Anal.[21] Calcd. for $C_{14}H_{16}NOCl$: C, 67.33; H, 6.46; N, 5.61; Cl, 14.20. Found: C, 66.55; H, 6.62; N, 5.52; Cl, 14.16.

p-Nitrodibenzylamine Hydrochloride.—The procedure described by Busch[22] for the preparation of o-nitrodibenzylamine was used in this reaction.

A solution of 53.6 g. (0.50 mole) of benzylamine and 42.9 g. (0.25 mole) of p-nitrobenzyl chloride in 250 ml. of ethanol was heated under reflux for four hours. It was then diluted with 900 ml. of water and the red oil which separated was extracted with ether. After the ether had been evaporated, the residue was treated with boiling 2% hydrochloric acid solution. The p-nitrodibenzylamine hydrochloride which precipitated from this solution was recrystallized first from boiling 2% hydrochloric acid and then three times from absolute ethanol. After the final recrystallization, the compound weighed 29.6 g. (42.4%) and melted at 248° dec.

Anal. Calcd. for $C_{14}H_{15}N_2O_2Cl$: C, 60.32; H, 5.43; N, 10.05. Found: C, 60.43; H, 5.85; N, 10.26.

p-Carbomethoxydibenzylamine Hydrochloride.—The method described above for the preparation of p-nitrodibenzylamine hydrochloride was used to synthesize this compound. Benzylamine and methyl α-bromo-p-toluate furnished a 34.2% yield of p-carbomethoxydibenzylamine hydrochloride, m.p. 233–234°

Anal. Calcd. for $C_{16}H_{18}NO_2Cl$: C, 65.86; H, 6.22; N, 4.80. Found: C, 65.95; H, 6.21; N, 4.59.

p-Nitro-p'-methoxydibenzylamine Hydrochloride.—The method used to prepare p-nitrodibenzylamine hydrochloride was used to prepare this compound from p-methoxybenzylamine and p-nitrobenzyl chloride. The two reactants gave a 31.6% yield of p-nitro-p'-methoxydibenzylamine hydrochloride, m.p. 222–223°.

(21) The values reported for all chlorine analyses are the averages of three individual determinations.

(22) M. Busch, *J. prakt. Chem.*, **159**, 257 (1894).

Anal. Calcd. for $C_{15}H_{17}N_2O_3Cl$: Cl, 11.48. Found: Cl, 11.55.

p-Carbomethoxy-p'-methoxydibenzylamine Hydrochloride.—The method described for the preparation of p-nitrodibenzylamine hydrochloride was used to prepare p-carbomethoxy-p'-methoxydibenzylamine hydrochloride in 24.6% yield from p-methoxybenzylamine and methyl α-bromo-p-toluate. The compound melts at 245–246°.

Anal. Calcd. for $C_{17}H_{20}NO_3Cl$: Cl, 11.02. Found: Cl, 11.12.

p-Carbomethoxybenzylhexaminium Bromide.—To a solution of 18.6 g. (0.133 mole) of hexamine dissolved in 175 ml. of chloroform was added 30.6 g. (0.133 mole) of methyl α-bromo-p-toluate. Precipitation began after the solution had been heated for about five minutes and within 15 minutes the contents of the flask had become semi-solid. After the reaction mixture had been cooled, the quaternary salt was filtered from the solution, washed with chloroform and dried. The p-carbomethoxybenzylhexaminium bromide weighed 45.4 g. (92.3%), m.p. 175° dec.

Sommelet Reaction on p-Carbomethoxybenzylhexaminium Bromide.—A solution of 14.84 g. (0.04 mole) of p-carbomethoxybenzylhexaminium bromide in 40 ml. of 50% acetic acid was heated for 2.75 hours, and was then made strongly acidic by the addition of concentrated sulfuric acid. The aldehyde was extracted from the cooled reaction mixture by treatment with three 50-ml. portions of ether and the ether extracts were neutralized with 20% sodium carbonate solution. Evaporation of the ether left a residue of 5.4 g. of p-carbomethoxybenzaldehyde, m.p. 60–62°. Recrystallization from low-boiling petroleum ether afforded 4.9 g. (74.7%) of pure aldehyde, m.p. 62–63°. Fuson and Cooke[23] report a m.p. of 61–62° for this compound.

(23) R. C. Fuson and H. G. Cooke, Jr., THIS JOURNAL, **62**, 1180 (1940).

URBANA, ILLINOIS

Unsaturated Amines. V. The Attack of Ternary Iminium Compounds by Nucleophilic Reagents[1,2]

BY NELSON J. LEONARD AND ALLAN S. HAY[3]

$\Delta^{5(10)}$-Dehydroquinolizidinium perchlorate has been used as a model for the study of the attack of the ternary iminium grouping ($>C=\overset{+}{N}< \longleftrightarrow >\overset{+}{C}-N<$) by nucleophilic reagents including Grignard reagents, lithium alkyls, metal hydrides, potassium cyanide and RSK and ROK types. Certain reactions of the unconjugated $>C=\overset{+}{N}<$ system have been recognized for the first time.

It has been established that the mild dehydrogenation of quinolizidine with mercuric acetate yields $\Delta^{1(10)}$-dehydroquinolizidine (I), the salts of which have been shown to be of the $\Delta^{5(10)}$-dehydroquinolizidinium type (II).[4] $\Delta^{5(10)}$-Dehydroquinolizidinium perchlorate therefore presents, in its cation, an ideal model of a symmetrical, unconjugated ternary iminium grouping ($>C=\overset{+}{N}< \longleftrightarrow >\overset{+}{C}-N<$),[5] analogous to $>C=O \longleftrightarrow >\overset{+}{C}-O^-$, for the study of

(1) Paper IV in this series: N. J. Leonard, Paul D. Thomas and V. W. Gash, THIS JOURNAL, **77**, 1552 (1955).

(2) Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 11–16, 1955; see Abstracts of Papers, p. 9-O.

(3) Monsanto Chemical Co. Fellow, 1953–1954.

(4) N. J. Leonard, A. S. Hay, R. W. Fulmer and V. W. Gash, THIS JOURNAL, **77**, 439 (1955).

(5) We prefer the designation of M. Lamchen, W. Pugh and A. M. Stephen, *J. Chem. Soc.*, 4418 (1954), for the grouping to other suggestions which have been made.
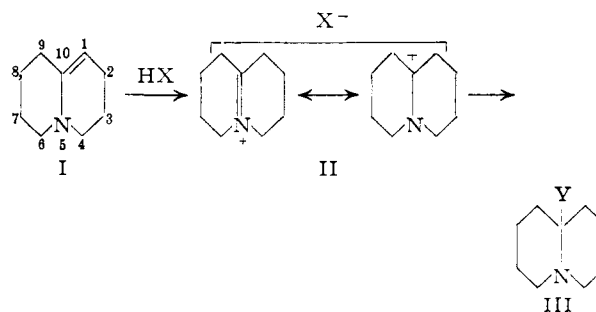
attack by nucleophilic reagents.[6] The introduction of a bridgehead substituent at C-10 (III) by attack of the anionic moieties of Grignard reagents, lithium alkyls, metal hydrides, and potassium cyanide, mercaptides and alkoxides on II has now been

(6) N. J. Leonard and V. W. Gash, THIS JOURNAL, **76**, 2781 (1954).

shown to be general, subject to the steric requirements of the system.

Conversions of ternary iminium salts to the corresponding saturated bases (e.g., III, Y = H) by means of lithium aluminum hydride and sodium borohydride have been reported for $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate[4] and for similarly constituted salts in the tetracyclic series.[1] Other closely related examples can be found.[7] Moreover, the reduction of $\Delta^{1(10)}$-dehydroquinolizidine (I) to quinolizidine[8] by formic acid bears formal resemblance to hydride reduction of a ternary iminium cation intermediate.[1,9] The action of methylmagnesium iodide on the ternary iminium salt II yields 10-methylquinolizidine (III, Y = CH_3), a fact which served to establish the structures of I and II.[4] It has now been found that other Grignard reagents[1] (ethylmagnesium iodide, n-propylmagnesium iodide, benzylmagnesium chloride) react readily with $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate to give the corresponding 10-substituted quinolizidines (III, Y = C_2H_5, n-C_3H_7, $C_6H_5CH_2$), and that the anion of α-picolyllithium also attacks the unconjugated $>\overset{+}{C}=N<$ grouping[10] in II (X = ClO_4) to give 10-(α-picolyl)-quinolizidine. The failure of isopropylmagnesium iodide and phenylmagnesium bromide to yield 10-substituted products with II may be attributed to increased steric hindrance of attack at C-10, with abstraction of a proton from C-1 (C-9) becoming an important competing reaction.

The product obtained from the reaction of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate with potassium cyanide was assigned the structure 10-cyanoquinolizidine (III, Y = CN) on the basis of its nearly quantitative conversion to 10-methylquinolizidine on treatment with methylmagnesium iodide. The combination of cyanide ion with the ternary iminium cation[1] is reminiscent of reactions of the same anion with the $>\overset{+}{C}=N<$ grouping as part of a conjugated system.[11,12] There is similar precedent[12,13] for the replacement of cyano by methyl by means of the Grignard reagent. In the present study this route from II (X = ClO_4) to 10-methylquinolizidine is preferred over the non-homogeneous reaction involving II and the methyl Grignard. 10-

Cyanoquinolizidine (III, Y = CN) was converted with efficiency to quinolizidine (III, Y = H) by treatment with lithium aluminum hydride,[14,15] and to $\Delta^{5(10)}$-dehydroquinolizidinium periodide (II, X = I_3) by treatment with excess iodine[12] in ether.

Further examples of the attack of nucleophilic reagents on the ternary iminium grouping in II (X = ClO_4) were found in the reactions of II with mercaptans, as their potassium salts. Although the products obtained from the lower molecular weight mercaptans could not be isolated in a pure state due to their facile decomposition to $\Delta^{1(10)}$-dehydroquinolizidine (I) and mercaptan, the potassium salts of p-thiocresol and α-naphthylmethyl mercaptan with II gave solids which could be recrystallized from ether at low temperature. The structures of the products were assigned as 10-(p-thiocresyl)-quinolizidine (III, Y = p-$CH_3C_6H_4S$) and 10 - (α - naphthylmethylmercapto) - quinolizidine (III, Y = α-$C_{10}H_7CH_2S$) on the basis of analysis and analogy with the compounds discussed earlier. The structures of both products were verified by an alternative synthesis based upon direct addition of the appropriate mercaptan to $\Delta^{1(10)}$-dehydroquinolizidine (I). This addition should produce the
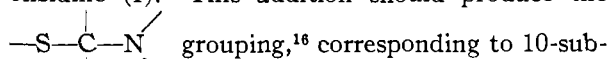
$$-\text{S}-\overset{|}{\text{C}}-\text{N}\overset{/}{\underset{\backslash}{}}$$ grouping,[16] corresponding to 10-substitution. The instability of the adducts is illustrated by their infrared spectra; for example, in Nujol 10-(α-naphthylmethylmercapto)-quinolizidine exhibits a spectrum satisfactory for the adduct structure, whereas in chloroform solution double bond absorption appears at 1652 cm.$^{-1}$.[4] The existence of an equilibrium between these adducts and their component mercaptans and $\Delta^{1(10)}$-dehydroquinolizidine is in accord with the chemistry of the thiazolidines.[17] Attempts to obtain the analogous oxygen compounds from $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate and potassium alkoxides or phenoxides resulted, in the case of the higher members, in the formation of solid compounds which were less stable than their sulfur analogs.[18]

The reactions of $\Delta^{4(9)}$-hexahydropyrrocolinium perchlorate (IV, X = ClO_4)[19] were found to be analogous to those of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate. For example, treatment of IV with methylmagnesium iodide gave 9-methyloctahydropyrrocoline (V, Y = CH_3) and with potassium cyanide, 9-cyanoöctahydropyrrocoline (V, Y = CN). The 9-cyano compound was converted to the 9-

(7) Cf. H. Schmid and P. Karrer, Helv. Chim. Acta, 32, 960 (1949); J. J. Panouse, Compt. rend., 233, 260, 1200 (1951); W. M. Whaley and C. N. Robinson, THIS JOURNAL, 75, 2008 (1953); B. Witkop, ibid., 75, 3361 (1953); B. Witkop and J. B. Patrick, ibid., 75, 4474 (1953); O. E. Edwards, F. H. Clarke and B. Douglas, Can. J. Chem., 32, 235 (1953); A. P. Gray, E. E. Spinner and C. J. Cavallito, THIS JOURNAL, 76, 2792 (1953); K. T. Potts and Sir Robert Robinson, J. Chem. Soc., 2675 (1955); R. Torossian and C. Sannié, Compt. rend., 236, 824 (1953).

(8) N. J. Leonard and R. R. Sauers, unpublished results.

(9) See also: P. L. de Benneville and J. H. Macartney, THIS JOURNAL, 72, 3073 (1950); P. L. de Benneville, U. S. Patent 2,578,787 (Dec. 18, 1951); R. Lukeš and J. Jizba, Chem. Listy, 47, 1366 (1953), and earlier articles in the Lukeš series.

(10) For reactions of Grignard reagents with the conjugated $>\overset{+}{C}=N<$ function see, for example, M. Freund and K. Lederer, Ber., 44, 2356 (1911), and earlier articles of Freund; E. Späth and J. Gangl, Monatsh., 44, 103 (1923); K. Wiesner, Z. Valenta, A. J. Manson and F. W. Stonner, THIS JOURNAL, 77, 675 (1955).

(11) See A. Kaufmann, J. Chem. Soc., 114, 187 (1918), for leading reference.

(12) D. A. Haworth and W. H. Perkin, Jr., ibid., 127, 1434 (1925).

(13) T. Thomson and T. S. Stevens, ibid., 2607 (1932).

(14) Similarly, lithium aluminum hydride reduction of 6-cyanosparteine[1] gives sparteine (A. S. Hay, Ph.D. Thesis, University of Illinois, 1955).

(15) See also Z. Welvart, Abstract No. 114, XIVth International Congress of Pure and Applied Chemistry, Zürich, Switzerland, July, 1955.

(16) Cf. J. W. Copenhaver, British Patent 642,253 (Aug. 30, 1950); E. Levas, Ann. chim. Paris, [12] 3, 145 (1948); M. F. Shostakovskiĭ, Zhur. Obshchei Khim., 20, 608 (1950); J. L. Szabo and E. T. Stiller, THIS JOURNAL, 70, 3667 (1948); W. E. Vaughan and F. F. Rust, U. S. Patent 2,522,590 (Sept. 19, 1950); R. R. Chambers, Ph.D. Thesis, University of Illinois, 1947.

(17) S. Ratner and H. T. Clarke, THIS JOURNAL, 59, 200 (1937); M. P. Schubert, J. Biol. Chem., 114, 341 (1936); M. P. Schubert, ibid., 121, 539 (1937); M. P. Schubert, ibid., 130, 601 (1939).

(18) C. M. McLeod and G. M. Robinson, J. Chem. Soc., 119, 1470 (1921).

(19) N. J. Leonard, W. J. Middleton, P. D. Thomas and D. Choudhury, J. Org. Chem., in press, article VI in this series.

IV   V
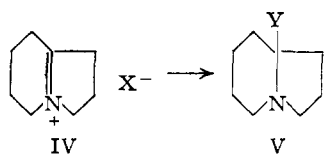
methyl compound by methylmagnesium iodide and to $\Delta^{4(9)}$-hexahydropyrrocolinium periodide (IV, X $= I_3$) by iodine in ether. The facility of reaction of these representative ternary iminium compounds (II, IV) with selected nucleophilic reagents suggests a certain versatility for their use in synthesis. The failure of some typical carbonyl reagents to react with II indicates possible limitations of the analogy of
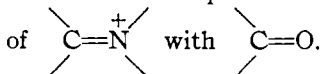
Experimental[20]

Reaction of $\Delta^{5(10)}$-Dehydroquinolizidinium Perchlorate[4] with Ethylmagnesium Iodide. 10-Ethylquinolizidine.—To the Grignard reagent prepared from 4.05 g. (0.026 mole) of ethyl iodide and 0.62 g. (0.026 gram atom) of magnesium in 150 ml. of anhydrous ether was added 3.0 g. (0.013 mole) of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate, and the mixture was stirred under reflux for 1 hour. The reaction mixture was then worked up as in the procedure given for 10-methylquinolizidine.[4] Distillation gave a colorless oil, b.p. 115° (25 mm.), yield 1.55 g. (71%).

Anal. Calcd. for $C_{11}H_{21}N$: C, 78.97; H, 12.65; N, 8.38. Found: C, 79.42; H, 12.37; N, 8.45.

The picrate was prepared in and recrystallized from ethanol as yellow needles, m.p. 220–221°.

Anal. Calcd. for $C_{17}H_{24}N_4O_7$: C, 51.51; H, 6.10; N, 14.14. Found: C, 51.47; H, 5.85; N, 14.33.

Reaction with n-Propylmagnesium Iodide. 10-n-Propyl-quinolizidine.—The Grignard reaction was conducted in the same manner using n-propylmagnesium iodide, giving a colorless oil, b.p. 132° (25 mm.), $n^{20.5}D$ 1.4908, yield 69%.

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.78. Found: C, 78.98; H, 12.39.

The picrate crystallized from ethanol as yellow needles, m.p. 185–186°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.66; H, 6.39; N, 13.65. Found: C, 52.88; H, 6.57; N, 13.47.

The hydriodide was prepared in the usual manner and was recrystallized from ethanol as colorless needles, m.p. 188–189°.

Anal. Calcd. for $C_{12}H_{24}IN$: C, 46.61; H, 7.82; N, 4.53. Found: C, 46.72; H, 7.60; N, 4.82.

When addition of isopropylmagnesium iodide to $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate was attempted, $\Delta^{1(10)}$-dehydroquinolizidine was recovered, along with a small amount of quinolizidine, indicating that some reduction had taken place. No 10-phenylquinolizidine could be isolated from the attempted reaction of phenylmagnesium bromide with $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate.

Reaction with Benzylmagnesium Chloride. 10-Benzyl-quinolizidine.—$\Delta^{5(10)}$-Dehydroquinolizidinium perchlorate was treated with three molar equivalents of benzylmagnesium chloride in the manner described above. The colorless oil, b.p. 117–119° (0.3 mm.), solidified on standing, m.p. 60–62°, yield 68%.

Anal. Calcd. for $C_{16}H_{23}N$: C, 83.78; H, 10.11. Found: C, 83.89; H, 9.99.

The picrate crystallized from ethanol as yellow prisms, m.p. 203–204°.

Anal. Calcd. for $C_{22}H_{26}N_4O_7$: C, 57.63; H, 5.72; N, 12.22. Found: C, 57.65; H, 5.75; N, 12.45.

(20) All melting points are corrected. We are indebted to Mrs. Esther Fett, Mrs. Lucy Chang and Mr. Joseph Nemeth for micro-analyses, and to Miss Helen Miklas and Mr. James Brader for determination of the infrared absorption spectra, using a Perkin-Elmer automatic recording infrared spectrometer, model 21.

Reaction with α-Picolyllithium. 10-(α-Picolyl)-quinolizidine.—A solution of 3.72 g. (0.04 mole) of α-picoline in 50 ml. of anhydrous ether was added slowly to a phenyllithium solution prepared from 6.28 g. (0.04 mole) of bromobenzene and 0.56 g. (0.08 g. atom) of lithium in 100 ml. of ether. To the orange-brown α-picolyllithium solution was added 3.56 g. (0.015 mole) of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate, and the mixture was stirred under reflux for 2 hours. Concentrated aqueous sodium hydroxide solution was added, and the ether layer was separated and washed with dilute hydrochloric acid. The aqueous acid layer was basified and extracted with ether. The combined ether extracts, following drying and removal of ether, furnished a viscous liquid, b.p. 137° (0.3 mm.), which crystallized to an almost colorless solid, m.p. ca. 50°, on standing, yield 2.23 g. (65%).

Anal. Calcd. for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63. Found: C, 78.08; H, 9.82.

The dipicrate crystallized from ethanol as yellow prisms, m.p. 152.5–153.5°.

Anal. Calcd. for $C_{27}H_{28}N_8O_{14}$: C, 47.09; H, 4.10; N, 16.28. Found: C, 47.34; H, 3.88; N, 16.50.

The monomethiodide separated from ethanol as colorless crystals, m.p. 212–213°.

Anal. Calcd. for $C_{16}H_{25}IN_2$: C, 51.62; H, 6.77; N, 7.53. Found: C, 51.40; H, 6.77; N, 7.52.

Reaction of $\Delta^{5(10)}$-Dehydroquinolizidinium Perchlorate with Potassium Cyanide. 10-Cyanoquinolizidine.—To a solution of 3.3 g. (0.051 mole) of potassium cyanide in 50 ml. of water contained in a separatory funnel was added 4.0 g. of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate, and the resulting mixture was extracted three times with ether. The product obtained from the ether extracts was distilled at 118–119° (16 mm.), $n^{21}D$ 1.4893, yield 2.43 g. (88%).

Anal. Calcd. for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06. Found: C, 73.45; H, 9.99; N, 16.92.

The infrared spectrum (pure liquid) showed absorption characteristic of $C\equiv N$ at 2210 cm.$^{-1}$. Attempts to form the perchlorate salt resulted in elimination of hydrogen cyanide. The picrate crystallized from ethanol as yellow needles, m.p. 128–129°.

Anal. Calcd. for $C_{16}H_{19}N_5O_7$: C, 48.85; H, 4.87; N, 17.81. Found: C, 48.67; H, 4.86; N, 17.85.

Reactions of 10-Cyanoquinolizidine. (a) With Methyl-magnesium Iodide.—To the Grignard reagent prepared from 7.25 g. (0.051 mole) of methyl iodide and 1.25 g. (0.051 gram atom) of magnesium in 200 ml. of ether was added 2.82 g. (0.017 mole) of 10-cyanoquinolizidine with stirring, and the mixture was heated 2 hours under reflux. The excess Grignard reagent was decomposed with 50 ml. of saturated aqueous ammonium chloride solution. Excess of a saturated aqueous solution of sodium fluoride was added to the aqueous layer, and the precipitated magnesium fluoride was separated by centrifugation. The supernatant was made strongly basic with sodium hydroxide and extracted with ether. The combined ether extracts were dried and the ether was removed. Addition of a saturated ethanolic solution of picric acid to the residue gave 5.87 g. (90%) of yellow powder, m.p. 261.5–262° dec., identified by mixed melting point determination as **10-methylquinoli-zidine picrate.** Phenylmagnesium bromide appeared not to react with 10-cyanoquinolizidine under the same conditions.

(b) **With Iodine.**—Treatment of 10-cyanoquinolizidine with excess of a solution of iodine in ether[12] caused the precipitation of a brown solid. Recrystallization from ethanol furnished dark maroon needles, m.p. 155–156°, of $\Delta^{5(10)}$-dehydroquinolizidinium periodide, yield 86%, infrared maximum (Nujol) at 1686 cm.$^{-1}$ ($>C\overset{+}{=}N<$). The corresponding iodide absorbs at 1688 cm.$^{-1}$.[4]

Anal. Calcd. for $C_9H_{16}I_3N$: I, 73.37. Found: I, 73.44.

(c) **With Lithium Aluminum Hydride.**—To a slurry of 1.0 g. of lithium aluminum hydride in 200 ml. of anhydrous ether was added 0.67 g. of 10-cyanoquinolizidine in 50 ml. of ether, and the mixture was stirred under reflux for one hour. The reaction mixture was worked up in the usual manner,[4] and the undistilled base was converted to the picrate in ethanol, m.p. 198–199°, yield 1.25 g. (97%),

which gave no depression in melting point upon admixture with an authentic sample[21] of quinolizidine picrate.

Further Reactions of $\Delta^{5(10)}$-Dehydroquinolizidinium Perchlorate. (a) With p-Thiocresol, Potassium Salt.—To a solution of 0.66 g. (0.018 mole) of potassium hydroxide and 1.46 g. (0.018 mole) of p-thiocresol in 35 ml. of methanol was added 2.80 g. (0.018 mole) of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate dissolved in 50 ml. of methanol. The potassium perchlorate formed was removed by filtration, and the filtrate was evaporated to dryness *in vacuo*. The 10-(p-thiocresyl)-quinolizidine was recrystallized from anhydrous ether using a Dry Ice–acetone-bath, colorless crystals, m.p. 61–63°.

Anal. Calcd. for $C_{16}H_{23}NS$: C, 73.31; H, 8.87; S, 12.27. Found: C, 74.09; H, 8.70; S, 12.11.

The material darkened rapidly on exposure to air and was decomposed to its component parts by dilute acid. The compound was also prepared by mixing equivalent parts of p-thiocresol and $\Delta^{1(10)}$-dehydroquinolizidine in ether.

(b) With α-Naphthylmethyl Mercaptan, Potassium Salt. Similar conditions resulted in the preparation of 10-(α-naphthylmethylmercapto)-quinolizidine from α-naphthylmethyl mercaptan; colorless needles, m.p. 98–99°.

Anal. Calcd. for $C_{20}H_{25}NS$: C, 77.11; H, 8.09; N, 4.50; S, 10.30. Found: C, 77.09; H, 8.14; N, 4.72; S, 10.06.

The compound darkened slowly on exposure to air. It was also prepared by mixing equivalent parts of α-naphthylmethyl mercaptan and $\Delta^{1(10)}$-dehydroquinolizidine in ether. The infrared spectrum in chloroform showed C=C absorption at 1655 cm.$^{-1}$ (reversal), but the band was absent when the spectrum was taken in Nujol mull.

The products resulting from the combination of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate and the potassium salts of n-propyl mercaptan and benzyl mercaptan were unstable and liberated mercaptan readily.

(c) With Potassium Alkoxides or Phenoxides.—The combination of $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate with a mole equivalent of potassium methoxide or phenoxide in methanol caused the precipitation of potassium perchlorate. The evaporation of the filtrate in each case left a colorless oil which darkened rapidly on standing and decomposed on attempted distillation to $\Delta^{1(10)}$-dehydroquinolizidine. When the potassium salt of 4-hydroxybiphenyl was used, a solid of m.p. *ca.* 65° was obtained at the evaporation stage, but this darkened quickly and could not be purified by recrystallization.

Under similar conditions, potassium hydroxide, potassium thiocyanate, potassium benzoate, potassium fluoride,

potassium p-toluenesulfonate and the potassium salt of malonic ester failed to yield stable products.

Reaction of $\Delta^{4(9)}$-Hexahydropyrrocolinium Perchlorate with Potassium Cyanide. 9-Cyanoöctahydropyrrocoline.—A solution of 6.71 g. (0.03 mole) of $\Delta^{4(9)}$-hexahydropyrrocolinium perchlorate[19] in water was added to an aqueous solution containing 1.96 g. (0.03 mole) of potassium cyanide. Sodium carbonate was added and the mixture was extracted with ether. The residue left after drying the ether extracts and removing the ether was distilled at 98° (14 mm.), $n^{28.5}$D 1.4790, yield 4.21 g., 96%.

Anal. Calcd. for $C_9H_{14}N_2$: C, 71.96; H, 9.39. Found: C, 72.50; H, 9.20.

The compound reverted to hexahydropyrrocoline on treatment with acids.

Reaction of 9-Cyanoöctahydropyrrocoline with Iodine. $\Delta^{4(9)}$-Hexahydropyrrocolinium Periodide.—To a solution of iodine (5 g.) in anhydrous ether was added 1.47 g. (0.01 mole) of 9-cyanoöctahydropyrrocoline. The brown precipitate which resulted was recrystallized from ethanol as brown-purple needles, m.p. 90–91°, yield 3.11 g. (63%), infrared maximum at 1678 cm.$^{-1}$ (Nujol mull).

Anal. Calcd. for $C_8H_{14}I_3N$: I, 75.42. Found: I, 75.57.

Reaction of 9-Cyanoöctahydropyrrocoline with Methylmagnesium Iodide. 9-Methyloctahydropyrrocoline.—The reaction with the Grignard reagent was carried out as in the case of 10-cyanoquinolizidine. The product was distilled at 68° (18 mm.), n^{28}D 1.4753.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31. Found: C, 77.25; H, 12.26.

9-Methyloctahydropyrrocoline picrate crystallized from ethanol as yellow plates, m.p. 274° dec.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47; N, 15.21. Found: C, 48.89; H, 5.35; N, 15.59.

9-Methyloctahydropyrrocoline hydriodide was prepared in the usual manner and recrystallized from ethanol–ether, m.p. 256.5–257.5° dec.

Anal. Calcd. for $C_9H_{18}IN$: C, 40.46; H, 6.79; N, 5.24. Found: C, 40.46; H, 6.61; N, 5.36.

2-Methylpyrrocolinium Perchlorate.—To an ethanol solution of 2-methylpyrrocoline, prepared according to the directions of Tschitschibabin,[22] was added 68% perchloric acid until the solution was acid to congo red paper. The precipitated salt was recrystallized from ethanol, m.p. 95.5–96°, infrared maxima at 1638, 2020 and 3100 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{10}ClNO_4$: C, 46.66; H, 4.35; N, 6.05. Found: C, 46.82; H, 4.45; N, 5.90.

(21) N. J. Leonard and W. C. Wildman, THIS JOURNAL, **71**, 3100 (1949).

(22) A. E. Tschitschibabin, *Ber.*, **60**, 1607 (1927).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Synthesis and Reactions of 1,1,2-Tribenzoylethylene and Related Compounds[1]

BY CHI-KANG DIEN[2] AND ROBERT E. LUTZ

1,1,2-Tribenzoylethylene has been prepared from 3-benzoyl-2,5-diphenylfuran by nitric acid oxidation. It is reduced to the saturated triketone or to the furan, and undergoes typical addition–cyclizations to the chloro and acetoxy furans. In the additions of hydrogen halide and morpholine, the halide and morpholinyl groups go to the 2-position as shown by subsequent furanizations of the addition compounds and oxidations of the furans to the chloro and morpholinyl unsaturated triketones. Chlorinations of both the saturated and unsaturated triketones appear to be straightforward. Bromination of 1,1,2-tribenzoylethane is at the 1-position but is followed by facile rearrangement to the 2-bromo compound. Bromination of the unsaturated triketone involves reduction of the 1-bromine of the dibromide and furanization. Prohibitive steric hindrance to halogenation in the 1-position of 1,2-tribenzoylethane is offered by a previously substituted halogen in the 2-position.

This paper is the first of a series dealing with the broad study of the conjugation of the 1,1,2-tribenzoylethylene type (II and VI) and it includes

investigation of the parent compound and the related saturated triketones and furans.

3-Benzoyl-2,5-diphenylfuran (IV),[3] an important intermediate for synthesis of the compounds in this

(3) (a) E. P. Kohler and W. N. Jones, THIS JOURNAL, **41**, 1249 (1919); (b) R. E. Lutz and J. M. Smith, *ibid.*, **63**, 1148 (1941); (c) H. Kleinfeller and H. Trommsdorff, *Ber.*, **71**, 2448 (1938).