phenols from alkyl halides and alkali phenolates in good yields is demonstrated.

3. The method for the preparation of substituted phenols by the condensation of olefins with phenols by means of sulfuric acid is improved to give high yield with a shortened reaction time.

4. Rearrangement of alkyl ethers, condensations of unsaturated compounds, alcohols, acids, alkyl halides, acid chlorides, aldehydes and ketones with phenols, and a stripping of alkyl groups from the phenol nucleus are considered as special cases of a quinoid–benzenoid dynamic equilibrium which may be shifted in either direction by varying conditions.

NEW YORK CITY RECEIVED APRIL 10, 1934

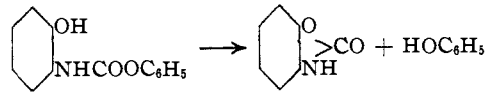
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Benzoxazolone Formation in the Attempt to Prepare Certain Mixed Diacyl Derivatives of *o*-Aminophenol

BY L. CHAS. RAIFORD AND GERALD O. INMAN

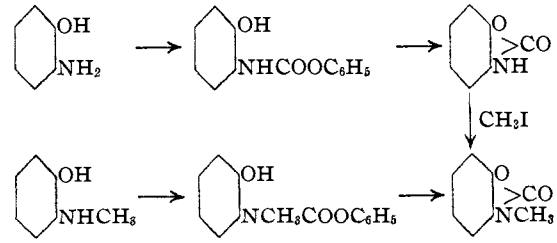
When two different acyl radicals are introduced into *o*-aminophenol the positions taken by these groups are determined by a number of factors.[1] If the acyls are R—C(=O)— and R'—C(=O)—,[2] the heaviest and most acidic radical is usually found attached to nitrogen, regardless of the order of introduction.[3] To meet this requirement the migration of acyl from nitrogen to oxygen must occur in one of these reactions. When the acyls are R—C(=O)— and R—O—C(=O)— the latter is most frequently[4] found on nitrogen. If one of these radicals is Ph—S(=O)(=O)— no rearrangement takes place[5] regardless of the structure of the other radical or the order of introduction of the two groups.

In previous work with the R—O—C(=O)— radical, R has always been represented by alkyl. In the present study we have examined the behavior of derivatives in which R is aromatic. To do this a number of aryl chlorocarbonates were prepared and converted into the N-carboaryloxy derivatives of *o*-aminophenol and several of its substitution products, following the method of Groenvik.[6] When these compounds were mixed with caustic alkali solution for the purpose of acylating them[7] they were converted into the corresponding benzoxazolones[8] while the required phenols were eliminated.



It is now shown that warming 2-N-carboaryloxyaminophenol with pyridine and with acetic anhydride, respectively, causes ring closure, and that in the latter instance N-acetylbenzoxazolone[9] is obtained. Likewise, when 2-benzoylaminophenol, in caustic soda or in pyridine solution, is treated with phenyl chlorocarbonate, phenol is liberated and N-benzoylbenzoxazolone is obtained in yields of 95 and 86%, respectively. No diacyl derivatives could be isolated.

The behavior of derivatives of 2-methylaminophenol was examined. Acylation of the base with phenyl chlorocarbonate gave 2-carbophenoxymethylaminophenol, m. p. 146°. This reacted with dilute caustic alkali solution to give 2-methylbenzoxazolone, m. p. 87.5°, which was also obtained by alkylation of benzoxazolone



(1) Raiford and Clark, THIS JOURNAL, **48**, 483 (1926). This paper gives important references to other work.

(2) R and R' may be aliphatic or aromatic.

(3) Exceptions have been noted by Raiford and others [THIS JOURNAL, **46**, 2308 (1924)]; Nelson and co-workers [*ibid.*, **53**, 997 (1931)]; Bell [*J. Chem. Soc.*, 2962 (1931)].

(4) Ransom and Nelson, THIS JOURNAL, **36**, 393 (1914); Nelson and others, *loc. cit.*

(5) Raiford and Lankelma, *ibid.*, **47**, 1123 (1925); Raiford and Grosz, *ibid.*, **53**, 3425 (1931).

(6) Groenvik, *Bull. soc. chim.*, [2] **25**, 177 (1876).

(7) Schotten-Baumann, *Ber.*, **17**, 2544 (1884); **19**, 3218 (1886).

(8) In previous work the formation of benzoxazolone from an acyl derivative of *o*-aminophenol has, with a single exception, been noted only in those cases where the starting material was heated to temperatures of 150 to 250°. Groenvik, *Bull. soc. chim.*, [2] **25**, 178 (1876); Kalckhoff, *Ber.*, **16**, 1828 (1883); Bender, *ibid.*, **19**, 2269 (1886); Ransom, *ibid.*, **31**, 1063 (1898), and *Am. Chem. J.*, **23**, 19 (1900).

(9) Kalckhoff, *Ber.*, **16**, 1828 (1883).

TABLE I

PREPARATION AND PROPERTIES OF ARYL CHLOROCARBONATES

Substituted phenyl	B. p., °C., and pressure, mm.		Yield, %	Formula	Halogen analyses, % Calcd.	Found
2,4-Dichloro-	115–20	16	64	$C_7H_3O_2Cl_3$	47.22	47.27
2,4,6-Tribromo-	193–7	34[a]	74	$C_7H_2O_2ClBr_3$	70.00	70.25
2-Nitro-	148	15	24	$C_7H_4O_4NCl$	17.61	17.72
4-Phenyl-	173–5	13[b]	77	$C_{13}H_9O_2Cl$	15.26	15.00
3-Methyl-4-chloro-6-isopropyl-	158–60	34	80	$C_{11}H_{12}O_2Cl_2$	28.74	27.26[c]
3-Methyl-4-bromo-6-isopropyl-[d]	158–62	24	76	$C_{11}H_{12}O_2ClBr$	39.62	38.91

[a] At room temperature this is a solid that melts at 47–50°. [b] Standing gave a solid that melted at 40–41°. [c] The benzoxazolone derivative obtained from this compound gave a satisfactory analysis. [d] Obtained from *p*-bromothymol which was prepared by a modification of Plancher's method [*Gazz. chim. ital.*, II, **23**, 76 (1893)].

as directed by Ransom.[10] The mono- and dibromo substitution products of this aminophenol gave similar results. The structures of these products were confirmed by preparing them from the aminophenols and phosgene.[11]

These compounds also undergo acylation readily, as shown by the action of 4-methyl-6-bromobenzoxazolone toward several acid chlorides as indicated below.

To learn whether ring closure can occur under these conditions when R—O—C(=O)— contains alkyl, *o*-hydroxyphenylurethan and 2-carboethoxyamino-4-methyl-6-bromophenol, respectively, were subjected to the action of ethyl chlorocarbonate as described. In each case the required diacyl derivative was obtained and no benzoxazolone was isolated.

Finally, mixed acetyl-benzoyl derivatives of 2-methylaminophenol and its bromine substitution products were studied. Introduction of these radicals in different orders gave isomers, and no rearrangement was observed.

Experimental Part

Preparation of Aryl Chlorocarbonates.—The method used was that briefly indicated by Oesper, Broker and Cook,[12] adapted from a German patent,[13] here slightly modified. To a 20% solution of phosgene in benzene, a mixture of one molecular proportion of the required phenol, if liquid,[14] and 5% excess of dimethylaniline was run in with stirring during half an hour, at a temperature not above 25°, and the mixture allowed to stand for an hour, which usually caused a separation into two layers. In some cases it was necessary to add a small amount of water to cause separation. The benzene layer was washed with dilute hydrochloric acid, with water, dried with calcium chloride, benzene distilled off and the residue distilled under reduced pressure.[15] Data for the new ones are given in Table I.

Preparation of Carbophenoxy Derivatives of *o*-Aminophenols.—To a cold aqueous solution of the hydrochloride[16] of the aminophenol, which was covered with a layer of ether, ammonium carbonate solution was added with stirring until effervescence ceased. The mixture was then repeatedly extracted with ether, the extract dried with anhydrous sodium sulfate, and to it was added slowly, with

TABLE II

CARBOPHENOXY DERIVATIVES OF *o*-AMINOPHENOL

No.	Substituted phenol	Solvent	Crystal form	Yield, %	M. p., °C.
1	2-Amino-	Chloroform–ligroin	Brown microscopic plates	88	150
2	2-Amino-4-bromo-	Ether	Colorless plates	60	181–182
3	2-Amino-4,6-dibromo-	Chloroform	Irregular masses	45	158
4	2-Methylamino	Chloroform–ligroin	Irregular masses	43[a]	146

No.	Formula	Analyses, % Halogen Calcd.	Halogen Found	Nitrogen Calcd.	Nitrogen Found
1	$C_{13}H_{11}O_3N$	...	...	6.11	6.04
2	$C_{13}H_{10}O_3NBr$	25.97	26.39	..	..
3	$C_{13}H_9O_3NBr_2$	41.34	41.21	..	..
4	$C_{14}H_{13}O_3N$[b]	...	...	5.76	5.60

[a] Refers to purified material. [b] Treatment with dilute alkali solution eliminated phenol and gave 2-methylbenzoxazolone, m. p. 87.5°, which did not depress the melting point of the product synthesized as directed by Ransom [*Am. Chem. J.*, **23**, 33 (1900)], who found 86°.

(10) Ransom, *Am. Chem. J.*, **23**, 33 (1900).

(11) Chelmicki, Dissertation, Bern, 1887; *Ber.*, **20**, 177 (1887).

(12) Oesper, Broker and Cook, THIS JOURNAL, **47**, 2609 (1925).

(13) German Patent, 251,805; *Friedländer*, **11**, 82 (1912).

(14) Solid phenols were dissolved or suspended in the phosgene solution, and dimethylaniline was run in slowly.

(15) An attempt to prepare 2,4-dinitrophenyl chlorocarbonate gave an oily product that decomposed violently in an effort to distil it under reduced pressure. A second lot deposited some solid on standing for several hours, and crystallization of this from benzene gave coarse, light yellow needles, m. p. 149°. It contained no halogen, and reacted with hot water to give carbon dioxide and 2,4-dinitrophenol, which suggested di-(2,4-dinitrophenyl) carbonate. Kempf [*J. prakt. Chem.*, [2] **1**, 408 (1870)] obtained by direct nitration of diphenyl carbonate a product that melted at 125.5° and was decomposed by water as indicated. The compound here in question was analyzed for nitrogen. *Anal.* Calcd. for $C_{13}H_6O_{11}N_4$: N, 14.2. Found: N, 13.88. When 2,4,6-trinitrophenol was treated with phosgene as described, the product obtained melted at 81°. *Anal.* Calcd. for $C_7H_2O_8N_3Cl$ and $C_6H_2O_6N_3Cl$: Cl, 12.16 and 14.33. Found: Cl, 13.75. Treatment with benzylamine gave the picramide, m. p. 141–142°. James, Jones and Lewis [*J. Chem. Soc.*, **117**, 1275 (1920)] found 144.8°. The first product was picryl chloride.

(16) In place of this an ethereal suspension of the free base may be used.

cooling, one-half a molecular proportion of phenyl chlorocarbonate. After one to two hours water was added to dissolve the amine hydrochloride, the solution separated, the ether distilled from the remainder and the residue crystallized from a suitable solvent. Analytical data and other properties are given in Table II.

2-Amino-4-methyl-6-bromophenol[17] was converted into a number of substituted carbophenoxy derivatives for which properties are given in Table III.

TABLE III

CARBOARYLOXY DERIVATIVES OF 2-AMINO-4-METHYL-6-BROMOPHENOL

No.	Acyl radical	Solvent	Crystal form
1	Carbophenoxy-	Chloroform–ligroin	Fine colorless needles
2	*o*-Tolyloxy-	Chloroform–ligroin	Clusters of small plates
3	*p*-Tolyloxy-	Chloroform–ligroin	Small colorless octahedrons
4	4-Diphenoxy-	Chloroform	Fine colorless plates

No.	Yield,[a] %	M. p., °C.	Formula	Halogen analyses, % Calcd.	Found
1	70	107	$C_{14}H_{12}O_3NBr$	24.84	25.03
2	60	124	$C_{15}H_{14}O_3NBr$	23.81	24.11
3	67	139–141	$C_{15}H_{14}O_3NBr$	23.81	23.76
4	77	162–163	$C_{20}H_{16}O_3NBr$	20.10	20.34

[a] These percentages are for purified material.

cipitated. Crystallization from alcohol, using "Norite," gave nearly colorless needles, m. p. 215°. Phenol was identified in the filtrate.

Anal. Calcd. for $C_7H_4O_2NBr$: Br, 37.38. Found: Br, 37.60.

Treatment of the N-carbophenoxy derivative of 4,6-dibromo-*o*-aminophenol as indicated gave the required dibromobenzoxazolone, m. p. 252°. This did not depress the melting point of the compound prepared from 3,5-dibromosalicylamide[18] as directed by McCoy.[19] The product was characterized further by conversion into its acetyl derivative that crystallized from alcohol in colorless plates; m. p. 160.5°.

Anal. Calcd. for $C_9H_5O_3NBr_2$: Br, 47.74. Found: Br, 47.43.

Portions of the carbophenoxy derivatives indicated in Table III were dissolved in dilute potassium hydroxide solution, the liquid acidified and the precipitates (A) collected. Addition of bromine water to the first filtrate gave 2,4,6-tribromophenol. The second precipitate was washed with a little ether, the filtrate was extracted with ether, and from the combined extract and washings *o*-cresol was isolated and identified as the *p*-bromobenzene-

TABLE IV

N-ACYL DERIVATIVES OF 4-METHYL-6-BROMOBENZOXAZOLONE

Acyl radical	Yield, %	Solvent	Crystal form	M. p., °C.	Formula	Halogen analyses, % Calcd.	Found
Acetyl-[a]	76	Ligroin	Colorless prisms	114–115	$C_{10}H_8O_3NBr$	29.62	29.66
Benzoyl-	34	Alcohol	Fine needles	176–176.5	$C_{15}H_{10}O_3NBr$	24.08	23.89
Benzenesulfonyl-[b]	41	Alcohol	Colorless needles	188–189	$C_{14}H_{10}O_4NBrS$	21.72	21.68
Carbomethoxy-	78[c]	None	Small plates	145 dec.	$C_{10}H_8O_4NBr$	27.95	28.56
Ethoxy-	34	Alcohol	Microscopic needles	87	$C_{11}H_{10}O_4NBr$	26.65	26.69
n-Propoxy-	96[c]	None	Small plates	99.5	$C_{12}H_{12}O_4NBr$	25.46	25.83
n-Butoxy-[b]	42	Alcohol	Microscopic needles	56	$C_{13}H_{14}O_4NBr$	24.37	24.47
Phenoxy-	30	Alcohol	Brown needles	145–146	$C_{15}H_{10}O_4NBr$	22.97	23.07
o-Tolyloxy-	50	Chloroform–ligroin	Colorless needles	168–169	$C_{16}H_{12}O_4NBr$	22.08	22.36
m-Tolyloxy-	31	Chloroform–ligroin	Colorless prisms	149.5–150	$C_{16}H_{12}O_4NBr$	22.08	22.66
p-Tolyloxy-	21	Chloroform–ligroin	Microscopic needles	128–129	$C_{16}H_{12}O_4NBr$	22.08	22.49
2-Nitrophenoxy-	43	Chloroform–ligroin	Colorless needles	198	$C_{15}H_9O_6N_2Br$	20.34	20.84
2,4-Dichlorophenoxy-[b]	41	Chloroform–ligroin	Fine needles	165	$C_{15}H_8O_4NCl_2Br$	36.18	36.91
2,4,6-Tribromophenoxy-	39	Chloroform–ligroin	Pink prisms	202–203	$C_{15}H_7O_4NBr_4$	54.68	54.38
3-Methyl-6-isopropylphenoxy-	18	Alcohol	Small plates	110–111	$C_{19}H_{18}O_4NBr$	19.79	20.28
3-Methyl-4-chloro-6-isopropylphenoxy-	35	Methyl alcohol	Colorless needles	149	$C_{19}H_{17}O_4NClBr$	26.32	26.61
3-Methyl-4-bromo-6-isopropylphenoxy-	80	Chloroform–ligroin	Colorless needles	156	$C_{19}H_{17}O_4NBr_2$	33.11	33.37
4-Diphenoxy-	27	Carbon tetrachloride	Microscopic needles	195.5	$C_{21}H_{14}O_4NBr$	18.86	19.37
α-Naphthoxy-[b]	28	Alcohol	Fine needles	170	$C_{19}H_{12}O_4NBr$	20.09	19.99
β-Naphthoxy-	47	Chloroform–ligroin	Fine needles	182–183	$C_{19}H_{12}O_4NBr$	20.09	20.16

[a] Prepared by refluxing a mixture of starting material and acetic anhydride.
[b] Acylation was done in the presence of caustic alkali solution.
[c] Refers to total yield; other figures refer to purified material.

Conversion of Carbophenoxy Derivatives into Benzoxazolones.—When 2-carbophenoxyamino-4-bromophenol was dissolved in 5% solution of potassium hydroxide, and the solution acidified, 4-bromobenzoxazolone was pre-

sulfonate, m. p. 82°. Similarly, the third case gave the *p*-cresyl derivative, m. p. 104°.[20] Crystallization of each

(17) Thiele and Eichwede, *Ann.*, **311**, 376 (1900).

(18) Spilker, *Ber.*, **22**, 2769 (1889).

(19) McCoy [*Am. Chem. J.*, **21**, 118 (1899)] recorded 250°.

(20) Sekera [THIS JOURNAL, **55**, 421 (1933)] reported 78–79° for the first and 100° for the second.

precipitate (A) from alcohol gave small colorless plates, m. p. 222°, and identical with 4-methyl-6-bromobenzoxazolone described below. From the mother liquor of the fourth, water precipitated 4-hydroxydiphenyl, obtained in silky needles from chloroform; m. p. 162°.

Second Synthesis of 4-Methyl-6-bromobenzoxazolone.—Twelve grams of 2-amino-4-methyl-6-bromophenol was added to a solution of 7 g. of phosgene in 100 cc. of chloroform, the liquid was refluxed for half an hour, and the solvent distilled off. The hydrochloride of the aminocresol was removed by extraction with 200 cc. of water. Crystallization of the residue from alcohol gave colorless plates of m. p. 222°; yield, 57%.

Anal. Calcd. for $C_8H_6O_2NBr$: Br, 35.08. Found: Br, 35.24.

N-Acyl Derivatives of 4-Methyl-6-bromobenzoxazolone.—To a pyridine solution of the benzoxazolone 10% excess of the acylating agent was added, the mixture heated at 50–60° for about twenty minutes, then acidified with dilute hydrochloric acid. The precipitated products were washed with dilute alkali, then with water and crystallized from a suitable solvent. When pyridine was replaced by 5% solution of potassium hydroxide and the mixture shaken until the odor of the acylating agent had disappeared, the products separated as oils that required cooling in an ice-bath, from a few minutes to two hours, to give solids. Data for these products are indicated in Table IV.

2-Carboethoxyaminophenyl Ethyl Carbonate.—To a solution of 2 g. of *o*-hydroxyphenylurethan in 20 cc. of pyridine, 1.5 g. of ethyl chlorocarbonate was added slowly with constant shaking at room temperature and then allowed to stand half an hour. The mixture was cooled in an ice-bath, acidified with hydrochloric acid, extracted with ether, and the extract dried with anhydrous sodium sulfate. Distillation of the ether left a brown sirup that did not crystallize when further dried under partial vacuum for more than a week, and later chilled in an ice box for ten days; yield, 91%.

Anal. Calcd. for $C_{12}H_{15}O_5N$: N, 5.53. Found: N, 5.53.

Hydrolysis of this product by dilute caustic alkali solution gave *o*-hydroxyphenylurethan.

2-Carboethoxyamino-4-methyl-6-bromophenyl Ethyl Carbonate.—One gram of the required 2-carboethoxyaminophenol was dissolved in 6 cc. of 5% solution of potassium hydroxide, and treated with ethyl chlorocarbonate as above. Crystallization of the product from alcohol gave colorless prisms, m. p. 109°; yield, 64%.

Anal. Calcd. $C_{13}H_{16}O_5NBr$: Br, 23.12. Found: Br, 23.57.

TABLE V

ACYL DERIVATIVES OF 2-METHYLAMINOPHENOL

Position[a] of acyl group unsubstituted	Solvent	Crystal form	M. p., °C.	Formula	Analyses, % Nitrogen Calcd.	Found
N-acetyl-O-acetyl[b]	Ligroin	Colorless plates	62–63[c]	$C_{11}H_{13}O_3N$	6.76	6.74
N-Acetyl-O-benzoyl	Ligroin	Colorless plates	96	$C_{16}H_{15}O_3N$	5.20	5.05
N-Benzoyl-O-acetyl	Ligroin	Irregular masses	63–64[c]	$C_{16}H_{15}O_3N$	5.20	5.06
N-Benzoyl-O-carbophenoxy	Alcohol	Colorless plates	103	$C_{21}H_{17}O_4N$	4.04	3.84
4-Bromo-					Halogen, %	
Acetylaminophenol[d]	Alcohol	Fine colorless needles	185–185.5	$C_9H_{10}O_2NBr$	32.77	32.73
N-Acetyl-O-benzoyl	Chloroform–ligroin	Colorless prisms	129	$C_{16}H_{14}O_3NBr$	22.97	23.35
N-Benzoyl-O-benzoyl	Chloroform–ligroin	Colorless microscopic needles	137	$C_{21}H_{16}O_3NBr$	19.50	19.80
Benzoylaminophenol	Chloroform–ligroin	Colorless microscopic needles	174	$C_{14}H_{12}O_2NBr$	26.13	26.21
N-Benzoyl-O-acetyl	Chloroform–ligroin	Microscopic prisms	109	$C_{16}H_{14}O_3NBr$	22.97	23.05
4,6-Dibromo-						
Acetylaminophenol[e]	Alcohol	Colorless needles	197	$C_9H_9O_2NBr_2$[f]	49.52	50.00
N-Acetyl-O-benzoyl	Alcohol	Microscopic plates	145[g]	$C_{16}H_{13}O_3NBr_2$	37.45	37.54
N-Benzoyl-O-benzoyl	Alcohol	Colorless prisms	144–145[g]	$C_{21}H_{15}O_3NBr_2$	32.70	32.77
Benzoylaminophenol	Alcohol	Colorless prisms	183	$C_{14}H_{11}O_2NBr_2$	41.54	41.74
N-Benzoyl-O-acetyl	Dilute alcohol	Colorless prisms	99	$C_{16}H_{13}O_3NBr_2$	37.45	37.12

[a] Position of acyl was determined by hydrolysis of diacyl derivative by alkali.

[b] Hydrolysis gave N-acetylmethylaminophenol, m. p. 150°, obtained by Lees and Schedden [*J. Chem. Soc.*, **83**, 756 (1903)] in a different way.

[c] A mixture of these products liquefied at room temperature.

[d] When heated with twice its weight of concentrated hydrochloric acid in a sealed tube for four hours at 140° it gave the hydrochloride of 2-methylamino-4-bromophenol. *Anal.* Calcd. for $C_7H_9ONClBr$: hal., 48.40. Found: hal., 48.42.

[e] Obtained in 80% yield by bromination of the required phenol in acetic acid solution in presence of iodine as a carrier.

[f] Hydrolysis, as indicated in 4, gave the hydrochloride of 2-methylamino-4,6-dibromophenol, m. p. 216°, with decomposition. *Anal.* Calcd. for $C_7H_8ONClBr_2$: hal., 61.55. Found: hal., 61.88.

[g] A mixture of these products melted over a range of 123–135°.

Derivatives of 2-N-Methylaminophenol

2-Acetylmethylaminophenyl Acetate.—A mixture of 10 g. of *o*-methylaminophenol sulfate, 10 g. of fused sodium acetate and 10 cc. of acetic anhydride was heated until liquid, cooled, 50 cc. of water added, and the liquid extracted with ether. The ether was distilled from the dried extract, and the residue that distilled at 195-200° and 30 mm. solidified slowly in the refrigerator. Data for this and other derivatives obtained by standard methods are given in Table V.

2-Methyl-4-bromobenzoxazolone.—When a solution of 2 g. of 2-methylamino-4-bromophenol in 36 cc. of 10% solution of sodium hydroxide was shaken with 2.6 g. of phenyl chlorocarbonate, it gave a pasty solid that was removed by extraction with ether. The extract was shaken with alkali solution, then with water, and the ether evaporated at room temperature. Crystallization of the residue from alcohol gave nearly colorless needles, m. p. 137.5°. The structure of this was proved by preparing it in a different way. A solution of 4.2 g. of 4-bromobenzoxazolone, 1.2 g. of potassium hydroxide and 6.2 g. of methyl iodide in 50 cc. of methyl alcohol was refluxed for three hours and the volatile material distilled off. The residue was extracted with 50 cc. of water, then triturated with potassium hydroxide solution, and the mixture filtered. Crystallization of the solid from alcohol gave colorless needles; m. p. 137.5; yield, 75%. A mixture of these products melted without depression.

Anal. Calcd. for $C_8H_6O_2NBr$: Br, 35.07. Found: Br, 35.18.

2-Methyl-4,6-dibromobenzoxazolone.—This was prepared as indicated above under the monobromo compound. Crystallization from alcohol gave colorless crystalline irregular masses, m. p. 124–125°. The same product was obtained by refluxing for three hours a mixture of 4 g. of the 4,6-dibromobenzoxazolone, previously described, and 5 g. of methyl iodide with 1.2 g. of potassium hydroxide in 50 cc. of methyl alcohol.

Anal. Calcd. for $C_8H_5O_2NBr_2$: Br, 52.10. Found: Br, 51.98.

Summary

1. Several new aromatic chlorocarbonates have been prepared by the action of phosgene on the required phenols. Under the conditions 2,4-dinitrophenol gave di-(2,4-dinitrophenyl) carbonate, while picric acid gave picryl chloride.

2. When the N-carboaryloxy derivatives of *o*-aminophenol and its substitution products are dissolved in alkali they are converted into the corresponding benzoxazolones and a phenol is liberated. The same change occurs when the derivatives of *o*-methylaminophenol are used. The structures of these products were confirmed by synthesis from the required aminophenol and phosgene.

3. 2-Acetylmethylaminophenol was converted into a mono and a dibromo derivative, and their structures were proved. Each of these gave mixed isomeric acetyl-benzoyl derivatives that showed no tendency to rearrange.

4. Under the conditions of these experiments *o*-aminophenol could not be converted into a diacyl derivative containing the radical Ph—O—C(=O)—.

5. Further work is in progress.

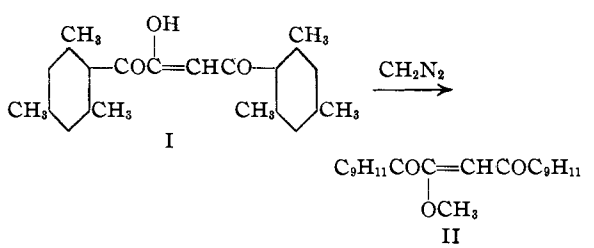
IOWA CITY, IOWA RECEIVED APRIL 16, 1934

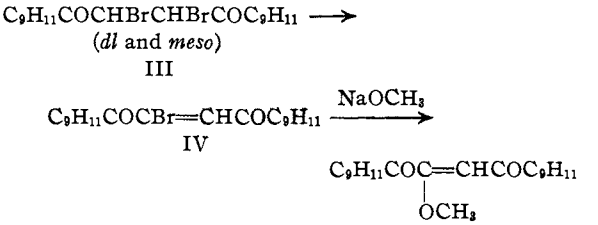
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 133]

The Alkyl Ethers of 1,2-Di-(trimethylbenzoyl)-ethenol

BY ROBERT E. LUTZ

Two stereomeric methyl ethers of di-(trimethylbenzoyl)-ethenol I are known,[1] one (yellow) II obtained by methylation of the enol with diazomethane, and the other (colorless) prepared by the action of sodium methylate on di-(trimethylbenzoyl)-dibromoethane III.





The latter reaction has been found to give mixtures of both stereomeric ethers (methyl[1a] and ethyl) with the ratio of yields depending on conditions. The colorless isomers are the chief

(1) (a) Lutz, THIS JOURNAL, **48**, 2905 (1926); (b) Conant and Lutz, *ibid.*, **47**, 881 (1925).