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# The Synthesis of 4-Chloro-3-benzoyl-2-azetinone Derivatives and Their Conversion into *N*-Benzoyl-2,4-azetidinedione Derivatives

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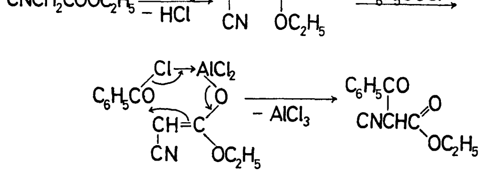
The treatment of ethyl α-cyanophenylacetate with benzoyl chloride in the presence of 2 equivalents of aluminum chloride in nitrobenzene afforded 4-chloro-3-benzoyl-3-phenyl- (6% yield) and 4-chloro-3-benzoyl-3-(*p*-benzoylphenyl)-2-azetinone (28%) at 50 °C. The same treatment of ethyl α-cyanopropionate afforded 4-chloro-3-benzoyl-3-methyl-2-azetinone (37%). The hydrolytic splitting of the chlorine atoms from the first two azetinones resulted in the formation of *N*-benzoyl-2,4-azetidinedione derivatives (36 and 20% respectively), whereas from the last we obtained *N*-benzoyl-α-carboxypropionamide (18%). These azetinone derivatives, when warmed with sodium methoxide in methanol, were converted into α-benzoyl α-cyano esters. The treatment of α-benzoyl α-cyano esters with aluminum chloride also afforded the azetinone derivatives in low yields.

Earlier studies of the aluminum chloride-catalyzed acylation[1] of active methylene compounds with acid chlorides were extended to the use of α-cyano esters as substrates. Thus, it was found that 4-chloro-3-benzoyl-2-azetinone derivatives could be formed from α-benzoylated α-cyano esters. The reconversion of the azetinone derivatives to the latter esters and their transannular, hydrolytic rearrangement to *N*-benzoyl-2,4-azetidinedione derivatives (*N*-benzoylmalonimides) were encountered.

When ethyl cyanoacetate was treated with benzoyl chloride in the presence of aluminum chloride in nitrobenzene at 55 °C, ethyl benzoylcyanoacetate was obtained as the main product. According to our previously-proposed mechanism,[1] the acylation can be explained in terms of an intramolecular condensation reaction which proceeds by means of the elimination of aluminum chloride from the coordination complex between acyl chloride and dichloroaluminum enolate as is shown in Scheme 1.



Scheme 1.

The benzoylation of ethyl α-cyanophenylacetate afforded a substance (Ia) in the presence of one equivalent of aluminum chloride at 50 °C, but the use of a larger amount of the condensing agent led to the formation of another substance (Ia′) besides Ia, while the benzoylation of ethyl α-cyanopropionate afforded only one product (Ib). The IR spectra of Ia, Ia′, and Ib are comparable to each other, none showing any band due to the cyano group. Their molecular formulas indicate that the α-benzoylated cyano ester is converted into Ia or Ib by losing its ethoxyl group and gaining a chlorine atom, and that Ia′ is a benzoylated

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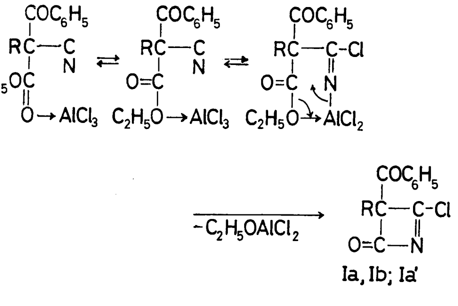
[1] T. Nojiri and K. Matsui, *Nippon Kagaku Zasshi*, **87**, 880 (1966); T. Nojiri, I. Hashimoto, M. Motoi, and K. Matsui, This Bulletin, **42**, 3359 (1969); K. Matsui, M. Motoi, and T. Nojiri, *ibid.*, **46**, 562 (1973).

product from the Ia. Thus, each of the structures seems to have a 4-chloro-3-benzoyl-2-azetinone ring. The reaction seems to be a novel case of the Ritter reaction[2] known as the nucleophilic addition of a nitrile to a carbonium ion in the presence of sulfuric acid. By analogy with the mechanism proposed for the aluminum chloride-catalyzed transacylation[3] between $\beta$-diketones and esters, the mechanism for the present reaction can be depicted as in Scheme 2.

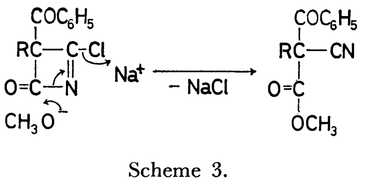


a: $R=C_6H_5$; b: $R=CH_3$; a': $R=p\text{-}C_6H_5COC_6H_4$

Scheme 2.

The formation of Ia′ can be ascribed to the Friedel-Crafts benzoylation at the *para* position of the phenyl group of Ia, because the hydrolysis of Ia′ gives *p*-benzoylated compounds, as will be described in the Experimental section. The facile formation of the four-membered ring from the $\alpha$-substituted, but not from the unsubstituted cyanoacetic ester, seems to be ascribable to a deviation from the normal valence angle by the introduction of a benzoyl group into the $\alpha$ position of the ester.

The treatment of 4-chloro-3-benzoyl-3-phenyl- (Ia), 4-chloro-3-benzoyl-3-(*p*-benzoylphenyl)- (Ia′), and 4-chloro-3-benzoyl-3-methyl-2-azetinone (Ib) with sodium methoxide in methanol gave their respective products, all of which show the IR spectra characteristic of $\alpha$-benzoyl $\alpha$-cyano esters, but the treatment of ethyl $\alpha$-benzoyl-$\alpha$-cyanophenylacetate and -$\alpha$-cyanopropionate with aluminum chloride in nitrobenzene gave Ia and Ia′, and Ib, respectively, in low yields. These findings support the assigned structures. The formation of this Ia′ suggests that free benzoyl chloride is liberated from the reactants during the reaction because of the reversibility[1] of the aluminum chloride-catalyzed acylation with acyl chlorides. The formation of $\alpha$-benzoyl $\alpha$-cyano ester by ring-opening can be explained in terms of the 1,4 attack of sodium methoxide on the 4-chloro-2-azetinone ring, as is illustrated in Scheme 3.

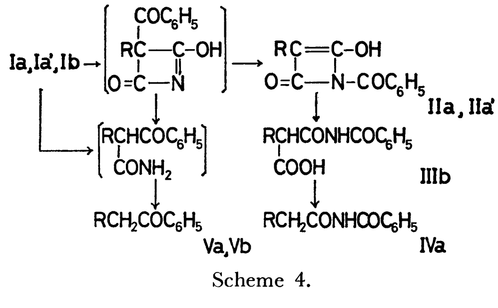


Scheme 3.

The hydrolytic splitting of the chlorine atom from Ia with glacial acetic acid containing a few drops of concentrated hydrochloric acid resulted in small amounts of *N*-benzoylphenylacetamide (IVa) and another substance (IIa), together with the unaltered Ia (47%), without giving a detectable amount of benzoic acid. The product IIa, with the composition of the expected 3-benzoyl-3-phenyl-2,4-azetidinedione, melts at 228.5—229.5 °C and is soluble in an aqueous sodium bicarbonate solution. In this solution, the IIa is partly converted into IVa on standing at room temperature, but remains unchanged to a certain extent. Obviously, the benzoyl group migrates from the carbon to the nitrogen atom.

The IR spectrum of Ia is somewhat similar to that of IIa, as will be described in the Experimental section. In the frequency region higher than 1200 cm$^{-1}$, however, a comparison of the two spectra shows that the absorption bands for Ia at 1745 cm$^{-1}$ and at 1238 and 1217 cm$^{-1}$, which may be due to ClC=N and Ar–CO–C respectively, are replaced by the bands at 1660 and 1629 cm$^{-1}$, and at 1426, 1402, and 1276 cm$^{-1}$, which may be assigned mainly to NC=O and $N\equiv C_3$ respectively, in IIa, which has no absorption due to N–H. Thus, the benzoyl group in IIa must be situated on the nitrogen atom; hence, IIa may be characterized as *N*-benzoyl-3-phenyl-2,4-azetidinedione. A similar acidic hydrolysis of Ia′ provided a chlorine-free substance (IIa′) (mp 228—230 °C), which was characterized as *N*-benzoyl-3-(*p*-benzoylphenyl)-2,4-azetidinedione by its IR spectrum, which is similar to that of IIa. Moreover, under more drastic conditions, Ia′ as well as Ia was hydrolyzed to give benzamide derived from the rearranged products.

A solution of Ia in methanol containing sodium carbonate, on standing at room temperature, also afforded a small amount of IIa, a trace of IVa, and an oil which was soluble in an aqueous sodium hydroxide solution but not in a sodium bicarbonate solution. This oil reacted to give an unidentified 2,4-dinitrophenylhydrazone which was not formed from Ia, and it was converted into desoxybenzoin (Va) and benzil upon treatment with sodium nitrite and sulfuric acid. The formation of such a hydrazone or ketones suggests that, in an alkaline medium, a part of either Ia or intermediate 3-benzoyl-3-phenyl-2,4-azetidinedione can be hydrolyzed with ring-opening prior to the rearrangement, as is shown in Scheme 4.



Scheme 4.

The rearrangement, being independent of the acidities of media, seems to proceed intramolecularly through both resonance-stabilized anions from the 3-benzoyl-

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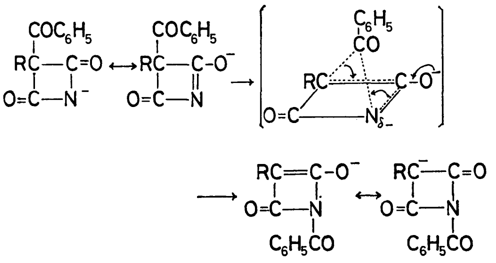
[2] L. I. Krimen and D. J. Cota, "Organic Reactions," Vol. 17, p. 213 (1969).

[3] K. Matsui and M. Motoi, This Bulletin, **46**, 565 (1973).

and *N*-benzoyl-azetidinedione derivatives. Accordingly, the transannular migration of the benzoyl group can be considered as being due to the relative unstability of the former anion which has a quaternary carbon atom linked to the three carbonyl groups. For this electrophilic rearrangement, the transition state shown in Scheme 5 may be passed through.



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Ib, under conditions similar to those in the above acidic hydrolysis of Ia, was converted into *N*-benzoyl-α-carboxypropionamide (IIIb) (18%), benzoic acid, and a mixture, giving the unaltered Ib (75%). The acidic hydrolysis of the mixture gave a slight amount of propiophenone (Vb). It can be seen that Ib undergoes the same rearrangement and subsequent ring-opening to give IIIb; it is also subject to some acid cleavage.

Further work is required on the general preparation of *N*-acyl-2,4-azetidinediones.

## Experimental

*Materials.* Commercial ethyl cyanoacetate was distilled at 206—207 °C before use. The ethyl α-cyanopropionate[4] and ethyl α-cyanophenylacetate[5] were prepared according to the literature, boiling at 86.4—87 °C/17 mmHg and at 125—127 °C/3.5 mmHg respectively. IR of the latter: 2250, 1747, 1240, 1028 cm$^{-1}$. Ethyl α-benzoyl-α-cyanophenylacetate was prepared from ethyl α-cyanophenylacetate by a modification of the method described in the literature[6]; bp 135—136 °C/0.03 mmHg. Found: C, 73.48; H, 5.13; N, 4.71%. Calcd for $C_{18}H_{15}NO_3$: C, 73.7; H, 5.17; N, 4.78%. IR: 2264, 1763—1749, 1696, 1218—1184, 1005 cm$^{-1}$. Ethyl α-benzoyl-α-cyanopropionate was also prepared as above; bp 116—117 °C/0.4 mmHg. Found: C, 67.54; H, 5.63; N, 5.94%. Calcd for $C_{13}H_{13}NO_3$: C, 67.51; H, 5.68; N, 6.06%. IR: 2207, 1752, 1709, 1259—1229, 1014 cm$^{-1}$.

*General Procedure for Preparing Crude Ethyl Benzoylcyanoacetate and 4-Chloro-3-benzoyl-2-azetinone Derivatives.* To a cold solution of aluminum chloride in dry nitrobenzene (10 ml), which was placed in a 50-ml flask equipped with a calcium chloride tube, we added the cyano ester (15 mmol) and then benzoyl chloride (4.2 g, 30 mmol) with cooling. The mixture was kept, with occasional swirling, in a thermostat. The reaction mixture was then stirred into a mixture of crushed ice and hydrochloric acid, after which the mixture was shaken with ether. The upper layer was washed with water to remove the aluminum chloride, and then shaken occasionally with a sodium bicarbonate solution until the Beilstein test for benzoyl chloride showed negligible results. The upper layer was then concentrated and steam-distilled *in vacuo* to leave a crude crystalline product.

*a) Ethyl Benzoylcyanoacetate*: The crude product obtained from ethyl cyanoacetate (1.7 g) by using aluminum chloride (4 g, 30 mmol) at 55 °C for 20 hr was found to consist of slight amounts of dibenzoyl- and tribenzoyl-methane by the use of the procedures described in our previous papers.[1] The aqueous sodium bicarbonate extract, after having been acidified with hydrochloric acid, was shaken with ethyl acetate. The upper layer was shaken with an aqueous copper acetate solution, and then the resulting product was filtered from copper benzoate. The upper layer of the filtrate was dried over sodium sulfate and concentrated to give a copper complex (mp 231—233 °C, ethanol), which was usually decomposed to give ethyl benzoylcyanoacetate. The aqueous solution containing aluminum chloride, after standing for a week, was extracted with ether. The evaporation of the ether extract gave an oil which was subsequently crystallized from ethanol to give ethyl benzoylcyanoacetate; mp 39—40 °C, (Found: N, 6.16%). The total yield was 41%.

*b) 4-Chloro-3-benzoyl-3-phenyl-2-azetinone, Ia*: The crude product obtained from ethyl α-cyanophenylacetate (2.84 g) by using aluminum chloride (15 mmol) at 50 °C for 48 hr was dissolved in a slight amount of benzene; then the solution was transferred onto a column packed with silica gel (60—200 mesh). Ia, eluted with benzene–petroleum ether (1 : 1), was recrystallized from ethanol as colorless needles (0.65 g, 15%), mp 184—185 °C. Found: C, 67.33; H, 3.56; Cl, 12.91; N, 4.91%. Calcd for $C_{16}H_{10}ClNO_2$: C, 67.73; H, 3.56; Cl, 12.49; N, 4.94%. MS: $M^+=283$, 285 (intensity ratio, 3 : 1). IR(KBr): 1745(s), 1707(sh), 1601(sh), 1592(s), 1567(s), 1547(s), 1491(m), 1446(m), 1350 (s), 1314(w), 1238(s), 1217(m), 1176(w), 1043(m), 1020(m) cm$^{-1}$.

*c) 4-Chloro-3-benzoyl-3-(*p*-benzoylphenyl)-2-azetinone, Ia′*: The crude product from the same treatment with 30 mmol of aluminum chloride was chromatographed successively with benzene–petroleum ether (1 : 1) and benzene–ether (3 : 1), giving 0.26 g (6%) of Ia and 1.64 g (28%) of Ia′ respectively. The latter, on recrystallization from ethanol, melts at 164.5—165 °C. Found: C, 71.30; H, 3.68; Cl, 8.89; N, 3.64%. Calcd for $C_{23}H_{14}ClNO_3$: C, 71.23; H, 3.64; Cl, 9.14; N, 3.61%. MS: $M^+=387$, 389 (3 : 1). IR(KBr): 1754(s), 1704(sh), 1669(s), 1598(s), 1570(s), 1535(s), 1502(m), 1447(m), 1355(s), 1315(m), 1279(s), 1239(s), 1227(m), 1175(w), 1041(m), 1020(w) cm$^{-1}$.

*d) 4-Chloro-3-benzoyl-3-methyl-2-azetinone, Ib*: The crude product obtained from ethyl α-cyanopropionate (1.9 g) by using 30 mmol of aluminum chloride at 50 °C for 48 hr was recrystallized from ethanol to give Ib(1.22 g, 37%), mp 123—124 °C (ethanol). It decomposes, with the formation of benzoic acid, over a long period in air. Found: C, 60.22; H, 3.74; Cl, 16.06; N, 6.36%. Calcd for $C_{11}H_8ClNO_2$: C, 59.64; H, 3.61; Cl, 16.03; N, 6.32%. MS: $M^+=221$, 223 (3 : 1). IR(KBr): 1750(s), 1707(sh), 1603 (s), 1575(m), 1554(s), 1489(w), 1448(m), 1387(m), 1349(m), 1313(w), 1247(m), 1223(m), 1050(m), 1015(w) cm$^{-1}$.

*Ia and Ia′, or Ib from the α-Benzoyl α-Cyano Ester.* When ethyl α-benzoyl-α-cyanophenylacetate (2.9 g, 10 mmol) in a nitrobenzene solution (10 ml) of aluminum chloride (1.6 g, 12 mmol) was kept at 50 °C for 22 hr (as in the case of *c*) above), Ia and Ia′ were obtained from the reaction mixture in trace and 7-mg amounts respectively. The yields were

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[4] N. Zelinsky, *Ber.*, **21**, 162 (1888).

[5] E. C. Horning and A. F. Finelli, "Organic Syntheses," Coll. Vol. IV, p. 461 (1963).

[6] A. Haller, *C. R. Acad. Sci. Paris*, **105**, 169 (1887).

increased to 0.5 mg and 12 mg respectively when the amount of aluminum chloride and the reaction temperature were decreased to 5 mmol and to 40 °C respectively. Under the former conditions, 70 mg of Ib were obtained from 2.3 g (10 mmol) of ethyl α-benzoyl-α-cyanopropionate. These azetinones were identified by the mixed-melting-point method.

*α-Benzoyl α-Cyano Ester from Ia, Ia′, or Ib.* A benzene solution (2 ml) of Ia (2 mmol) was added to a sodium methoxide solution made from sodium (0.002 g atom) and methanol (3 ml). After 1 hr, the mixture was warmed at 40 °C for 1 hr. The cooled reaction mixture was acidified with an aqueous acetic acid and then shaken with ether. The ether layer, after having been washed with a sodium bicarbonate solution, was dried and concentrated; then the remaining oil was placed in a column packed with silica gel. Benzene-ether (14 : 1) was used as the eluent. The fractions, each showing a single spot on tlc, were collected. The resulting product was concentrated to leave an oil. The IR spectra for the oils from Ia and Ib were similar to those of ethyl α-benzoyl-α-cyanophenylacetate and -α-cyanopropionate respectively. In the same way, the IR spectrum of the oil from Ia′ was found to be similar to that for Ia, so it seems to be due to methyl α-benzoyl-α-cyano-*p*-benzoylphenylacetate. No search for compounds with a methoxyl group in the products was made because of the small amounts involved.

*Hydrolysis of Ia. a)*: Two drops of concd hydrochloric acid were added to a solution of Ia (0.3 g) in benzene (1 ml) and glacial acetic acid (5 ml); then the solution was warmed at 50—51 °C for 2 hr. The cooled reaction mixture was diluted with water and then shaken with ether-benzene (5 : 1). The upper layer, freed from acetic acid by washing with water, was shaken with a saturated sodium bicarbonate solution. The upper layer was then dried and evaporated to leave a crystalline mass, which was subsequently recrystallized from ethanol to give Ia (0.14 g). The lower layer, after the removal of the ether dissolved, was acidified to precipitate crude *N*-benzoyl-3-phenyl-2,4-azetidinedione (IIa) (0.1 g, 36%, mp 226—228 °C), which was collected by filtration. The crude IIa in ether was washed with an aqueous solution of a slight amount of sodium bicarbonate; then it was dried and concentrated by passing a stream of dry air, giving colorless crystals; mp 228.5—229.5 °C. Found: C, 72.67; H, 4.19; N, 5.42%. Calcd for $C_{16}H_{11}NO_3$: C, 72.44; H, 4.19; N, 5.28%. IR(KBr): 1710(sh), 1660(s), 1629(m), 1612(m), 1579(m), 1552(s), 1496(w), 1448(m), 1426(s), 1402(s), 1352(s), 1309(m), 1276(s), 1115(m) cm$^{-1}$.

The filtrate separated from the above crude IIa was extracted with ether. The resulting extract was dried and concentrated to give colorless crystals (20 mg, 8%), which were subsequently recrystallized from ether to give *N*-benzoylphenylacetamide; mp 138.5—139.5 °C. This melting point was undepressed on admixture with a synthesized sample melting at 139—140 °C (lit.[7] 129—130 °C). Found: N, 5.8%. IR(KBr): 3287, 1732, 1686, 1605 cm$^{-1}$.

*b)*: A solution of Ia (50 mg) in benzene (1 ml) and ethanol (10 ml) was added to a mixture of an aqueous solution (4 ml) of sodium carbonate (35 mg) and methanol (30 ml). The resulting solution was stirred with a magnetic stirrer at room temperature for 6 hr. The reaction mixture was then steam-distilled *in vacuo* to remove the organic solvent. The residue was separated as above into an oil, IIa (7 mg), and *N*-benzoylphenylacetamide (a trace). The oil, containing a small amount of Ia, gave a 2,4-dinitrophenylhydrazone. The isolated products were identified by mixed-melting-point method.

*c)*: A solution of Ia (100 mg) in benzene (2 ml) and ethanol (20 ml) was added to a warm mixture of methanol (40 ml) and an aqueous solution (5 ml) of sodium carbonate (100 mg). The resulting solution was warmed at 60—65 °C for 8 hr. The reaction mixture, after the removal of the organic solvent, was shaken with ether. The lower layer, on acidification, gave phenylacetic acid (mp 79—80 °C (water)) and benzoic acid (mp 119—120 °C). The upper layer, after extraction with a sodium hydroxide solution, was evaporated to give benzamide (mp 129—130 °C (ether)). The alkaline extract, after acidification, was reextracted with ether. The evaporation of the ether extract gave an oil. An excess amount of sodium nitrite powder was added in small portions to a solution of this oil in 80% sulfuric acid over a 12-hr period with occasional heating up to 50—60 °C; then the reaction mixture was diluted with warm water. The ether extract from the sulfuric acid solution was concentrated and then steam distilled. The residue was alkalized with a sodium hydroxide solution and then extracted with ether. An oil obtained from the ether extract gave a 2,4-dinitrophenylhydrazone melting at $<$195 °C (ethanol). A similar treatment of the above distillate led to crystals melting at $<$185 °C. The first and last melting points were undepressed on admixture with the 2,4-dinitrophenylhydrazone of benzil (mp 200—202 °C) and that of desoxybenzoin (mp 203—204 °C) respectively.

*Acid Hydrolysis of Ia′. a)*: Ia′, when treated as has been described in the case of the hydrolysis of Ia, *a)*, was converted into *N*-benzoyl-3-(*p*-benzoylphenyl)-2,4-azetidinedione (20%); mp 228—230 °C (tetrahydrofuran). Found: C, 74.82; H, 4.03; N, 3.55%. Calcd for $C_{23}H_{15}NO_4$: C, 74.78; H, 4.10; N, 3.79%. IR(KBr): 1705(sh), 1662(sh), 1652(s), 1630(m), 1605(m), 1580(m), 1563(s), 1495(w), 1447(w), 1425(s), 1400(s), 1353(s), 1314(s), 1280(s), 1262(m), 1173(m), 1115(m) cm$^{-1}$.

*b)*: To a solution of Ia′ (100 mg) in glacial acetic acid (2 ml), we added one drop each of concd sulfuric acid and water; then the solution was refluxed for 0.5 hr. The reaction mixture was subsequently diluted with water, neutralized with sodium bicarbonate, and then shaken with ether. The evaporation of the upper layer left crystals, which were then triturated with water. The water-insoluble crystals were recrystallized from ether-methanol to give *p*-benzoylphenylacetamide; mp 140—141 °C (lit.[8] 136—137 °C). Found: C, 75.34; H, 5.66; N, 5.70%. From the aqueous solution, benzamide was separated; it was then crystallized from ether-petroleum ether; mp 127—128 °C. The above lower layer was acidified and then extracted with ether. The ether extract, freed from acetic acid, was evaporated to give crystals, which were then triturated with water. The water-insoluble crystals were recrystallized from benzene to give *p*-benzoylphenylacetic acid; mp 113—114 °C (lit.[8] 112—114 °C). Found: C, 75.18; H, 5.15%. From the aqueous solution, benzoic acid was isolated. The benzoic acid and benzamide were identified by the mixed-melting-point method.

*Acid Hydrolysis of Ib.* Six drops of concd hydrochloric acid were added to a solution of Ib (2 g) in benzene (5 ml) and glacial acetic acid (30 ml); then the solution

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[7] H. L. Wheeler, T. B. Johnson, and D. F. McFarland, *J. Amer. Chem., Soc.* **25**, 787 (1903).

[8] R. P. Zelinski, B. W. Turnquest, and E. C. Martin, *ibid.*, **73**, 5521 (1951).

was warmed at 65—66 °C for 0.5 hr. The reaction mixture was separated as in the case of the hydrolysis of Ia, *a*). The unaltered Ib weighed 1.5 g. The sodium bicarbonate extract, after acidification, was extracted with ether. The ether extract was evaporated to give a crystalline mass, which was triturated with ether-petroleum ether (1 : 4); then the insoluble crystals were collected by filtration. From the filtrate, benzoic acid was obtained. The organic solvent-insoluble crystals were treated with a sodium bicarbonate solution; then the product was filtered from an insoluble substance. The filtrate on acidification gave crystals. A solution of these crystals in ether was concentrated by passing dry air to give *N*-benzoyl-α-carboxypropionamide (0.36 g, 18%) in the form of colorless needles, which melted at 129 °C with decomposition. Found: C, 59.71; H, 5.04; N, 6.20%. Calcd for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.01; N, 6.33%. IR (KBr): 3400—3370, 3306, 1712, 1682, 1602 cm$^{-1}$. The thermal decomposition of this carboxy amide gave *N*-benzoylpropionamide. It was crystallized from petroleum ether (mp 98—98.5 °C), giving no depression on admixture with a synthesized sample (lit.[9] mp 98 °C). IR(KBr): 3295, 1713, 1683, 1602 cm$^{-1}$.

The mother liquor from the crystallization of the above carboxy amide, the sodium bicarbonate-insoluble substance, and the aqueous acidic filtrates were combined; then the mixture, after the addition of a few mls of concd hydrochloric acid, was steam-distilled. The distillate gave 2,4-dinitrophenylhydrazone of propiophenone. It was recrystallized from ethanol (mp 197—199 °C), giving no depression on admixture with an authentic sample melting at 199—200 °C.

The present authors wish to express their thanks to Professor Hiroshi Suda and to Miss Michiko Araki of this faculty for their elemental analyses.

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9) H. L. Wheeler, P. T. Walden, and H. F. Metcalf, *ibid.*, **20**, 64 (1898).