

chloro-6-( $\alpha$ -methylallyl)-phenol, whose structure was proved by reduction to 2,4-dichloro-6-(*s*-butyl)-phenol and synthesis of this compound. Heating the acid in dimethylaniline gives cleavage and very little rearrangement; methyl 3,5-dichlorosalicylate and the corresponding acid are present in the reaction product.

2. O-Allylsalicylic acid rearranges to give 64% of 3-allylsalicylic acid and 23% of 2-allylphenol.

3. O-Allyl-3,5-dichlorosalicylic acid rearranges more slowly than the crotyl compound, and allyl 2,4-dichlorophenyl ether also rearranges more slowly than crotyl 2,4-dichlorophenyl ether.

4. The relation of these observations to the mechanism of the Claisen rearrangement is discussed.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

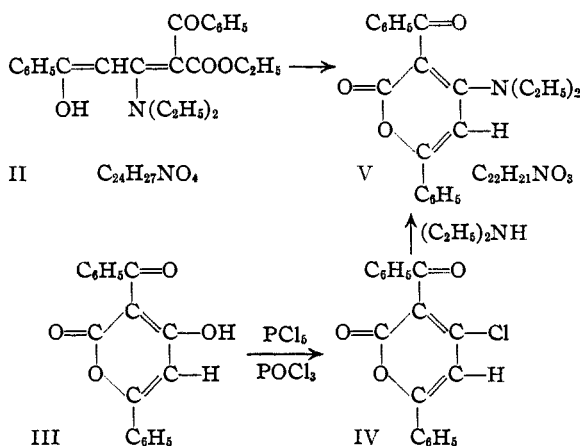
## The Action of Benzoyl Chloride on Ethyl $\beta$ -Diethylaminocrotonate

BY WALTER M. LAUER AND NORMAN H. CROMWELL<sup>1,2</sup>

The acylation of  $\beta$ -aminocrotonic esters has not been extensively investigated, but examples of both C- and N-acylation have been reported.<sup>3,4</sup> The present study is concerned with the action of benzoyl chloride on ethyl  $\beta$ -diethylaminocrotonate (I). Instead of the expected monobenzoyl derivative, ethyl  $\beta$ -diethylamino- $\alpha,\gamma$ -dibenzoylcrotonate (II)  $C_6H_5-CO\overset{\gamma}{CH_2}-\overset{\beta}{C}=\overset{\alpha}{C}(COC_6H_5)COOC_2H_5$

was obtained. That benzoylation actually produced ethyl  $\beta$ -diethylamino- $\alpha,\gamma$ -dibenzoylcrotonate was established in the following manner.

Hydrolysis of the dibenzoyl derivative ( $C_{24}H_{27}NO_4$ ) in the presence of acids produced the compound  $C_{22}H_{21}NO_3$  which was synthesized. Dehydrobenzoylacetic acid (III) upon treatment with



(1) An abstract of a thesis submitted for the Ph.D. degree, June, 1939.

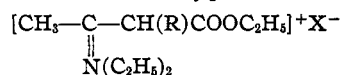
(2) Present address: The University of Nebraska, Lincoln, Nebraska.

(3) Collie, *Ann.*, **226**, 309 (1884).

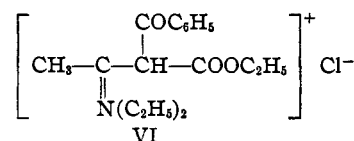
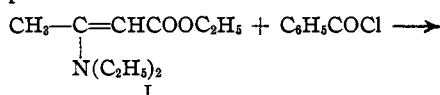
(4) Benary, *et al.*, *Ber.*, **42**, 3912 (1909); **50**, 65 (1917); **59**, 2548 (1926).

phosphorus pentachloride yielded the monochloro derivative (IV) which in turn was transformed to 3-benzoyl-4-diethylamino-6-phenylpyrone (V).

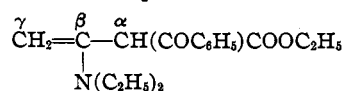
Earlier work,<sup>5</sup> dealing with the alkylation of ethyl  $\beta$ -diethylaminocrotonate, has shown that alkyl halides react in a manner requiring direct attachment of the alkyl group to the  $\alpha$ -carbon atom to form a salt of the type



If benzoylation with benzoyl chloride in dry ether follows this same course, then the initial step in the process can be formulated as



The introduction of the benzoyl group should decrease the basicity of the aminocrotonate and, therefore, a proton transfer from VI to I is to be expected. Presumably, the free base, derived from VI by the loss of a proton, upon benzoylation yields the hydrochloride of the dibenzoyl derivative, ethyl  $\beta$ -diethylamino- $\alpha,\gamma$ -dibenzoylcrotonate, which was actually isolated. Since the second benzoyl group attaches itself to the  $\gamma$ -carbon, it seems likely that the immediate precursor of the dibenzoyl derivative possesses the structure



(5) Lauer and Jones, *THIS JOURNAL*, **59**, 232 (1937).

All attempts to isolate a monobenzoylation product failed, however.

The benzoylation of ethyl  $\beta$ -di-*n*-propylaminocrotonate was also investigated. The results were similar to those obtained in the case of ethyl  $\beta$ -diethylaminocrotonate.

### Experimental

**Benzoylation of Ethyl  $\beta$ -Diethylaminocrotonate** was carried out in dry ether with benzoyl chloride. The description of a typical benzoylation follows. A solution of the diethylamino-crotonic ester (45 g.) in dry ether (220 ml.) was treated dropwise with benzoyl chloride (33 g.). The reaction mixture was stirred and cooled in an ice-bath. After the addition of the benzoyl chloride was complete, the reaction mixture (in a well-stoppered container) was placed in a refrigerator and allowed to stand. A mixture of hydrochlorides separated out slowly; 27 g. separated out on standing overnight, and during a period of four months an additional 40 g. of material was obtained.

It was not possible to obtain pure compounds by the direct crystallization of this mixture of hydrochlorides, but it was noted that a portion of the product was hydrolyzed by shaking with water.

**Treatment of mixed hydrochlorides with water** was conducted in the following way. A sample (16 g.) of the mixed hydrochlorides was shaken with water and the light-yellow solid (7.8 g.) which precipitated out, was extracted with ether. Crystallization from a mixture of ether and petroleum ether (b. p. 60–68°) yielded colorless crystals (m. p. 76–78°) which were soluble in both dilute hydrochloric acid and dilute sodium hydroxide solutions. Ferric chloride produced a deep purple color with a solution of this crystalline material. After repeated crystallization from a mixture of ether and petroleum ether, the crystalline compound,  $C_{24}H_{27}NO_4$ , melted at 76.5–77.5°. Aqueous ethanol also can be used for purification purposes.

*Anal.* Calcd. for  $C_{24}H_{27}NO_4$ : C, 73.24; H, 6.91; N, 3.56. Found: C, 73.34; H, 6.65; N, 3.93.

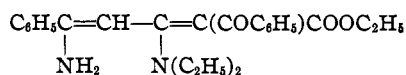
The hydrochloride of this amine, ethyl  $\beta$ -diethylamino- $\alpha,\gamma$ -dibenzoyl crotonate, was prepared by passing dry gaseous hydrochloric acid into an ether solution of the amine. Crystallization from a mixture of dry ether and alcohol yielded the pure hydrochloride (m. p. 125–126°).

*Anal.* Calcd. for  $C_{24}H_{28}NO_4Cl$ : C, 67.02; H, 6.58; Cl, 8.26. Found: C, 66.92; H, 6.57; Cl, 8.37.

The hydrochloride (0.48 g.) shaken with water (40 ml.) produced a precipitate (m. p. 76–77°; 0.35 g.) of the free amine,  $C_{24}H_{27}NO_4$ , which was separated by ether extraction.

Treatment of the mixed hydrochlorides, produced by the benzoylation of ethyl  $\beta$ -diethylaminocrotonate, with water therefore produced the amine,  $C_{24}H_{27}NO_4$ . After the removal by ether extraction of the material, which separated out upon the simple treatment of the mixed hydrochlorides with water, the clear aqueous solution was made alkaline with ammonia. The solution then became cloudy and a yellow precipitate,  $C_{24}H_{28}N_2O_3$ , gradually appeared. Thus, in one experiment, a sample (40 g.) of the mixed hydrochlorides, produced by benzoylation, gave upon treatment with water  $C_{24}H_{27}NO_4$  (10.1 g.) and, after its removal by

ether extraction, the treatment with ammonia produced  $C_{24}H_{28}N_2O_3$  (4.0 g.; m. p. 129–131°, after crystallization from ether). The compound,  $C_{24}H_{28}N_2O_3$ , produced in this manner, is sparingly soluble in ether, soluble in benzene, alcohol and dilute hydrochloric acid, but insoluble in dilute sodium hydroxide. A probable formula for this compound, which showed no color with ferric chloride, is



*Anal.* Calcd. for  $C_{24}H_{28}N_2O_3$ : C, 73.41; H, 7.25; N, 7.14. Found: C, 73.45; H, 7.23; N, 7.23.

**The Hydrolysis of  $C_{24}H_{27}NO_4$  (Ethyl  $\beta$ -Diethylamino- $\alpha,\gamma$ -dibenzoylcrotonate).**—The following experiment is typical of the behavior of  $C_{24}H_{27}NO_4$  upon treatment with acids. The amine (0.91 g.) was heated to boiling for twenty minutes with dilute sulfuric acid (20 ml., 1.4%). An oil separated (0.055 g.), which solidified upon cooling. Crystallization from a mixture of ether and petroleum ether produced a colorless crystalline compound (m. p. 126–127°). The compound, obtained in this manner, is insoluble in dilute hydrochloric acid, in aqueous sodium carbonate and does not produce a color with ferric chloride.

*Anal.* Calcd. for  $C_{22}H_{21}NO_3$ : C, 76.03; H, 6.11; N, 4.03. Found: C, 75.97; H, 6.01; N, 4.29.

A portion (0.233 g.) of the starting material was recovered.

Hydrolysis in the presence of acetic acid also produced the compound  $C_{22}H_{21}NO_3$ . The dibenzoylated amine,  $C_{24}H_{27}NO_4$ , yielded with aqueous sodium hydroxide (15%) a yellow sparingly soluble sodium derivative, which was converted into the original substance on treatment with carbon dioxide. Hydrolysis with aqueous sodium hydroxide (1%) slowly produced the compound  $C_{22}H_{21}NO_3$ , (3-benzoyl-4-diethylamino-6-phenylpyrone) along with some benzoic acid.

**Synthesis of 3-benzoyl-4-diethylamino-6-phenylpyrone** was accomplished by converting dehydrobenzoylacetic acid to 3-benzoyl-4-chloro-6-phenylpyrone, followed by replacement of the chlorine atom with the diethylamino group. The first step has been described by Perkin.<sup>6</sup> The 3-benzoyl-4-chloro-6-phenylpyrone (0.22 g.) was dissolved in absolute ethanol (25 ml.), diethylamine (0.102 g.) was added and the solution was boiled under reflux for ten minutes. A portion (15 ml.) of the alcohol was then removed by distillation, a small amount (1 ml.) of water was added and the solution cooled. Colorless crystals (0.176 g.; m. p. 126–127° after crystallization from a mixture of benzene and petroleum ether) separated out. Mixed with a sample of  $C_{22}H_{21}NO_3$  obtained from the acid hydrolysis of ethyl  $\beta$ -diethylamino- $\alpha,\gamma$ -dibenzoylcrotonate, the melting point was unchanged.

**Benzoylation of Ethyl  $\beta$ -Di-*n*-propylaminocrotonate.**—The aminocrotonate (13.5 g.), dissolved in ether (150 ml.), was treated at 0° with benzoyl chloride (9.3 g.). No visible reaction took place, so the mixture was placed in an ice-chest. After five weeks, a precipitate (15 g.) had separated. The mixed hydrochlorides obtained in this way were treated with water and the insoluble material produced by hydrolysis was extracted with ether. An oil

(6) Perkin, *J. Chem. Soc.*, 47, 262–297 (1885).

(3.85 g.) which upon cooling in the presence of petroleum ether (b. p. 60–68°) produced a solid product (2.70 g.; m. p. 50–65°), was obtained. Crystallization of the solid material from a mixture of ether and alcohol yielded a pure compound (m. p. 71–72°), which gave a dark purple color with a ferric chloride solution.

*Anal.* Calcd. for  $C_{26}H_{31}NO_4$ : C, 74.07; H, 7.42; N, 3.33. Found: C, 73.94; H, 7.44; N, 3.38.

The Hydrolysis of Ethyl  $\beta$ -Di-*n*-propylamino- $\alpha,\gamma$ -dibenzoylcrotonate was carried out as follows. The dibenzoylated amine (1.0 g.), dissolved in acetic acid (10 ml.), was boiled for ten minutes. After cooling, water was added, and a precipitate (0.51 g.) was obtained. Crystallization from a mixture of benzene and petroleum ether produced the pure product (m. p. 147–147.5°).

*Anal.* Calcd. for  $C_{24}H_{28}NO_3$ : C, 76.76; H, 6.71; N, 3.73. Found: C, 77.08; H, 6.66; N, 3.87.

**Synthesis of 3-Benzoyl-4-di-*n*-propylamino-6-phenylpyrone.**—This synthesis was conducted in the manner described above for the preparation of the corresponding diethylamino compound. The melting point (147–147.5°) of the synthetic specimen was unchanged by the addition of the compound produced by the acid treatment of the ethyl  $\beta$ -di-*n*-propylamino- $\alpha,\gamma$ -dibenzoylcrotonate.

### Summary

It was found that benzylation of ethyl  $\beta$ -diethylaminocrotonate and of ethyl  $\beta$ -di-*n*-propylaminocrotonate yields  $\alpha,\gamma$ -dibenzoyl derivatives. These dibenzoylation products undergo ring closure to produce substituted pyrones, which were synthesized.

MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 22, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

## Electric Moments of Inorganic Halides in Dioxane. I. Phosphorus, Arsenic and Antimony Trihalides<sup>1</sup>

BY P. A. McCUSKER AND B. COLUMBA CURRAN

Molecular complexes of inorganic halides with donor compounds are commonly interpreted as resulting from the formation of coördinate bonds between the acceptor and donor molecules. Studies of the dielectric properties of solutions of coördination complexes enable the persistence of coördination in solution to be detected and an estimate of the extent of coördination to be made. In the majority of previous investigations<sup>2</sup> of this kind, solutions of crystalline complexes in non-polar solvents were studied. Electric moments calculated from such data are of significance for only those complexes which are not dissociated in non-polar solvents. This work has thus been limited to those halides in which the central atoms form strong bonds with donor molecules.

Complexes of inorganic halides with dioxane are not subject to this limitation. Dioxane has, among ordinarily available solvents, the unique characteristic of being a donor compound and at the same time non-polar. This latter character permits the use of the Debye equation in calculating the electric moments of dioxanates in dioxane solution, and in estimating therefrom the extent of coördination. A knowledge of the extent of coördination affords a means of comparing the relative tendencies of certain elements to use

available bond orbitals in forming coördinate linkages with donor compounds.

Halides were chosen in this series of investigations because in these compounds the residual positive charge on the central atoms promotes coördination. Electric moments of some trihalides of members of the nitrogen family are reported in this first paper. The saturated character of nitrogen in its trihalides and the low solubility of bismuth halides in dioxane have limited the compounds investigated to the phosphorus, arsenic and antimony halides.

Incidental to the main purpose of the present work, but confirming the conclusions as to the formation of molecular coördination compounds between the halides studied and dioxane, definite crystalline compounds of dioxane with certain of these halides were isolated. Further studies on these crystalline dioxanates are being carried out and will be reported in a later paper.

### Experimental

**Preparation and Purification of Compounds.**—Phosphorus trichloride, phosphorus tribromide and arsenic trichloride were purified by fractional distillation of the c. p. liquids directly into weighing bottles under moisture-free conditions in an all glass system.

Arsenic tribromide, an Eastman Kodak Co. product, was fractionally distilled, a middle fraction being used in sample preparation.

(1) The material in this paper was presented in part at the Detroit meeting of the American Chemical Society, September, 1940.

(2) Ulich and Nespital, *Z. angew. Chem.*, **44**, 750 (1931).