-resorcinol did the ketimine salt fail to crystallize, a circumstance very probably the result of failure to introduce hydrogen chloride for a sufficient period. However, slight modification of the general procedure used in handling the reaction product permitted isolation of the corresponding glyoxylic acids in a pure state.

(6) Bulow and Wagner [*Ber.*, **36**, 1941 (1903)] established the position of the COCO<sub>2</sub>H group in 2,4-dihydroxyphenylglyoxylic acid by their preparation of this compound from 2-phenyl-7-hydroxy-1,4-benzopyranol-4-carboxylic acid.



cinol lends strength to the proposed formulation. That the initial insoluble reaction products are ketimine hydrochlorides is indicated by their solubility in water and insolubility in ether. The condensation therefore is related closely to the familiar Gattermann and Houben-Hoesch syntheses.

Since neither the ketocarboxyl nor resorcylic fragment of the 2,4-dihydroxyphenylglyoxylic acid molecule is strongly chromophoric, the bright yellow color exhibited by such compounds is considered to be the result of a contribution of the *ortho* (such as IIb) or possibly the *para* (such as IIa) methylenequinone structure.<sup>7</sup> By supposing chelation to exert a color-deepening effect (resonance stabilization of the *ortho*-quinonoid form<sup>8</sup>), a rather satisfactory correlation between structure and the color of numerous hydroxy-substituted acetophenones, benzophenones, benzoquinones, naphthoquinones, anthraquinones and phenylglyoxylic acids, as compared to the respective unsubstituted compounds, can be drawn.

All 2,4-dihydroxy-5-alkylphenylglyoxylic acids prepared in this investigation gave dark red-brown

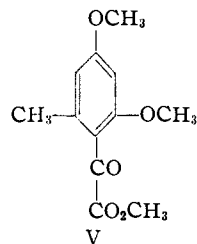
(7) Chromophoric character is an attribute of such a structure not without precedent, for almost twenty years ago Robertson and Robinson [*J. Chem. Soc.*, 2106 (1927)] used a similar assumption to explain the bright yellow color of 2,6-dihydroxy-3,5-dimethylbenzaldehyde. Furthermore, it is expected that the two *ortho-para* orienting ring substituents would combine their influence with that of the carboxyl group on the methylene carbon atom to stabilize the methylenequinone structure [cf. Gomberg and West, *THIS JOURNAL*, **34**, 1529 (1912)] in the case of 2,4-dihydroxyalkylphenylglyoxylic acids.

(8) Cf. J. R. Johnson, "Modern Electronic Concepts of Valence," Vol. II, chapter 25, of "Organic Chemistry," H. Gilman, editor-in-chief, second edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1870; Geissman, Schlatter, Webb and Roberts, *J. Org. Chem.*, **11**, 741 (1946).

colorations with ferric chloride and colors ranging from light yellow-brown to dark bluish-green with a mixture of thiophene-benzene and concentrated sulfuric acid.

An attempt to form a 2,4-dinitrophenylhydrazone of the hexyl acid failed. This result is in accord with Karrer and Ferla's<sup>3</sup> inability to form either an oxime or phenylhydrazone from 2,4-dihydroxyphenylglyoxylic acid and also bespeaks an interaction of the carbonyl and the *ortho* hydroxyl group. The many earlier reports of facile oxime, hydrazone, phenylhydrazone and bisulfite addition product formation<sup>9</sup> can be understood more readily when it is recalled that none of the early acids contained both *ortho* and *para* hydroxyl groups.

We have not been able to isolate any pure crystalline materials from the diazomethane methylation of the acids of series I. Whereas the relationship between IIa and b well may involve the phenomenon of resonance, we felt that with IVa and b the equilibrium should be rather of the tautomeric type; hence, the isomer IVb conceivably might have real and independent existence. Thus, methylation with diazomethane under essentially anhydrous conditions (avoiding lactone hydrolysis) could yield both colorless (from IVa) and colored (from IVb) methyl ethers. We were successful in isolating only the latter and in small yields. The material possessed a deep yellow color with analytical data corresponding to that calculated for a monomethyl ether of IV. Moist diazomethane yielded an orange-red crude product from which was isolated the colorless trimethylated derivative V, which corresponded in every detail to the product obtained by Karrer<sup>3</sup> with dimethyl sulfate and alkali. Both methylation and hydrolysis undoubtedly proceeded simultaneously during this wet methylation. We believe the orange-red color of the crude product was due to the presence of materials which first were methylated and then perhaps hydrolyzed and further methylated. However, we were unable to isolate any such products in a pure state.



Work along the general lines outlined in this paper is being continued.

All the compounds prepared were tested for antibacterial activity against *S. aureus*, *E. coli* and *B. subtilis* by both the broth serial dilution (BSD) and agar streak plate (ASP) techniques. The so-

(9) Schad, *Ber.*, **26**, 216 (1893); Tiemann, *ibid.*, **24**, 2877 (1891); Vorländer, *ibid.*, **44**, 2463 (1911); Bouveault, *Bull. soc. chim.*, [3] **18**, 1014 (1896).

dium salt of the 5-*n*-octyl-2,4-dihydroxyphenylglyoxylic acid was the most active, completely inhibiting the growth of *S. aureus* at 1:12,500 dilution (BSD) and *B. subtilis* at 1:25,000 dilution (ASP). None of the compounds had significant action against *E. coli*. The octyl compound was also active at 1:8,000 dilution against the fungi *Epidermophyton floccosum*, *Microsporon canis* and *Trichophyton rubrum*.

**Acknowledgments.**—The authors wish to express their appreciation to the Wm. S. Merrell Company for financial assistance and to Drs. M. G. Van Campen, Jr., and Milton Foter for arranging the antibacterial and antifungal tests. We also appreciate the assistance rendered by Sharp and Dohme who generously supplied us with hexylresorcinol, and Mr. V. Warren Fox, who prepared some of the glyoxylic acid from hexylresorcinol.

### Experimental<sup>10</sup>

**4-Alkylresorcinols.**—All 4-alkylresorcinols used in this work were prepared by Clemmensen reduction of the ketone formed by condensation of resorcinol with the proper carboxylic acid in the presence of zinc chloride. Only in the purification of 4-*n*-dodecylresorcinol was modification of the standard procedure<sup>11</sup> necessary.

**2-Ethyl-4-methylresorcinol.**—2,6-Dihydroxyacetophenone was prepared by alkaline cleavage of 4-methyl-7-hydroxy-3-acetylcoumarin<sup>12</sup> and reduced to 2-ethylresorcinol by a slight modification<sup>13</sup> of Clemmensen's method. The latter compound was transformed to 2,4-dihydroxy-3-ethylbenzaldehyde by a modification<sup>14</sup> of the Gattermann aldehyde synthesis. Another Clemmensen reduction then produced the desired 2-ethyl-4-methylresorcinol, which was purified according to Robinson and Shah.<sup>15</sup>

**2,4-Dihydroxyphenylglyoxylic Acid.**—The preparation of this acid illustrates the general procedure for all hydroxyphenylglyoxylic acids.

In a flask equipped with reflux condenser, stirrer and gas inlet tube were placed 11.0 g. (0.100 mole) of vacuum dried resorcinol, 10.8 g. (0.109 mole) of ethyl cyanofornate<sup>16</sup> and 100 ml. of absolute ether (dried over sodium). A rapid stream of dry hydrogen chloride was introduced for two hours, cold water being used at intervals to dissipate the heat generated. Hot water hydrolyzed the precipitated ketimine salt directly to a mixture of the crude keto acid (2.2 g.) and its ethyl ester (14.6 g.), the two being separated by extraction of an ethereal solution with sodium bicarbonate. The ester formed yellow-orange crystals, m. p. 65–68°, after recrystallization from water; it is soluble in benzene, ethanol, ether and chloroform, but insoluble in low-boiling petroleum ether.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>5</sub>: C, 57.1; H, 4.80. Found: C, 57.6; H, 5.12.

Saponification of this ester with 10% potassium hydroxide produced more of the desired acid as mustard-yellow

crystals, m. p. 161.5–163°,<sup>17</sup> after recrystallization from water.<sup>18</sup>

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>O<sub>5</sub>: C, 52.8; H, 3.32. Found: C, 52.7; H, 3.32.

On standing six days the ethereal mother liquor from the original insoluble ketimine salt deposited a small quantity of light yellow crystals. The ether was decanted and the crystals covered with fresh ether which was neutralized with sodium bicarbonate. Evaporation of the ether produced orange crystals, presumably the ketimine ethyl ester, which did not melt below 330°. This product was slightly soluble in ether but quite insoluble in water; it gave no halogen test with silver nitrate but evolved ammonia when treated with 50% potassium hydroxide.

We found that satisfactory neutral equivalents of the acids prepared in this investigation could be determined by visual titration in water or aqueous alcohol using phenolphthalein as indicator (two acid hydrogens titrated per mole) when the end-point was not obscured by fluorescence.<sup>19</sup>

**2,4-Dimethoxy-6-methylphenylglyoxylic Acid Methyl Ester (V).**—An ethereal solution, not previously dried, containing about 2.8 g. (0.065 mole) of diazomethane was added gradually to a solution of 2.3 g. (0.013 mole) of pure 2,4-dihydroxy-6-methylphenylglyoxylic acid lactone (IV) in 60 ml. of ordinary ether at 0°. Evaporation of the ether produced an orange-red solid from which 0.4 g. (14%) of pure ester (V) was obtained as snow-white crystals, m. p. 73–74°, by repeated fractional crystallization from aqueous acetic acid. Saponification of the ester yielded the colorless free acid, m. p. 138.8–139.2°. <sup>20</sup>

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>5</sub> (acid): C, 58.93; H, 5.40. Found: C, 59.12; H, 5.66.

**Monomethyl Ether of 2,4-Dihydroxy-6-methylphenylglyoxylic Acid Lactone.**—An ethereal solution containing ca. 2.1 g. (0.050 mole) of diazomethane (previously dried for three hours over potassium hydroxide and thirty minutes over sodium wire) gradually was added to 3.0 g. (0.017 mole) of 2,4-dihydroxy-6-methylphenylglyoxylic acid lactone (IV) dissolved in 70 ml. of absolute ether which had been dried over sodium. After six hours, the ether was evaporated to an oil which crystallized on standing overnight in a refrigerator. This solid was refluxed thirty minutes (nitrogen atmosphere) with excess 3% sodium hydroxide. The cold alkaline solution was filtered and acidified, whereupon 1.1 g. of crude product, m. p. 143–153°, separated.<sup>21</sup> This material was extracted twice with boiling water and the insoluble residue dissolved in hot 10% sodium bicarbonate solution and reprecipitated with acid. The yellow product thus obtained was extracted fractionally and crystallized with carbon tetrachloride to yield four fairly pure fractions (melting between the extremes of 163° and 171°), which after combination and retreatment with sodium bicarbonate and acid, as before, produced a small amount of pure monomethyl ether of IV as a bright yellow precipitate, m. p. 168–170.5°. There was no color with ferric chloride.

(17) Karrer and Ferla (ref. 3) listed 168° and stated that the value of 194° (ref. 6) was probably a typographical error.

(18) A few drops of concentrated hydrochloric acid added to an almost saturated solution hastened crystallization.

(19) Titrations performed with a Beckmann pH meter produced curves having well defined equivalence points corresponding to titration of one acid hydrogen ion. These equivalence points fell in a pH range of 5.12 to 5.80, indicating the strongly acidic nature of the compounds. However, the neutral equivalents calculated from such points were almost invariably 18 to 70 units too high. These results may be due to the presence of a phenolic group ortho to the ketocarboxyl side chain, since Anschütz [*Ann.*, **366**, 80 (1909)] found *o*-acetoxyphenylglyoxylic acid to behave normally on visual titration.

(20) Karrer and Ferla (ref. 3) reported 73–74° and 138–139° for the ester and acid, respectively.

(21) A considerable quantity of unreacted starting material (m. p. 206–209°) was recovered by ether extraction of the filtrate from the crude product. More starting material was recovered during later fractionations.

(10) All melting points are corrected for stem emergence unless specified otherwise.

(11) Dohme, Cox and Miller, *THIS JOURNAL*, **48**, 1688 (1926).

(12) Russell and Frye, "Organic Syntheses," **21**, 22 (1941).

(13) Russell, Frye and Mauldin, *THIS JOURNAL*, **62**, 1441 (1940).

(14) Adams and Levine, *ibid.*, **45**, 2373 (1923).

(15) Robinson and Shah, *J. Chem. Soc.*, 1491 (1934). They found that the intermediate 2,4-dihydroxy-3-ethylbenzaldehyde melted at 115–118°; we found 119.5–121°. The higher value probably can be attributed to the superiority of water to benzene as recrystallization solvent.

(16) Gluud, Nussler and Keller, German Patent 592,539; *Chem. Zentr.*, **105**, II, 3437 (1934).

*Anal.* Calcd. for  $C_{10}H_8O_4$ : C, 62.49; H, 4.20. Found: C, 62.89; H, 4.64.

### Summary

1. The condensation of ethyl cyanofornate with alkyl derivatives of resorcinol has been used to prepare a number of new 2,4-dihydroxyalkyl-phenylglyoxylic acids.

2. The use of ethyl cyanofornate is proposed

as a general method for introducing the ketocarboxyl (COCOOH) group into activated positions on aromatic nuclei.

3. All hydroxyphenylglyoxylic acids prepared in this work have been subjected to antibacterial and antifungal testing but none showed exceptional activity.

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RECEIVED JUNE 9, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGIA SCHOOL OF TECHNOLOGY]

## Alkoxyaryloxyketones and their Condensation with Isatins

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To continue our work<sup>1,2</sup> on the preparation of keto ethers and their conversion into substituted quinoline acids we have prepared a series of ketones from alkoxyphenols by the procedure of Hurd and Perletz.<sup>3</sup> The resulting alkoxyaryloxyketones have been condensed with both isatin and 5-methylisatin, by the method of Pfitzinger,<sup>4</sup> to produce 3-alkoxyaryloxy-4-quinaldinecarboxylic acids.

The yields of the ketones prepared ranged from 47.6%, in the case of the 2-methoxy-4-methylphenoxyacetone, to 73% for the 4-propoxyphenoxyacetone. All of the ketones were obtained, after purification, as light yellow, low-melting solids, which darkened on standing.

The potassium salts of the quinaldinecarboxylic acids were salted out by high concentrations of potassium hydroxide. In every instance, decarboxylation of these acids was observed to start well below the melting point, hence melting point values changed with the rate of heating and are of little significance.

### Experimental

**Preparation of Alkoxyaryloxyacetones.**—The procedure for the condensation of chloroacetone with the alkoxyphenols was based on the method of Hurd and Perletz.<sup>3</sup>

To a vigorously stirred and refluxing suspension of 0.4 mole of the alkoxyphenol and 57 g. (0.41 mole) of anhydrous potassium carbonate in 150 ml. of dry acetone was added over a period of thirty minutes a solution of 50 g. (0.54 mole) of chloroacetone and 3 g. of potassium iodide in 50 ml. of dry acetone. The chloroacetone mixture had

been allowed to stand for twenty hours prior to addition. After refluxing for seven hours, stirring was continued for an additional twenty hours at room temperature. The mixture was filtered and the salt washed well with dry acetone. To obtain the ketone from the filtrate it was diluted with water and cooled with ice. The precipitate was recrystallized twice from methanol and water, and again from cyclohexane. The essential data on the ketones and derivatives are tabulated in Table I.

**Preparation of 3-(4-Methoxyphenoxy)-4-quinaldinecarboxylic Acid.**—Fourteen and seven-tenths grams (0.1 mole) of isatin was dissolved in 200 ml. of 33% aqueous potassium hydroxide solution and 17 g. (0.1 mole) of 4-methoxyphenoxyacetone was added. The resulting mixture was heated under reflux on the steam-bath for four hours, and upon cooling a solid cake of potassium 3-(4-methoxyphenoxy)-4-quinaldinecarboxylate separated in the reaction flask. The latter was disintegrated and dissolved in 800 ml. of hot water. The resulting solution was boiled with Nuchar, filtered, cooled in ice, and the quinoline acid precipitated by the addition of acetic acid (1:1). The product was separated by filtration, suspended in 600 ml. of hot water, and converted into the soluble potassium salt by the addition of 33% potassium hydroxide. The treatment with Nuchar was repeated, and 23 g. (74% yield) of the purified acid was obtained. The product was dried over phosphorus pentoxide in a vacuum desiccator.

The remaining 3-alkoxyaryloxy-4-quinaldinecarboxylic acids were formed in essential accordance with this general procedure. In each case a small sample was recrystallized from a large quantity of water and this material used for

TABLE II  
3-ALKOXYARYLOXY-4-QUINALDINECARBOXYLIC ACIDS

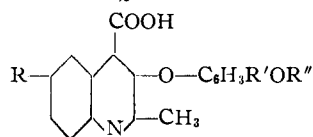


TABLE I  
ALKOXYARYLOXYACETONES,  $CH_3COCH_2OC_6H_4R'OR''$

R'	R''	Yield, %	M. p., °C.	2,4-Dinitrophenylhydrazone	Semicarbazone
H	4-CH <sub>3</sub>	64	48.5	149	192.3
H	4-C <sub>2</sub> H <sub>5</sub>	62	35.5	105.5	192
H	4-C <sub>3</sub> H <sub>7</sub>	73	39	91.5	188.8
H	4-C <sub>4</sub> H <sub>9</sub>	69	37	153	187.8
4-CH <sub>3</sub>	2-CH <sub>3</sub>	48	28.5	136	153

R	R'	R''	Yield, %	M. p. °C. (dec.)	Nitrogen, % Calcd.	Found
H	H	4-CH <sub>3</sub>	74	215	4.56	4.20
H	H	4-C <sub>2</sub> H <sub>5</sub>	56	214	4.33	4.19
H	H	4-C <sub>3</sub> H <sub>7</sub>	70	208	4.15	4.14
H	H	4-C <sub>4</sub> H <sub>9</sub>	77	150	3.99	3.70
H	4-CH <sub>3</sub>	2-CH <sub>3</sub>	75	232	4.33	4.14
CH <sub>3</sub>	H	4-CH <sub>3</sub>	67	234	4.33	4.25
CH <sub>3</sub>	H	4-C <sub>2</sub> H <sub>5</sub>	64	198	4.15	4.30
CH <sub>3</sub>	H	4-C <sub>3</sub> H <sub>7</sub>	62	204	3.99	4.01
CH <sub>3</sub>	H	4-C <sub>4</sub> H <sub>9</sub>	60	193	3.83	3.85
CH <sub>3</sub>	4-CH <sub>3</sub>	2-CH <sub>3</sub>	54	242	4.15	4.19

(1) Knight, Porter and Calaway, *THIS JOURNAL*, **66**, 1893 (1944).  
 (2) Newell and Calaway, *ibid.*, **69**, 116 (1947).  
 (3) Hurd and Perletz, *ibid.*, **68**, 38 (1946).  
 (4) (a) Pfitzinger, *J. prakt. Chem.*, **33**, 100 (1886); (b) **38**, 582 (1888); (c) **56**, 283 (1897).