

substitution at the more electronegative atom of the ambident anion.<sup>1-3,8,9</sup>

In the case of pyrrolylsodium, which is readily soluble in tetrahydrofuran, slow addition of a solution of the salt to a solution of the alkylating agent (inverse addition) increased markedly the relative amount of N-alkylated product in the present reaction with allyl tosylate, just as in the previously reported reaction with allyl bromide.<sup>1</sup>

When reactions were run in the same solvent (Table I, tetrahydrofuran), the position of substitution of the pyrrolyl anion was affected by the nature of the cation, in agreement with the findings that in aprotic solvents of low dielectric constant the proportion of alkylation at the more electronegative atom of the ambident anion increases as the cation is changed from Li<sup>+</sup> to Na<sup>+</sup> to K<sup>+</sup>.<sup>1,3,8,9</sup> In this connection the fact should be noted that pyrrolylmagnesium halides are alkylated almost exclusively on carbon.<sup>10</sup>

Table II shows that in the treatment of pyrrolyl-potassium with allyl tosylate an increase in the reaction temperature caused a small (dioxane) to moderate (toluene) increase of the relative percentage of N alkylation. The effect of temperature on the position of alkylation of ambident anions is not uniform. There was no clear-cut effect in the reaction of pyrrolylpotassium with allyl bromide,<sup>11</sup> but increased C alkylation was observed at a higher temperature with crotyl and benzyl halides.<sup>1</sup> A temperature increase has been reported to favor O alkylation of sodio-2-carbethoxycyclanones with isopropyl iodide in dimethyl sulfoxide,<sup>12</sup> O alkylation of ethyl acetoacetate with *n*-butyl chloride, and potassium carbonate in dimethyl sulfoxide, but C alkylation when the last reaction is run in *N*-methylpyrrolidine.<sup>5</sup>

The higher relative percentage of N-alkylated product generally obtained when *n*-propyl tosylate was substituted for allyl tosylate as the alkylating agent (Table III) is consistent with the greater selectivity of satu-

TABLE III  
REACTIONS OF PYRROLYLMETAL SALTS  
WITH *n*-PROPYL TOSYLATE AT 65°

Cation	Solvent	Relative %		
		1- <i>n</i> -Propyl-pyrrole	2- <i>n</i> -Propyl-pyrrole	3- <i>n</i> -Propyl-pyrrole
K <sup>+</sup>	Tetrahydrofuran	97	2.5	0.50
K <sup>+</sup>	Benzene	95	4.0	1.0
Na <sup>+</sup>	Tetrahydrofuran	65	32	3.0
Li <sup>+</sup>	Tetrahydrofuran	25	70	5.0

rated alkyl halides, compared with allyl halides, in alkylating pyrrolylmetal salts<sup>1</sup> and indolylsodium<sup>2</sup> predominantly on the nitrogen atom, and salts of phenols,<sup>3</sup> or ethyl acetoacetate<sup>6</sup> predominantly on the oxygen atom. The effect of the cation on product composition is again significant in this case (Table III), as in the case with allyl tosylate (Table I).

(8) D. Y. Curtin and D. H. Dybvig, *J. Amer. Chem. Soc.*, **84**, 225 (1962).

(9) N. Kornblum, R. Seltzer, and P. Haberfeld, *ibid.*, **85**, 1148 (1963).

(10) (a) P. S. Skell and G. P. Bean, *ibid.*, **84**, 4655 (1962); (b) C. E. Griffin and R. Obrycki, *J. Org. Chem.*, **29**, 3090 (1964); (c) A. J. Castro, J. F. Deck, N. C. Ling, J. P. Marsh, Jr., and G. E. Means, *ibid.*, **30**, 344 (1965).

(11) E. P. Papadopoulos, Ph.D. Thesis, University of Kansas, Lawrence, Kan., 1961; *Dissertation Abstr.*, **22**, 3858 (1962).

(12) S. J. Rhoads and R. W. Hasbrouck, *Tetrahedron*, **22**, 3557 (1966).

## Experimental Section

The reactions were run under nitrogen at 65° for 8 hr, and the products were analyzed by gas-liquid partition chromatography. A 275-cm column packed with Chromosorb W 60/80, containing 20% silicone oil was used in a model 154 Perkin-Elmer vapor fractometer with helium as the carrier gas. Bromobenzene was the internal standard, and the peak areas were measured with a planimeter.

**Procedure.**—To a solution of 0.25 mol of pyrrole in 100 ml of dry solvent,<sup>13</sup> 0.20 g-atom of potassium<sup>14</sup> was added and the mixture was refluxed with stirring until completion of the reaction. After addition of 100 ml of solvent, the temperature was adjusted to the desired value, and 0.20 mol of the alkyl tosylate,<sup>15</sup> dissolved in 100 ml of solvent, was added dropwise over a period of 1 hr.<sup>16</sup> The reaction mixture was stirred at constant temperature for a further 8 hr; then it was cooled to room temperature and filtered. After the solid material had been washed with ether, it was dissolved in 100 ml of water, and the aqueous solution was extracted with ether. The combined filtrate, ether washings, and extracts were then dried over anhydrous magnesium sulfate. After removal of the solvents by distillation under reduced pressure, the residue was analyzed by gas-liquid partition chromatography.

**Registry No.**—Allyl tosylate, 4873-09-0; *n*-propyl tosylate, 599-91-7; pyrrolylpotassium, 16199-06-7.

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(13) For the reactions run in dimethyl sulfoxide, pyrrolylpotassium was prepared in tetrahydrofuran. This solvent was subsequently removed by distillation under reduced pressure and replaced by dimethyl sulfoxide.

(14) Sodium hydride and lithium hydride were used for the preparation of the corresponding salts of pyrrole.

(15) Z. Foldi, *Chem. Ber.*, **53**, 1836 (1920).

(16) In the inverse addition reaction, a solution of 0.20 mol of pyrrolylsodium in 200 ml of tetrahydrofuran was added dropwise, over a period of 4 hr, to 0.20 mol of allyl tosylate dissolved in 100 ml of tetrahydrofuran, at 65°.

## The Benzene-Resorcinol-Phthaleinanhidride of v. Pechmann

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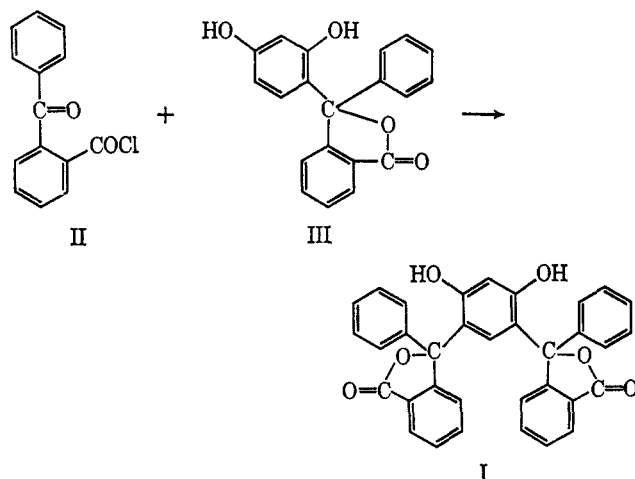
On heating *o*-benzoylbenzoic acid with resorcinol in sulfuric-acetic acid, v. Pechmann<sup>1</sup> obtained a compound of unestablished structure which he named benzene-resorcinol-phthaleinanhidride. This same compound (I) also resulted from the reaction of *o*-benzoylbenzoic acid with resorcinol in the presence of anhydrous zinc chloride.<sup>2</sup>

In this Note it is shown that I can also be obtained in high yields from 2 mol of *o*-benzoylbenzoyl chloride (II) and 1 mol of resorcinol by the method of Blicke<sup>3</sup> and in 94% yield and high purity in the reaction of equimolar quantities of II with 3-phenyl-3-(2,4-dihydroxyphenyl)-phthalide (III).

(1) H. v. Pechmann, *Ber.*, **14**, 1862 (1881).

(2) M. H. Hubacher, *J. Org. Chem.*, **23**, 1400 (1958).

(3) F. F. Blicke and R. D. Swishers, *J. Amer. Chem. Soc.*, **56**, 923 (1934).



On caustic fusion of I, 2,4-dihydroxybenzophenone, benzoic acid, and 4,6-dihydroxyisophthalic acid were obtained. Thus the structure of I is undoubtedly that of 4,6-bis(3-phenylphthalidyl)resorcinol, belonging to a class of compounds for which the name of diphthalein is suggested.

Orndorff and Murray<sup>4</sup> obtained two phthaleins in the reaction of 2-(4-hydroxybenzoyl)benzoic acid with resorcinol, which they believed to be isomers. Two phthaleins were also obtained in this laboratory from II and hydroquinone and from II and pyrogallol. It is quite possible that on reinvestigation one of each pair of compounds will be found to be a diphthalein.

#### Experimental Section<sup>5</sup>

**Preparation of I. A. From II and Resorcinol.**—To a solution of II, prepared from 45.2 g of *o*-benzoylbenzoic acid and 30 g of thionyl chloride, in 250 ml of benzene was added 11.0 g of powdered resorcinol. The suspension was heated to 80–85° for 4 hr. A fine, gray precipitate formed with the evolution of HCl. The mixture was filtered the next day and the cake washed with 50 ml of benzene and with six portions of 60 ml of ethanol, leaving 40.5–43.1 g (77–82%) of I, mp 278–290°.

**B. From II and III.**—To II, prepared from 22.6 g of *o*-benzoylbenzoic acid and 15 g of thionyl chloride, in 170 ml of benzene, was added 31.8 g of III,<sup>3</sup> mp 199–200°. The mixture was slowly heated to 80°, yielding 49.4 g (94%) of I, mp 290–292°.

I (1 g) required 650 ml of acetic acid or 2 l. of ethanol for recrystallization. The crystals from acetic acid sintered with gas evolution at 227–235°, solidified, and remelted at 292–294°.

Crystals from acetic acid, dried at 20–25°, were analyzed. *Anal.* Calcd for  $C_{34}H_{22}O_6 \cdot CH_3COOH \cdot H_2O$ : C, 71.46; H, 4.67. Found: C, 71.26; H, 5.03.

After being dried under vacuum at 230–235°, I was again analyzed. *Anal.* Calcd for  $C_{34}H_{22}O_6$ : C, 77.56; H, 4.21. Found: C, 77.20; H, 4.14.

A solution of 16 mg of I in 50 ml of 0.1 *N* sodium hydroxide is of strong reddish orange color.

**Alkaline Degradation of I. A.**—A solution of 10 g of I in 30 ml of 2.5 *N* sodium hydroxide was kept for 3 weeks over nitrogen, then acidified, yielding 5.19 g of *o*-benzoylbenzoic acid and 1.3 g of resorcinol.

**B.**—A solution of 10 g of I in 100 ml of 0.1 *N* sodium hydroxide was refluxed for 30 min, yielding 5.9 g of *o*-benzoylbenzoic acid and 1.1 g of resorcinol.

**C.**—I (10 g) was added to 50 g of molten potassium hydroxide at 240–245°. The melt was stirred for 10 min, then cooled, and dissolved in water. The solution yielded 4.77 g of benzoic acid, 0.67 g of 2,4-dihydroxybenzophenone (mp 142–143°), and two nonsublimable acids, which were separated from each other by fractional crystallization from 50% acetic acid. One melted at

236.2–237.3° dec and the other at 298–300° dec. The latter proved to be 4,6-dihydroxyisophthalic acid, which when treated with diazomethane yielded the dimethyl 4,6-dimethoxyisophthalate, mp 145.0–147.5°, after sublimation under high vacuum and subsequent crystallization from methanol, and did not depress the melting point of authentic dimethyl 4,6-dimethoxyisophthalate,<sup>6</sup> mp 147.8–148.3°.

**Diacetyl Derivative of I.**—A mixture of 2.63 g of I, 10 ml of acetic acid, 5 ml of acetic anhydride, and 1 drop of concentrated sulfuric acid was refluxed for 1 hr. The mixture was poured on ice and the precipitate crystallized from ethanol (1 g in 100 ml). This diacetyl derivative melted at 253.0–256.3° (lit.<sup>1</sup> mp 245°). *Anal.* Calcd for  $C_{38}H_{26}O_8$ : C, 74.74; H, 4.29; mol wt, 611;  $2CH_3CO$ , 14.1. Found: C, 74.64; H, 4.24; mol wt,  $606 \pm 28$  (Rast);  $CH_3CO$ , 13.8 (lit.<sup>1</sup> C, 74.9, H, 4.3).

Dr. David N. Kendall reported on the infrared spectrum of compound I, scanned as Nujol and hexachlorobutadiene mulls: "An absorption band is observed at 893  $cm^{-1}$ , which is believed to arise from 1,2,4,5-tetrasubstituted benzene. Monosubstituted benzene absorptions are present at 695 and 749  $cm^{-1}$  and *ortho*-disubstituted benzene absorption at 765  $cm^{-1}$ . Compound I shows ketone carbonyl absorption of a  $\gamma$ -lactone with  $\alpha, \beta$ -unsaturation at 1721  $cm^{-1}$ ; aromatic hydroxyl at 3205, 1383, and 1292  $cm^{-1}$ ; aromatic C=C at 1610, 1597, 1517, and 1490  $cm^{-1}$ ; and C–O–C of the C–O–C=O grouping at 1259  $cm^{-1}$ . The infrared spectra of I and the known compound III are very similar in the 5000–1250- $cm^{-1}$  region."

**Registry No.**—I, 15791-04-5.

(6) F. v. Hemmelmayr, *Monatsh. Chem.*, **38**, 87 (1917); E. Spaeth, *et al.*, *Ber.*, **64**, 2211 (1931).

#### The Acetate-Catalyzed Enolization of 2-Butanone

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Recently, several papers have appeared on the relative rates of enolization at the two sites of simple unsymmetrical ketones, studied by deuterium exchange and nmr techniques.<sup>1–8</sup> Generally, the results obtained by different workers are in agreement, but our results<sup>1</sup> and those of Rappe,<sup>4,5</sup> on the enolization of 2-butanone differ in two important respects. We find that the relative rates for base-catalyzed enolization at the methylene and  $\alpha$ -methyl positions are *different* for different bases and that the rate of exchange in the absence of catalyst is negligible. Rappe finds the relative rates *the same* for different bases and an appreciable rate for the so-called uncatalyzed reaction. Because of this, we have recently studied the uncatalyzed and acetate-catalyzed reactions again and have re-determined the acetate catalysis constants using the buffer method suggested by Bell.<sup>9</sup> Our previous method involved the extraction of catalytic constants for acetate from over-all rate data by an extrapolation technique.<sup>1</sup>

(1) (a) J. Warkentin and O. S. Tee, *Chem. Commun.*, **7**, 190 (1966); (b) J. Warkentin and O. S. Tee, *J. Amer. Chem. Soc.*, **88**, 5540 (1966).

(2) C. Rappe, *Acta. Chem. Scand.*, **20**, 376 (1966).

(3) C. Rappe, *ibid.*, **20**, 1721 (1966).

(4) C. Rappe, *ibid.*, **20**, 2236 (1966).

(5) C. Rappe, *ibid.*, **20**, 2305 (1966).

(6) C. Rappe, *ibid.*, **21**, 857 (1967).

(7) A. A. Bothner-By and Colette Sun, *J. Org. Chem.*, **32**, 492 (1966).

(8) J. Hine, K. G. Hampton, and B. C. Menon, *J. Amer. Chem. Soc.*, **89**, 2664 (1967).

(9) R. P. Bell and P. Jones, *J. Chem. Soc.*, **88** (1953).

(4) W. R. Orndorff and R. R. Murray, *J. Amer. Chem. Soc.*, **39**, 683 (1917).

(5) All melting points are corrected.