reduction and acetylation led to compounds IIIc and IIId, respectively.

Since the anomalous hydrocyanation product appeared to be the consequence of a hydrocyanation process and a subsequent Michael condensation, it was of interest to ascertain whether the last reaction could be induced in a separate experiment. As a consequence, a base-catalyzed condensation of 2-cyclohexenone (I) and 3-cyanocyclohexanone (II), prepared by a previously prescribed method,[3] was executed under conditions similar to those of the preparation of IIIa. The reaction afforded the latter, although in low yield.

Experimental Section

Condensation Product IIIa.—A solution of 5.0 g of 2-cyclohexenone (I) and 4.0 g of potassium cyanide in 45 ml of 95% ethanol and 25 ml of water was refluxed for 3.5 hr. The pH of the mixture was *ca.* 12. The cooled solution was neutralized with hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The solid residue (5.4 g) was chromatographed on activity 4 alumina. Elution with benzene yielded 3.0 g of a yellow solid whose crystallization from water afforded pale yellow crystals of IIIa: mp 193–194°; infrared ($CHCl_3$), OH or NH 2.89 (m), 3.01 (m), C═O 5.89 (s), C═O and C═C 6.10 (s), 6.29 (s), 6.62 μ (s); ultraviolet $\lambda_{max}^{95\%\ EtOH}$ 310 mμ (ε 11,000).

Anal. Calcd for $C_{13}H_{17}O_2N$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.26; H, 7.92; N, 6.53.

Dry hydrogen chloride gas was bubbled into a methanolic solution of IIIa. Removal of the solvent and crystallization of the residual solid from acetone yielded crystalline IIIa hydrochloride: mp 135°; infrared spectrum (Nujol), OH or NH 2.92–3.02 (s, br), C═O 5.88 (s), C═O, C═C, C═N 6.03 (s), 6.09 (s), 6.25 (s), 6.41 μ (m). A solution of 1.5 g of 2-cyclohexenone (I) and 1.8 g of 3-cyanocyclohexanone (II) in 10 ml of a phosphate buffer mixture (pH 10.3) was refluxed for 0.5 hr at 50–60°. Work-up and as above yielded 0.9 g of IIIa, mp and mmp 193–194°; spectra were identical with those of IIIa prepared by the above method.

Ketoamide IIIb.—A mixture of 0.2 g of IIIa and 2 ml of acetic anhydride in 10 ml of pyridine was stirred at room temperature for 18 hr. Evaporation of the solution and crystallization of the residual solid (0.15 g) from hexane–ethyl acetate yielded colorless crystals: mp 117°; infrared ($CHCl_3$), C═O 5.84 (s), 6.06 (s), C═O, C═C 6.29 μ (s); ultraviolet $\lambda_{max}^{95\%\ EtOH}$ 301 mμ (ε 9400); pmr ($CDCl_3$), three-proton singlet at 2.16 ppm (acetyl Me).

Anal. Calcd for $C_{15}H_{19}O_3N$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.77; H, 7.43; N, 5.44.

Alcohol IIIc.—A solution of 0.5 g of IIIa and 30 mg of sodium borohydride in 15 ml of a phosphate buffer mixture (pH 7.0) was stirred at room temperature for 2 hr. Water was added and the mixture extracted with chloroform. The extract was dried over sodium sulfate and evaporated. Crystallization of the residual solid (0.2 g) from hexane–chloroform yielded colorless crystals of IIIc: mp 214–215°; infrared ($CHCl_3$), OH, NH 3.00 (s), 3.08 (s), 3.19 (s), C═O and C═C 6.10 (s), 6.20 μ (m); ultraviolet $\lambda_{max}^{95\%\ EtOH}$ 320 mμ (ε 13,200).

Anal. Calcd for $C_{13}H_{19}O_2N$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.54; H, 8.69; N, 6.25.

Amido Ester IIId.—A mixture of 0.2 g of IIIc and 2 ml of acetic anhydride in 10 ml of pyridine was stirred at room temperature for 18 hr. Evaporation of the solution under reduced pressure and crystallization of the residual solid (0.19 g) from ether yielded colorless crystals of IIId: mp 132–133°; infrared ($CHCl_3$), NH 3.07 (w), C═O 5.78 (s), 6.07 (s), C═O, C═C 6.30 μ (s); ultraviolet $\lambda_{max}^{95\%\ EtOH}$ 312 mμ (ε 10,000); pmr ($CDCl_3$), three-proton singlet at 2.06 and 2.16 ppm (acetyl Me).

Anal. Calcd for $C_{17}H_{23}O_4N$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.97; H, 7.50; N, 4.49.

Registry No.—IIIa, 13369-48-7; IIIa hydrochloride, 13369-49-8; IIIb, 13369-50-1; IIIc, 13369-51-2; IIId, 13369-52-3.

Acknowledgment.—The authors are indebted to the CIBA Pharmaceutical Co. for financial support of this work.

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[3] D. K. Banerjee, J. Dutta, and G. Bagavant, *Proc. Indian Acad. Sci.*, **A46**, 80 (1957).

Rearrangements Involving the Mixed Anhydride of o-Benzoylbenzoic and Methylcarbonic Acids[1]

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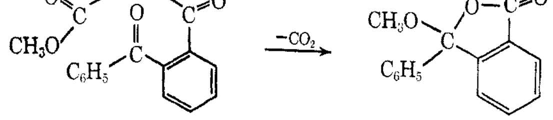
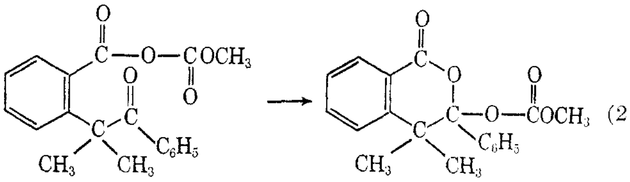
In earlier work, the pyrolysis at about 120° of the mixed anyhdride of methylcarbonic and *o*-benzoylbenzoic acids (I) to form ψ-methyl *o*-benzoylbenzoate (II) and carbon dioxide was reported[3] (eq 1). Subsequently, the pyrolysis of the mixed anhydride of methylcarbonic and *o*-(α,α-dimethylphenacyl)benzoic (III) was shown to yield a rearranged lactonic ester (IV) without loss of carbon dioxide[4] on heating near 130° (eq 2). Pyrolysis of IV at about 225° yielded the ψ-methyl ester of *o*-(α,α-dimethylphenacyl)benzoic acid and carbon dioxide.



I II (1)



III IV (2)

The above observations led us to reexamine the pyrolysis of I at lower temperatures. When I, mp 70–71°, is heated (neat) in the 70–80° range, rearrangement to the lactonic ester (V), mp 149°, occurs (Scheme I). Thus, the behavior of I parallels that[4] of III if the temperature of pyrolysis is kept low. The resulting compound (V) is stable until heated in the 170–235° range when it forms ψ ester (II), normal ester (VI), and the anhydride of *o*-benzoylbenzoic acid[3] (VII). The relative amounts of II, VI, and VII formed from V depend on the temperature of pyrolysis. The difference in the results herein reported with the previous ones[3] is probably due to the fact that extremely pure I was used and all traces of acid and basic contaminants were removed from the apparatus and solvents in question.

The rearrangement of I to V takes place almost quantitatively in 12 hr when I is heated (neat) at 70°, or in about 45 min when heated at 120–125°. In addition, 5–7% of II is produced at the higher tempera-

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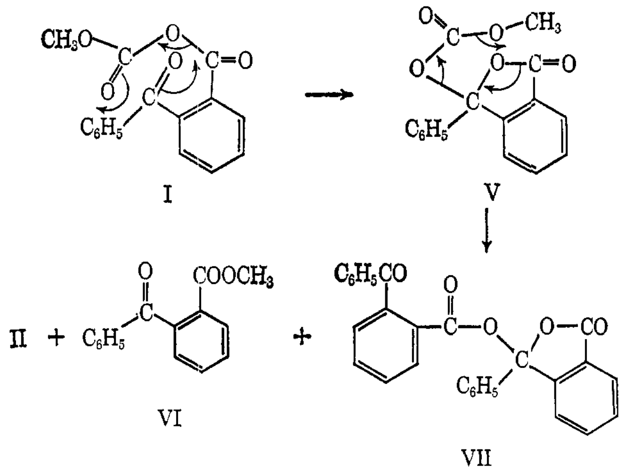
[1] This work was supported by Grant No. DA-ARO-D-31-124-G846 of the U. S. Army Research Office, Durham, N. C.

[2] Postdoctoral Research Assistant, The Ohio State University, 1966–1967.

[3] M. S. Newman and C. Courduvelis, *J. Am. Chem. Soc.*, **88**, 781 (1966).

[4] M. S. Newman and S. Mladenovic, *ibid.*, **88**, 4523 (1966).

SCHEME I



ture. However, if I is rapidly heated to temperatures higher than 140° the results shown in Table I are obtained. When pure V is heated no reaction occurs until temperatures near 180° are reached, at which point pyrolysis to yield II (12–15%), VI (18–35%), and VII (50–68%) occurs. Since these proportions of products are similar to those listed in Table I, I for the most part undoubtedly rearranges rapidly to V before other pyrolytic paths are followed. However, some VI may be formed directly from I *via* a [3.2.1] path accompanied by loss of carbon dioxide, as shown in formula V.[4a] Both methyl *o*-benzoylbenzoate (VI) and the ψ ester (II) are stable when heated at 230–240° for 45 min.

TABLE I

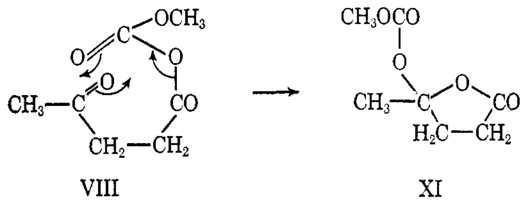
PYROLYSIS OF I

Temp,[a] °C	Products,[b] % VI	II	V	VII
123	...	6[c]	94	...
145	1	11	83	5
185	38	10	...	52
235	35	15	...	50

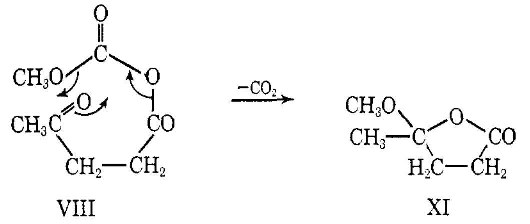
[a] The temperatures listed were accurate to ±2°. [b] All pyrolyses were for 45 min. [c] The percentages listed are accurate to ±2% as determined by nmr.

In order to see if the pyrolytic change of I to V takes place by a monomolecular path, solutions of I at two different concentrations in toluene (and in acetonitrile) were heated for equal times. Since the same percentages of I were converted to V in both experiments in each solvent, the rates are monomolecular. However, the rate of rearrangement was greater in acetonitrile. Judging from the products (II, VI, and VII) of pyrolysis of V at temperatures of 180° and higher, these reactions occur by a path which involves scission into at least two fragments.

Since the pyrolytic reaction of I was shown to proceed by different paths depending on the temperature of pyrolysis, we repeated the pyrolysis of the mixed anhydride of levulinic acid and methylcarbonic acid (VIII) previously reported[5] to yield ψ-methyl levulinate (IX) and normal methyl levulinate (X) in the ratio 92:8 at temperatures in the 120–140° range. We now find that, when the pyrolysis of VIII is conducted at 50–55° for 4–6 hr, a mixture of 40% of IX and 60% of the cyclic lactonic ester (XI) is obtained. The rearrangements of VIII to XI and to IX thus undoubtedly occur by the two [3.2.1] paths shown in eq 3 and 4. The low-temperature rearrangement of VIII to XI thus parallels the low-temperature rearrangement of I to V.



(3)



(4)

Experimental Section[6]

3-Carbomethoxy-3-phenylphthalide (V).—In a clean[6] test tube 1.0 g of pure I (mp 70–71° after several recrystallizations from methylene chloride–hexane) was just melted and held at 70 ± 2° for 12 hr. No loss in weight occurred and a solid, mp 138–142°, had formed. Recrystallization from methylene chloride–hexane afforded colorless crystals of V, mp 148–149°, in 90–95% yield. The nmr spectrum in $CDCl_3$ showed a singlet at δ 3.75 ppm (OCH_3) and nine aromatic protons at 7.45–7.65 (relative to TMS).

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.6; H, 4.2. Found:[7] C, 67.5; H, 4.1.

When two solutions each containing 500 mg of I in 5 and 20 ml of pure toluene were heated at 88 ± 1° for 2 hr, nmr analysis of the products showed each to consist of 82:18 mixtures of I and V by the OCH_3 singlet at δ 3.86 and 3.75, respectively. When similar experiments were done, except that the heating was at 70 ± 1° for 4 hr in acetonitrile, each solution afforded a 1:1 mixture of I and V.

Pyrolysis of V.—When samples of pure V were heated at the temperatures indicated neat for 45 min, there was obtained VI, II, and VII in the following amounts (as estimated by nmr analysis), respectively: 35, 12, and 53% (185 ± 2°); 29, 15, and 56% (203°); and 18, 14, and 68% (228°).

Pyrolysis of I.—Samples of pure I, mp 70–71°, in clean[6] test tubes were rapidly heated to the temperatures indicated in Table I for 45 min. The contents were then dissolved in $CDCl_3$ and the nmr spectrum taken with TMS as internal standard.

Pyrolysis of VIII.—On pyrolysis of VIII[5] at 50–55° for 4–6 hr (two experiments), there was obtained a liquid of which nmr analysis indicated that a mixture of 60% of XI (singlet at δ 3.74 (CH_3, 3 H), $CH_3C{=}O$ at 2.16; multiplet, 4 H at 2.70), and 40% of IX (OCH_3 at 3.21, CH_3 at 2.16, and 4 H at 2.70) was present.

Registry No.—I, 6158-51-6; II, 7335-63-9; V, 13369-55-6; VI, 606-28-0; VII, 13369-57-8; IX, 1487-57-6; XI, 13369-59-0.

[4a] NOTE ADDED IN PROOF.—Professor Robert L. Augustine, Seton Hall University, has informed us that he has obtained essentially the same results in the decomposition of I. He has also further established the intramolecular nature of the formation of V by use of crossover experiments using I and the mixed anhydride of ethylcarbonic and *o*-toluoylbenzoic acid. His results will be reported shortly in conjunction with other work in this area.

[5] M. S. Newman, N. Gill, and B. Darre, *J. Org. Chem.*, **31**, 2713 (1966).

[6] All glassware was steamed out for 30 min before use. Solvents were purified by conventional methods and were freshly distilled before use.

[7] Analysis was performed by Galbraith Microanalytical Laboratory, Knoxville, Tenn.