In earlier work[1] on the dehydrogenation of tetracyclohexylmethane (IV) to tetraphenylmethane, none of the latter could be isolated, although it was detected by gas chromatography. Tetraphenylmethane has now been obtained in 9.1% yield by aromaticization of IV thereby completing the structure proof for tetracyclohexylmethane.

The 60-Mcps proton magnetic resonance (pmr) spectra for the intermediate cyclohexyl and phenyl substituted methanes in deuteriochloroform displayed two absorption regions: a fairly sharp band at 2.65 and complex multiplets in the region 6.6–9.6 ppm. Quantitative band and coupling-constant assignments were impossible to determine. However, the ratio of the areas under the respective pmr bands agreed satisfactorily with the theoretical (see Table I) and supported the molecular structures proposed.

TABLE I

PROTON DISTRIBUTION IN $(c\text{-}C_6H_{11})_nC(C_6H_5)_{4-n}$

	Phenyl		Cyclohexyl		Cyclohexyl/phenyl	
n	Calcd	Found[a]	Calcd	Found[a]	Calcd	Found
1	15	14.8	11	11.2	0.73	0.75
2	10	9.7	22	22.2	2.20	2.26
3	5	4.7	33	33.5	6.60	7.09

[a] Based on the computed average area per proton.

Experimental Section

Gas chromatographic analysis was performed at *ca.* 210° using capillary columns coated with Carbowax 1540. Hydrogenations were carried out in a magnetically stirred autoclave. Stirring was maintained at 1000 rpm for all reactions. Thin layer chromatography was performed with Silica gel HF$_{254+366}$ (E. Merck A. G.). All reagents, solvents and catalyst are from commercial suppliers. Tetraphenylmethane was obtained from K & K Laboratories, Inc., and was purified by sublimation before use. Tetracyclohexylmethane was prepared as previously reported.[1]

Dehydrogenation of Tetracyclohexylmethane.—The dehydrogenation of IV was carried out as previously described[1] except refluxing methyl phthalate was used (bp 280°) as a heat bath. Three 100-mg batches furnished 25 mg (8%) of tetraphenylmethane, mp 284–285° (no depression), mol wt 311 (vapor osmometry), when the hot, filtered octadecane solutions were diluted with an equal volume of benzene.

Cyclohexyltriphenylmethane (I).—Tetraphenylmethane (1 g, 0.0031 mole) and 5% rhodium on charcoal (0.5 g) in methylcyclohexane (150 ml) were hydrogenated at 92° and 500-psi hydrogen pressure. Samples were taken at intervals and were analyzed by gas chromatography. After 35 hr of reaction the area under the peak for I on the chromatogram stopped increasing with respect to the total area of the reaction products and the hydrogenation was terminated. Preparative-scale, thin layer chromatography on silica gel, with 10% benzene in hexane as the developing solvent, yielded a fraction of crude I, which was further purified by recrystallization from hexane. Sublimation of the product gave 150 mg (15% of theory) of I, mp 137–138°.[5]

Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03; mol wt, 326.5. Found: C, 91.87; H, 8.06; mol wt (Mechrolab osmometer), 330.

Dicyclohexyldiphenylmethane (II).—Hydrogenation of 1 g (0.0031 mole) of tetraphenylmethane was carried out for 48 hr in 150 ml of methylcyclohexane with 1 g of 5% rhodium on charcoal at 95° and 500-psi hydrogen pressure. The reaction mixture was filtered to remove the catalyst and the components were separated by means of thin layer chromatography using hexane as the developing solvent. Sublimation of the product gave 0.77 g (74% of theory) of II, mp 195–196°.

Anal. Calcd for $C_{25}H_{32}$: C, 90.30; H, 9.70. Found: C, 90.63; H, 9.37.

Tricyclohexylphenylmethane (III).—Compound III was obtained by the hydrogenation of 1 g (0.003 mole) of II in 150 ml of methylcyclohexane with 1 g of 5% rhodium on charcoal as catalyst at 500-psi hydrogen pressure and 97.5°. Samples were taken periodically and examined by means of gas–liquid chromatography. When the peak corresponding to III reached a maximum, after approximately 7 days, the reaction was stopped and the catalyst was removed by filtration. After initial purification by thin layer chromatography on silica gel, with hexane as the developing solvent, the product was recrystallized from hexane. After sublimation, there was obtained 85 mg (19% of theory) of III, mp 240–242°.

Anal. Calcd for $C_{25}H_{38}$: C, 88.79; H, 11.31; mol wt, 338.5. Found: C, 88.69; H, 11.40; mol wt (Mechrolab osmometer), 300.

Registry No.—I, 13619-64-2; II, 13619-65-3; III, 13619-66-4; tetraphenylmethane, 630-76-2.

---

[5] Reference 4 reports a melting point of 143–145°. The cause and significance of the discrepancy in values is not known.

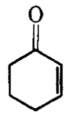
An Anomalous Hydrocyanation

ERNEST WENKERT, ROBERT L. JOHNSON, AND LINDA L. SMITH

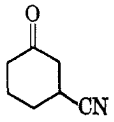
Departments of Chemistry, Iowa State University, Ames, Iowa, and Indiana University, Bloomington, Indiana

Received April 5, 1967

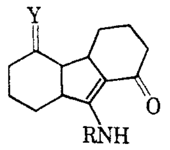
In an attempt to synthesize 3-cyanocyclohexanone (II), the unsaturated ketone I was exposed to an aqueous, alcoholic potassium cyanide solution. The sole isolable product was a crystalline substance whose elemental analysis ($C_{13}H_{17}O_2N$) revealed it to be an unexpected 2:1 enone–cyanide adduct. Its infrared spectrum (see Experimental Section) showed OH and/or NH bands and bands characteristic of a saturated keto function and a vinylogous amide unit,[1] but no C≡N absorption. The ultraviolet spectrum confirmed the presence of a vinylogous amide chromophore.[2] These facts and the mechanistic rationale of the complex reaction given by eq 1 suggest IIIa as the structure of the unusual product. Acetylation of the adduct yielded the derivative IIIb, while sodium borohydride



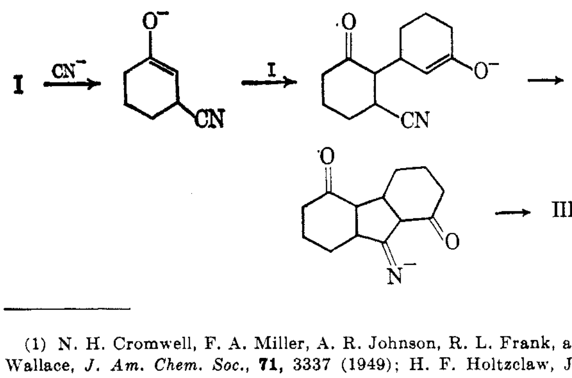
I



II



IIIa, R = H; Y = O
b, R = Ac; Y = O
c, R = H; Y = HOH
d, R = Ac; Y = HOAc



(1)

---

[1] N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *J. Am. Chem. Soc.*, **71**, 3337 (1949); H. F. Holtzclaw, Jr., J. P. Coleman, and R. M. Alire, *ibid.*, **80**, 1100 (1958).

[2] E. Wenkert and B. Wickberg, *ibid.*, **87**, 1580 (1965); E. Wenkert, K. G. Dave, and F. Haglid, *ibid.*, **87**, 5461 (1965).

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.

---

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

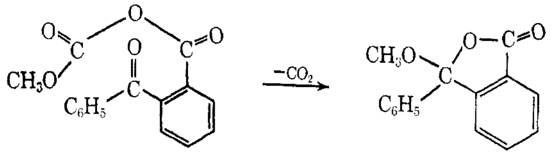
Rearrangements Involving the Mixed Anhydride of o-Benzoylbenzoic and Methylcarbonic Acids[1]

Melvin S. Newman and Lekhu K. Lala[2]

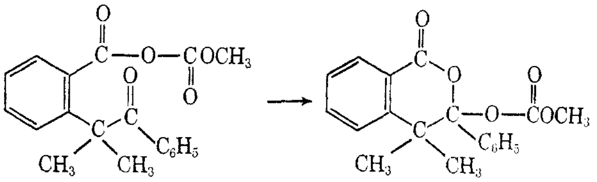
Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210

Received April 20, 1967

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-

---

[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).