Treatment of the acid chloride in dilute ether solution with triethylamine resulted in formation of pentamethyleneketene monomer and dimer in satisfactory yields. The relative yields of the monomer and dimer varied with the number of hours the reaction mixture was allowed to stand at room temperature; prolonged reaction time seemed to favor formation of the dimer.

The monomer was a slightly yellow colored liquid; the dimer a white solid which sublimed to form needle-like crystals. The monomer gave positive reaction with bromine in carbon tetrachloride and potassium permanganate, and reacted with aniline to form hexahydrobenzoanilide and with dilute alkali to yield hexahydrobenzoic acid.

The dimer reacted with hydroxylamine to form the monoxime and with hot dilute alkali to give dicyclohexyl ketone. Catalytic hydrogenation of the dimer at elevated temperature and high pressure produced a hydroxy ketone, which upon reaction with alkali formed dicyclohexyl ketone and formic acid.

Experimental[3]

Hexahydrobenzoyl Chloride.—The chloride was prepared from hexahydrobenzoic acid, m.p. 30–31°, by use of thionyl chloride. Boiling point of chloride was 65–65.5° (5 mm.) and 180–181° (750 mm.); reported b.p. 179° (760 mm.).[4] Observed m.p. of amide was 183–184°; reported m.p. 184°.[5]

Pentamethyleneketene Monomer and Dimer.—The monomer was prepared by treating 14.6 g. (0.10 mole) of hexahydrobenzoyl chloride dissolved in 300 ml. of diethyl ether with 11.4 g. (0.11 mole) of triethylamine. At the end of 16 hours, the hydrochloride was removed by inverted filtration. Removal of the ether by distillation left a dark colored residue which when distilled from a Claisen flask gave 3.6 g. (32%) of the monomer, b.p. 40–41° (3 mm.), d^{20}_4 1.0617, n^{20}_D 1.4680. *Anal.* Calcd. for $C_7H_{10}O$: mol. wt., 110. Found: mol. wt., 108.

The dimer was prepared by treating a solution of 36.6 g. (0.25 mole) of hexahydrobenzoyl chloride in 400 ml. of diethyl ether with 30.3 g. (0.30 mole) of triethylamine. The reaction mixture was allowed to stand for four days. At the end of this period, the precipitated triethylamine hydrochloride was separated by filtration. The filtrate was then concentrated by evaporation of the ether with a stream of dry, oxygen-free nitrogen. Prolonged chilling of the concentrated filtrate produced crystals of the dimer, which were removed by suction filtration. Repeated chilling of the filtrate caused additional crops of the dimer to separate. Finally, the filtrate was distilled, and 2 g. of the dimer, b.p. 175–180° (15 mm.), collected. The crude dimer was recrystallized from ethanol; yield was 15.5 g. (55%); m.p. 164–165°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09; mol. wt., 220. Found: C, 75.90; H, 9.00; mol. wt., 218.

Reaction of Monomer with Aniline.—One gram of pure monomer was added slowly to an equivalent amount of aniline in 10 ml. of anhydrous diethyl ether. The crude anilide was recrystallized from petroleum ether. Observed m.p. was 139–140°; reported[6] m.p. for hexahydrobenzoanilide is 141°; mixed m.p. was 140–141°.

Reaction of Monomer with Alkali.—To 1 g. of the monomer was added dropwise 10 ml. of 10% sodium hydroxide. The alkaline solution was extracted with diethyl ether and acidified with dilute hydrochloric acid. The acid solution was extracted with several small portions of ether and the combined extracts dried. Evaporation of the solvent left 0.7 g. of hexahydrobenzoic acid, m.p. 29.5–30.5°. Mixed m.p. with authentic sample of hexahydrobenzoic acid was 30–31°.

Reaction of Dimer with Hydroxylamine.—One gram of dimer, 10 ml. of ethanol and 1 g. of pyridine were warmed under reflux to 60°; and a solution of 0.3 g. of hydroxylamine in 5 ml. of water was added slowly. After heating for two hours, the reaction mixture was evaporated by a stream of dry air. The residue was triturated with a small portion of hot chloroform and filtered. Chilling of the filtrate precipitated 0.3 g. of the monoxime, m.p. 171–172°.

Anal. Calcd. for $C_{14}H_{21}O_2N$: N, 5.95. Found: N, 5.93.

Catalytic Hydrogenation of Dimer.—Two grams of the dimer and 50 ml. of ethanol, mixed with 0.5 g. of Raney nickel, were treated with hydrogen at 1,000 p.s.i. and 80° for two hours. After removal of the catalyst by filtration, the solution was concentrated by distillation. The solid residue was recrystallized from dilute ethanol. The hydrogenated product was further purified by sublimation; m.p. 121–122°; yield 1.64 g. (77%). This product formed a semicarbazone, m.p. 141–142°, and a phenylurethan, m.p. 151–152°.

Alkaline Hydrolysis of Hydrogenated Product.—To 2 g. of the hydrogenated product was added 10 ml. of 10% sodium hydroxide solution. The mixture was warmed over a water-bath. The oil which formed was extracted with ether. Removal of the ether left 1 g. of an oily liquid, b.p. 211–213° (755 mm.), which formed an oxime, m.p. 157–158°. Melting point of the oxime prepared from an authentic sample of dicyclohexyl ketone was 157–158°; mixed m.p. 158–159°.

Anal. Calcd. for $C_{13}H_{23}ON$: N, 6.70. Found: N, 6.77.

The alkaline solution from above was acidified with sirupy phosphoric acid and distilled. The distillate reacted acid to litmus, reduced potassium permanganate and mercuric nitrate solutions and gave a negative test with the Schiff reagent.

Reaction of Dimer with Sodium Hydroxide.—Two grams of the dimer was refluxed with 50 ml. of 15% sodium hydroxide solution for 48 hours. The cooled reaction mixture was extracted with diethyl ether. Removal of the ether by distillation gave 0.9 g. (53%) of an oil, b.p. 145–147° (12 mm.). Treatment of this oil with hydroxylamine produced an oxime, m.p. 158–159°; mixed m.p. with an authentic sample of dicyclohexyl ketone oxime was 157–158°.

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[3] All melting points are corrected.

[4] V. Meyer, *Ber.*, **30**, 1941 (1897).

[5] J. S. Lumsden, *J. Chem. Soc.*, **87**, 92 (1905).

[6] N. J. Edson, *J. Soc, Chem. Ind.*, **53**, 138 (1934).

Cyclization of N-β-Cyanoethylanilines

BY WILLIAM S. JOHNSON AND WILLIAM DEACETIS[1]

RECEIVED FEBRUARY 2, 1953

A recent publication of Braunholtz and Mann,[2] in which the monocyclization of N,N-bis-(β-cyanoethyl)-*m*-toluidine, II ($R=CH_3$) was mentioned, prompts us to announce our interest in this problem. Our studies, which are yet at a preliminary stage, have been aimed at finding a facile synthesis of 4-keto-7-chloro-1,2,3,4-tetrahydroquinoline III (R = Cl), which has recently been shown[3] to be easily converted to the important antimalarial, chloroquine.

We have been able to obtain III (R = Cl) by direct cyclization of I (R = Cl),[4] but since we have found that cyclizations of this type proceed more readily with cyanoethyl derivatives of alkylanilines (having a tertiary nitrogen atom),[5] we have considered the feasibility of monocyclization of II (R = Cl) to IV (R = Cl) followed by β-elimination of the N-cyanoethyl group to give III (R = Cl). Some of our experiments are reported below.

The addition of acrylonitrile to aniline and to *m*-

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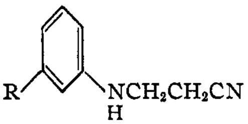
[1] Wisconsin Alumni Research Foundation Research Assistant, 1950–1952.

[2] J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 3046 (1952).

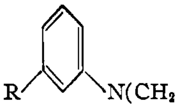
[3] W. S. Johnson and B. G. Buell, THIS JOURNAL, **74**, 4513 (1952).

[4] Details of this work will be reported in a future publication.

[5] *Cf.* French patent 806,715 [*C. A.*, **31**, 4991 (1937)].



I



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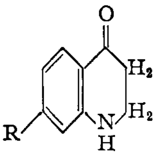
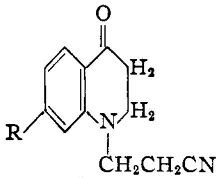


III



IV

chloroaniline according to the procedure of Smith and Yu[6] yielded the bis-cyanoethyl compounds II (R = H), and II (R = Cl), respectively. Braunholtz and Mann[2] have described an excellent procedure for the aluminum chloride-catalyzed double cyclization of the former substance to give the tricyclic diketone, 1,6-diketojulolidine, in 89% yield. Using a 5:1 instead of 6.7:1 molar ratio of aluminum chloride they obtained a "small yield" of a monocyclization product from II (R = CH$_3$). Employing essentially the procedure of Mann and Smith[7] for double cyclization, but reducing the ratio of catalyst to 2.5:1, we have effected monocyclization of II (R = H) into IV (R = H) in about 72% yield. The crude product thus obtained was converted into crystalline oxime in 79% yield. In the *m*-chloro series the same conditions, however, gave the monocyclization product, presumably IV (R = Cl), in only 6% yield isolated as the 2,4-dinitrophenylhydrazone, and considerable dicyano compound II (R = Cl) was recovered. When the temperature was raised to 175–200° (*o*-dichlorobenzene solvent) 7-chloro-1,6-diketojulolidine was produced in 47% yield; therefore it seems likely that some intermediate temperature will give improved yields of IV (R = Cl).

Preliminary attempts to eliminate the cyanoethyl group from IV (R = H) with base were not successful. Treatment with a mixture of concentrated hydrochloric acid and excess acetic anhydride however, yielded III (R = H), isolated as the N-acetyl derivative.

Experimental[8]

N-β-Cyanoethyl-4-keto-1,2,3,4-tetrahydroquinoline (IV, R = H).—A mixture of 3.0 g. of the dicyano compound II (R = H),[6] m.p. 82–83.5°, 5.02 g. of powdered aluminum chloride, 15 ml. of chlorobenzene and 0.5 ml. of concentrated hydrochloric acid was heated with stirring at 140–145° (oil-bath) for 6 hours. The mixture was cooled, and 100 ml. of water was added slowly with cooling. The chlorobenzene was removed by steam distillation and the residue extracted with chloroform. The chloroform extracts were washed with 10% sodium bicarbonate solution, water, saturated salt solution and dried over sodium sulfate. Evaporation of the solvent and evaporative distillation of the reddish oily residue at 75–85° (0.01 mm.) gave 2.17 g. (72% yield) of clear yellow oil which could not be induced to crystallize. The analysis for carbon was about 2.6% below that calculated for IV (R = H), but on treatment with hydroxylamine hydrochloride in pyridine, an oxime was produced in 79% yield. From 0.50 g. of the oil was thus obtained 0.426 g. of pale yellow **oxime**, m.p. 175–178° (dec.). Recrystallization from benzene–petroleum ether (60–68°) gave yellow prisms, m.p. 178–185° (dec.). Further recrystallization did not change the m.p. of this material which may consist of a mixture of *syn* and *anti* forms.

Anal.[9] Calcd. for $C_{12}H_{13}ON_3$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.62; H, 5.92; N, 19.35.

The pure ketone was isolated from the crude cyclization product by chromatography on alumina. The product came off the column with benzene, and after two recrystallizations from diisopropyl ether was obtained as pale yellow plates, m.p. 79–79.5°.

Anal. Calcd. for $C_{12}H_{12}ON_2$: C, 71.97; H, 6.04; N, 13.99. Found: C, 71.96; H, 6.10; N, 13.83.

N,N-Bis-(β-cyanoethyl)-*m*-chloroaniline (II, R = Cl) was prepared according to the procedure of Smith and Yu[6] for the parent compound (II, R = H) from 102 g. of *m*-chloroaniline, 95.4 g. of acrylonitrile, 20 ml. of acetic acid and 8.0 g. of cuprous chloride. The crude reddish oily product was dissolved in hot alcohol, and on cooling 14.9 g. of II (R = Cl) crystallized, m.p. 88–92°. The filtrate was concentrated and the residual reddish oil distilled through a 25-cm. Vigreux column to give 46.5 g. of N-β-cyanoethyl-*m*-chloroaniline, b.p. 135–150° (0.02–0.03 mm.), m.p. 41–47° and 14.5 g. of oil, b.p. 150–225° (0.02–0.03 mm.). Crystallization of the latter fraction from alcohol gave an additional 4.05 g. of II (R = Cl), m.p. 94–96°. A sample purified by repeated recrystallization from alcohol was obtained as long colorless needles, m.p. 98–99°.

Anal.[9] Calcd. for $C_{12}H_{12}N_3Cl$: C, 61.67; H, 5.18. Found: C, 61.85; H, 5.19.

N-β-Cyanoethyl-4-keto-7-chloro-1,2,3,4-tetrahydroquinoline (IV, R = Cl) was prepared from 3.0 g. of the dicyano compound II (R = Cl), m.p. 95.5–96.5°, 4.34 g. of aluminum chloride, 15 ml. of chlorobenzene and 0.5 ml. of concentrated hydrochloric acid as described above for IV (R = H). The heating period was 7 hours. The crude product obtained on evaporation of the chloroform was solid, m.p. 80–100°, and on crystallization from alcohol, yielded a total of 1.85 g. of uncyclized dicyano compound II (R = Cl). The filtrate was treated with 2,4-dinitrophenylhydrazine solution, and the **2,4-dinitrophenylhydrazone of IV (R = Cl)** separated immediately; yield 0.32 g.; m.p. 220–225° (dec.). Two recrystallizations from ethyl acetate gave red microcrystals, m.p. 242–243° (dec.) introduced at 220°.

Anal.[9] Calcd. for $C_{18}H_{15}O_4N_6Cl$: C, 52.12; H, 3.65; N, 20.26. Found: C, 52.14; H, 3.69; N, 19.78.

7-Chloro-1,6-diketojulolidine.—The cyclization described in the preceding experiment was repeated except that 20 ml. of *o*-dichlorobenzene was used in place of the chlorobenzene, and the mixture was heated for 0.5 hour at 200° and an additional 1.5 hours at 175°. Crystallization of the crude product from alcohol gave 1.09 g. of brown needles, m.p. 160–162° and a second crop amounting to 0.324 g. of darker material, m.p. 154–158°. Evaporative distillation of the residue from the filtrate at 120–130° (0.01 mm.) gave an additional 0.02 g., m.p. 159–162°, making the total yield of material of fair quality, 1.43 g.

Sublimation of a sample from the first crop, followed by repeated recrystallization from alcohol gave bright yellow needles, m.p. 164–165°.

Anal.[9] Calcd. for $C_{12}H_{10}O_2NCl$: C, 61.15; H, 4.28; N, 5.94. Found: C, 61.12; H, 4.42; N, 5.96.

Conversion of IV (R = H) into N-Acetyl-4-keto-1,2,3,4-tetrahydroquinoline.—A mixture of 0.490 g. of the keto nitrile IV (R = H), m.p. 79–79.5°, and 5 ml. of a solution of 100 g. of concentrated hydrochloric acid in 400 g. of acetic anhydride was heated under reflux for 3 hours. An additional 5 ml. of acetic anhydride was added and the refluxing was continued for another hour. The mixture was cooled, 20 ml. of water added, and the acids neutralized with solid potassium carbonate. The resulting basic solution was extracted with chloroform and the combined extracts were washed with saturated sodium bicarbonate solution, water, saturated salt solution and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 0.471 g. of a pale yellow oil which crystallized from benzene–petroleum ether (60–68°) in colorless prisms, m.p. 150–155°. The nature of this product is uncertain, but after standing in contact with the mother liquor for several days, the crystals, which had turned to a semisolid, were redissolved in benzene and chromatographed on 10 g. of Florisil. From the column

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[6] P. A. S. Smith and T. Yu, THIS JOURNAL, **74**, 1096 (1952).

[7] F. G. Mann and B. B. Smith, *J. Chem. Soc.*, 1898 (1951).

[8] Melting points are corrected for stem exposure.

[9] Microanalyses by E. J. Eisenbraun and G. Winestock.

there was obtained 0.228 g. (47% yield) of pale yellow crystals, m.p. 88–92°. Recrystallization from a small amount of methanol gave small colorless prisms, m.p. 91.5–92.5° (reported[10], 94°), undepressed on admixture with authentic N-acetyl-4-keto-1,2,3,4-tetrahydroquinoline prepared from the free quinolone.[11]

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(10) G. R. Clemo and H. J. Johnson, *J. Chem. Soc.*, 2133 (1930).

(11) W. S. Johnson, E. L. Woroch and B. G. Buell, This Journal, **71**, 1901 (1949).

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The Solubility of Lead Chloride in Sodium Chloride, Perchloric Acid and Hydrochloric Acid Solutions[1]

By S. Z. Lewin, John E. Vance and Lawrence B. Nelson

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In connection with an investigation of the crystal growth of lead chloride, measurements were made of the solubility of that compound at 25° in the media listed in Table I.

Table I

Solubilities of $PbCl_2$ at 25°

Medium (conc. in molality)	G. $PbCl_2$ per 1000 g. H_2O	Standard deviation	Lit. values (interpolated)
0.4723 *m* NaCl	1.870	0.008	1.87[a]
1.0125 *m* NaCl	1.784	.008	1.74[a]
2.0265 *m* NaCl	2.743	.010	2.72[a]
4.0216 *m* NaCl	8.367	.014	8.55[a]
0.5375 *m* HCl	1.561	.007	(3.68 g. at 0.50 *m*)[g]
0.5487 *m* $HClO_4$	10.88	.04	
1.0368 *m* $HClO_4$	10.56	.05	
2.3239 *m* $HClO_4$	7.421	.025	
3.4565 *m* $HClO_4$	5.183	.013	
6.4730 *m* $HClO_4$	1.781	.005	
Water	....	...	10.87[a], 10.84[b], 10.86[c], 10.75[d], 10.91[e], 10.76[f], 11.03[g], 10.84[h]

[a] G. E. R. Deacon, *J. Chem. Soc.*, 2063 (1927). [b] L. J. Burrage, *ibid.*, 1703 (1926). [c] W. R. Carmody, This Journal, **51**, 2909 (1929). [d] T. P. Goulden and L. M. Hill, *J. Chem. Soc.*, 447 (1945). [e] L. Wilkinson, N. O. Bathhurst and H. N. Parton, *Trans. Faraday Soc.*, **33**, 623 (1937). [f] F. Flöttman, *Z. anal. Chem.*, **73**, 1 (1938). [g] H. E. Armstrong and J. V. Eyre, *Proc. Roy. Soc. (London)*, **A88**, 238 (1913). [h] P. M. Lichty, This Journal, **25**, 469 (1903).

Sealed glass tubes containing solution and excess solid $PbCl_2$ were heated to about 100° for several hours, then placed into a thermostat and rotated at 25.00 ± 0.05° for at least 24 hours, after which samples were removed for analysis by suction through a plug of glass wool.

The concentration of acid was determined in each case by titration with standard NaOH to the brom cresol green end-point. Two procedures were used for the determination of lead chloride; (1) triple evaporation with sulfuric acid, followed by dilution with water and the usual gravimetric procedure with filtration on Selas crucibles, and (2) neutralization to the methyl orange end-point with ammonia, precipitation in hot solution with hydrogen sulfide, followed by solution of the precipitate in nitric acid and conversion to lead sulfate as before. Both procedures were followed in the case of the sodium chloride and hydrochloric acid solutions, and gave concordant results; only procedure (2) was used for the solutions containing perchloric acid. The concentration of sodium chloride was found as the difference between total chloride as obtained by the Volhard titration[2] and the amount of chloride as lead chloride calculated from the gravimetric determination of lead.

Demassieux[3] and Deacon[4] have reported that no double salts are formed between NaCl and $PbCl_2$, whereas Kendall and Sloan[5] offered analytical evidence that the solid phase in equilibrium with NaCl solutions of $PbCl_2$ is $NaCl{\cdot}2PbCl_2$ for all concentrations in excess of 0.5 *N* NaCl. The solid phases in equilibrium with the 1, 2 and 4 *m* NaCl solutions of Table I were analyzed for lead according to procedure (1) above. The solid was removed from the liquid phase by filtration, and dried by pressing between filter papers without washing. The analytical results are given in Table II.

Table II

Analyses of Solid Samples

Source of sample	$PbCl_2$, %
Mallinckrodt A.R. $PbCl_2$	100.16, 99.84, 99.96
1 *m* NaCl	98.36, 99.17
2 *m* NaCl	99.16, 98.05
4 *m* NaCl	98.13, 99.21

The analyses of the samples from the NaCl solutions are low as a result of contamination by NaCl, but the data clearly support the conclusion that no double salts form between NaCl and $PbCl_2$ for solutions up to 4 *m* in NaCl under the conditions of our experiments.

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(1) This work was supported in part under Contract No. AT (30-1)-1256 between the Atomic Energy Commission and New York University.

(2) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 546, procedure 2.

(3) N. Demassieux, *Ann. chim.*, **20**, 267 (1923).

(4) G. E. R. Deacon, footnote *a* of Table I.

(5) J. Kendall and C. H. Sloan, This Journal, **47**, 2306 (1925).

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Anion-exchange Studies. VII.[1,2] Separation of Sulfuric Acid from Metal Sulfates by Anion Exchange

By Kurt A. Kraus, Frederick Nelson and John F. Baxter[3]

Received January 2, 1953

A strong base anion-exchange resin in the sulfate form (or in combination with other polyvalent anions) might be considered a base which can react with (adsorb) acids according to reactions of the type

$$(SO_4^{=})_r + HX \rightleftharpoons (HSO_4^{-})_r + (X^{-})_r \qquad (1)$$

where subscript r stands for resin. In the case of the adsorption of sulfuric acid by a sulfate resin equation (1) becomes

$$(SO_4^{=})_r + H_3O^+ + HSO_4^- \rightleftharpoons 2(HSO_4^-)_r + H_2O \qquad (2a)$$

and

$$(SO_4^{=})_r + 2H_3O^+ + SO_4^{=} \rightleftharpoons 2(HSO_4^-)_r + 2H_2O \qquad (2b)$$

The fact that such acid adsorption, possibly according to equations (1) and (2), actually takes place can readily be demonstrated by passing sulfuric acid solutions through sulfate columns, and noting that a considerable volume of effluent is free of acid.

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus and G. E. Moore, This Journal, **75**, 1460 (1953).

(3) Summer Participant (1951) at Oak Ridge National Laboratory.