Velick[4] having prepared undecyne-10-al-1 ethyl acetal by reduction of 10,11-dibromoundecanoyl chloride and elimination of hydrogen bromide in 25% over-all yield.

Kharasch[5] has reported that sulfuryl chloride chlorination of butyric acid gives approximately 45% of γ-chlorobutyryl chloride and 45% of the β-chloro isomer. Using essentially his conditions, we obtained the desired γ-chloro compound in 31% yield (based on sulfuryl chloride), but the β-isomer was found only to the extent of 3%. Instead we isolated as much as 21% of α-chlorobutyryl chloride.

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Experimental

A mixture of 600 cc. of carbon tetrachloride, 665 cc. (7.28 moles) of technical butyric acid, 486 cc. (6 moles) of sulfuryl chloride and 10 g. of benzoyl peroxide was refluxed in the dark two hours. The mixture was cooled and 600 cc. (8.3 moles) of thionyl chloride was cautiously added. After eight more hours of refluxing, everything boiling below 100° (40 mm.) was removed by distillation. Redistillation through an 18-plate column gave the following fractions: 174 g. of **butyryl chloride**, b.p. 46–47.5° (100 mm.); 170 g. of **α-chlorobutyryl chloride**, b.p. 44–49° (40 mm.); 28 g. of **β-chlorobutyryl chloride**, b.p. 64–68° (40 mm.); and 263 g. of **γ-chlorobutyryl chloride**, b.p. 83–90° (40 mm.).

γ-Chlorobutyraldehyde.—A mixture of 168 g. (1.19 moles) of γ-chlorobutyryl chloride, 900 cc. of toluene, 16 g. of palladium–barium sulfate catalyst[2] and 1.66 cc. of poison[2] was refluxed and vigorously stirred in a two-liter, 3-neck flask. Hydrogen was passed through and the effluent gas bubbled through water. After nine hours the evolution of hydrogen chloride ceased at 94% of the theoretical. The toluene was washed with water, twice with sodium bicarbonate solution and twice more with water. Distillation through a Vigreux column at 35 mm. gave 58 g. (46%) of **γ-chlorobutyraldehyde**, b.p. 69–70° (35 mm.), n^{20}_{D} 1.4480. The dinitrophenylhydrazone recrystallized from alcohol had m.p. 130–131°.[6]

Anal. Calcd. for $C_{10}H_{11}O_4N_4Cl$: C, 41.89; H, 3.87. Found: C, 42.20; H, 3.65.

γ-Chlorobutyraldehyde Diethyl Acetal.—The aldehyde could be converted to the diethyl acetal in 63% yield by reaction with five parts of ethanol and calcium chloride. Better over-all yields were obtained if the aldehyde was not isolated. Thus, 250 cc. of absolute ethanol and 50 g. of calcium chloride were added to the cold Rosenmund reduction mixture and stirring was continued 16 hours. The mixture was filtered, the phases separated and the upper layer washed twice with sodium bicarbonate solution and once with water. Water was removed by brief boiling. Distillation yielded 118 g. (55% based on the acid chloride) of γ-chlorobutyraldehyde diethylacetal, b.p. 89–92° (14 mm.).

Anal. Calcd. for $C_8H_{17}O_2Cl$: C, 53.19; H, 9.49. Found: C, 53.76; H, 9.49.

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[4] J. English and S. F. Velick, THIS JOURNAL, **67**, 1413 (1945).

[5] M. Kharasch and H. Brown, *ibid.*, **62**, 925 (1940).

[6] R. Paul and S. Tchelitcheff (*Bull. soc. chim.*, [5] **15**, 197 (1948)) report a melting point of 135° for this dinitrophenyl hydrazone.

MASS. GEN. HOSP.
BOSTON, MASS.
RECEIVED OCTOBER 23, 1950

Pentafluorobenzoic Acid

BY E. T. MCBEE AND EDWARD RAPKIN

Pentafluorobenzoic acid has been synthesized in low yield by sulfuric acid hydrolysis of perfluorotoluene according to the method of LeFave.[1] The slow rate of hydrolysis and the low yield obtained may be attributed to the relatively low boiling point (103°) of the fluorocarbon as well as to its lack of solubility in sulfuric acid. Even with rapid stirring two layers were still apparent and neither the reaction rate nor the yield were appreciably increased.

Reduction of pentafluorobenzoic acid with lithium aluminum hydride gave pentafluorobenzyl alcohol in good yield. The alcohol was not isolated but was converted to the corresponding *p*-nitrobenzoate and isolated as such.

Experimental[2]

Pentafluorobenzoic Acid.—A mixture of 10 g. (0.042 mole) of perfluorotoluene[3] and 30 g. of concd. sulfuric acid was stirred vigorously at reflux temperature for one week. During this period the lower acid layer became black while the unreacted fluorocarbon layer remained colorless. Hydrogen fluoride evolution was extremely slow.

When the fluorocarbon layer had completely disappeared the black acid solution was poured on ice, diluted with water to a volume of 250 ml., and boiled with Norite for several minutes. After filtration, the resulting colorless solution was ether extracted and the extract dried with Drierite. Evaporation of the ether gave white crystals of pentafluorobenzoic acid. While the material can be recrystallized from water, a mixture of petroleum ether (90–100°) diluted with some toluene proved more satisfactory. From this solvent pair 2.2 g. (25% yield) of large square plates of pentafluorobenzoic acid, m.p. 106–107°, was obtained.

Anal. Calcd. for $C_7HF_5O_2$: C, 39.6; H, 0.47. Found: C, 39.4; H, 0.47.

Pentafluorobenzyl *p*-Nitrobenzoate.—Pentafluorobenzoic acid (0.5 g.) was added to a refluxing mixture of lithium aluminum hydride (0.5 g.) and 10 ml. of ether. The mixture was hydrolyzed with excess dilute hydrochloric acid and the ether layer removed and dried. Evaporation of the ether left a colorless, pleasant-smelling oil. This oil was converted to the *p*-nitrobenzoate (0.63 g.) which was alternately recrystallized four times from alcohol and petroleum ether (90–100°). The colorless crystals sintered at 108° and melted at 110–112°.

Anal. Calcd. for $C_{14}H_6F_5NO_4$: C, 48.4; H, 1.73; N, 4.03. Found: C, 48.6; H, 1.85; N, 4.11.

Acknowledgment.—The authors are indebted to the Moorman Manufacturing Co., Quincy, Ill., for financial support which made this work possible.

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[1] G. M. LeFave, THIS JOURNAL, **71**, 4148 (1949).

[2] Microanalyses by Dr. H. Galbraith.

[3] E. T. McBee, V. V. Lindgren and W. B. Ligett, *Ind. Eng. Chem.* **39**, 378 (1947).

PURDUE RESEARCH FOUNDATION AND
DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
W. LAFAYETTE, IND.
RECEIVED OCTOBER 21, 1950

Some Azoproteins and Their Isoelectric Points[1]

BY R. L. MCGEACHIN AND B. D. ASHLEY

Haurowitz[2] found that the introduction into proteins of azophenyl radicals containing acidic groups gave azoproteins whose isoelectric points were lower than those of the original proteins. We have coupled casein, ovalbumin, pumpkin seed globulin and beef serum protein with excess diazotized *p*-arsanilic acid and determined the isoelectric points of these azoproteins. In all cases, the isoelectric point of the azoprotein was lower than that of the original protein, confirming Haurowitz's findings on

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(1) Taken from the M. S. thesis of B. D. Ashley.

(2) F. Haurowitz, *Kolloid Z.*, **74**, 208 (1936).

other proteins. The greatest change in isoelectric point (from 4.6 to 3.2) was found in the azocasein, the product containing the most arsenic. This is to be expected since the isoelectric point of a protein is at least partially determined by the numbers of free acidic and basic groups.

Our results on the coupling of casein seem to agree with those of Kapeller-Adler and Boxer[3] who found an arsenic content of 8.20% (8.10, 8.19, 8.33), when an excess of diazotized *p*-arsanilic acid was used. Our product contained an average of 8.32% arsenic (8.10, 8.55).

Experimental

4-Arsonophenylazoproteins.—Casein, ovalbumin, pumpkin seed globulin and beef serum protein were coupled with *excess* diazotized *p*-arsanilic acid following the method of Landsteiner and van der Scheer.[4]

Anal.[5] Azocasein, Found: As, 8.10, 8.55. Azovalbumin, Found: As, 3.62, 3.43. Azopumpkin seed globulin, Found: As, 6.22. Azobeef serum protein, Found: As, 3.56.

Isoelectric point determinations on both the original proteins and the azoproteins were carried out using the method of Hawk, Oser and Summerson.[6]

ISOELECTRIC POINTS

	Original protein	Azoprotein
Casein	4.6	3.2
Ovalbumin	5.2	4.3
Pumpkin seed globulin	5.3	4.6
Beef serum protein	>6.2	<6.2

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[3] R. Kapeller-Adler and G. Boxer, *Biochem. Z.*, **285**, 55 (1936).

[4] K. Landsteiner and J. van der Scheer, *J. Exp. Med.*, **45**, 1045 (1927).

[5] A modification of the method of F. E. Cislak and C. S. Hamilton, THIS JOURNAL, **52**, 638 (1930), was used in the arsenic analyses.

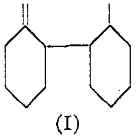
[6] P. B. Hawk, B. L. Oser and W. H. Summerson, "Practical Physiological Chemistry," Twelfth Edition, The Blakiston Company, Philadelphia, Pa., 1947, p. 160.

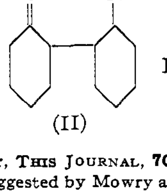
DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF LOUISVILLE SCHOOL OF MEDICINE
LOUISVILLE, KY.
RECEIVED SEPTEMBER 18, 1950

Acid-catalyzed Reactions of Nitriles. IV. Condensation of Cyclohexanone with Nitriles

BY EUGENE E. MAGAT

In a recent communication, Bruson, Riener and Riener[1a] have shown that cyclohexanone condenses with nitriles, in the presence of aluminum chloride, to yield compounds whose properties have suggested that they are imino-ethers of the aldol of cyclohexanone having the general formula (I). It is the purpose of this paper to report evidence which indicates that the products are in reality the isomeric amides of 1-(2-oxocyclohexyl)-cyclohexylamine (II).[1b]


(I)


(II)

R = CH_3

The following properties of the reaction product contradict the assignment of structure (I).

(1) Tertiary alcohols do not form imino-ethers as do primary and secondary alcohols; the tertiary alcohols rather lose water to form unsaturated compounds.[2] (2) Imino-ethers are usually unstable at high temperatures and gradually decompose to the original nitrile and alcohol,[3] whereas the condensation product can be distilled at 175–225° at 0.5–1 mm. without decomposition. (3) Imino-ethers are basic compounds which form stable salts with acids. If the condensation product were an imino-ether it should be necessary to neutralize the hydrochloric acid salt, which would form in the presence of aluminum chloride, before isolating the free imino-ether. However, no neutralization step is necessary in the isolation of (I). (4) The infrared absorption spectrum of the condensation product shows bands at 3.03, 3.25, 6.00 and 6.45 microns characteristic of the peptide linkage –CO–NH–.[4] These bands are sufficiently intense to show a high concentration of –CO–NH– groups. The infrared spectrum is shown in Fig. 1.

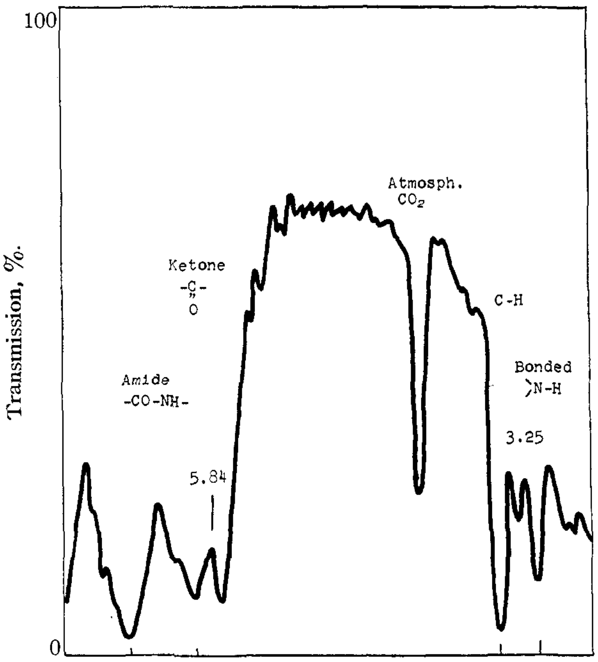


Fig. 1.—Infrared spectrum of reaction product of acetonitrile and cyclohexanone, 0.001 inch thick. Tracings of spectra recorded on Perkin-Elmer Infrared Spectrometer Model 12C with rock-salt prism in accordance with instruction manual.

These properties are in accord with structure (II). In addition, the following properties of the reaction product are also in accord with structure (II): (a) Ketone derivatives are formed. (b) Amides are, in general, soluble in concentrated hydrochloric acid and are reprecipitated unchanged

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[1] (a) Bruson, Riener and Riener, THIS JOURNAL, **70**, 483 (1948); (b) A similar formulation has been suggested by Mowry and Ringwald, *ibid.*, **72**, 4439 (1950).

[2] Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 86.

[3] *Ibid.*, p. 84.

[4] Richards and Thompson, *J. Chem. Soc.*, 1248 (1947).