Acknowledgment.—The authors are indebted to Mr. U. Stoeckli and his associates for microanalytical and instrumental data.

Heterocyclic Analogs of Fulvene and Fulvalene. II. 1,4-Diazafulvenes[1]

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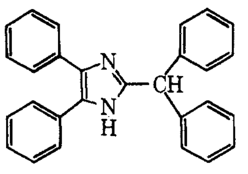
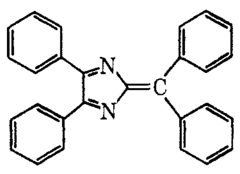
Several recent publications[2,3] dealing with nitrogen-containing analogs of fulvalene prompted us to present briefly some of our results in this general area. Earlier we showed[1] that $\Delta^{2,2'}$-bi-2H-benzimidazole could be readily prepared by oxidation of 2,2′-bibenzimidazole with lead peroxide. Recently the same method was used to prepare 2,3,6,7-tetraphenyl-1,4,5,8-tetraazafulvalene from 4,5,4′,5′-tetraphenyl-2,2′-biimidazole.[2] We have now found that examples of 1,4-diazafulvene derivatives can be prepared by oxidative methods and other reactions.

2-Benzhydryl-4,5-diphenylimidazole (I)[4] was converted into 2-benzhydrylidene-4,5-diphenyl-2H-imidazole (II) by two methods. Oxidation of I with freshly prepared lead peroxide gave an intense yellow solution from which II was isolated as orange needles. The spectroscopic properties were consistent with structure II: the infrared spectrum in CCl_4 showed no N-H absorption but had strong peaks at 3.25 and 3.29 μ (aromatic C-H) and at 6.02, 6.25, 6.71, and 6.92 μ (C=N and C=C). The visible spectra had maxima at 415 mμ (log ϵ 4.432) in ethanol and at 409 mμ (log ϵ 4.486) in cyclohexane. The nmr spectrum in $CDCl_3$ showed only a complex multiplet between τ 2.1 and 2.8 for the aromatic protons. An alternative though less efficient synthesis involved bromination of I with N-bromosuccinimide in $CHCl_3$ followed by dehydrobromination with triethylamine to yield a complex mixture from which II was isolated in low yield by column chromatography.

Behringer has recently described the properties of some 1,4-diazafulvenium ions obtained by the protonation with H_2SO_4 of 2-imidazolyldiphenyl carbinols, which were prepared by the reaction of aryl lithiums with 2-benzoylimidazoles.[5] When II was dissolved in concentrated H_2SO_4, a stable intense green solution resulted, with absorptions at 622 (log ϵ 4.396) and 458 mμ (log ϵ 4.006), which suggests that II was converted to a 1,4-diazafulvenium ion, presumably III. Quenching with water discharged the color and gave a product that was identified as 4,5-diphenyl-2-imidazolyldiphenyl carbinol (IV). In concentrated H_2SO_4, II and IV had identical absorption spectra. The easy reduction of II to I by $LiAlH_4$ indicated that no molecular rearrangement had occurred during oxidation.



I



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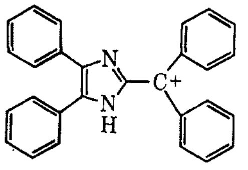
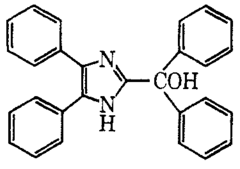
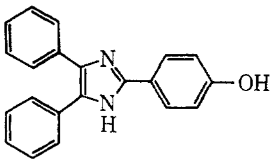


III

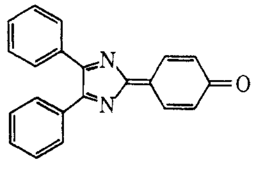


IV

2-(4-Hydroxyphenyl)-4,5-diphenylimidazole (V) was similarly oxidized by lead peroxide in warm $CHCl_3$ to 4-(4,5-diphenyl-2H-imidazol-2-ylidene)-2,5-cyclohexadien-1-one (VI).[3,6] Its infrared spectrum had intense absorption at 6.16 μ (C=O) and weaker absorptions at 3.22, 3.25, and 3.29 μ (=CH) and at 6.25, 6.77, and 7.00 μ (aromatic (C=C). The visible spectra had maxima at 432 mμ (log ϵ 4.396) in ethanol and at 421 mμ (log ϵ 4.746) in cyclohexane. The nmr spectrum in $CDCl_3$ showed the cyclohexadienide protons as an AB system, with doublets at τ 1.55 and 3.44 (4 H, J_{AB} = 10 cps) and the aromatic protons as a multiplet centered at τ 2.5 (10 H). Compound VI decomposed in concentrated H_2SO_4. It was reduced in poor yield by hydrazine and Raney nickel.



V



VI

2-(4-Pyridyl)-4,5-diphenylimidazole (VII) was alkylated with methyl benzenesulfonate to yield 4-(4,5-diphenylimidazolyl)-1-methylpyridinium benzenesulfonate (VIII). Treatment of VIII with sodium methoxide gave 1,4-dihydro-4-(4,5-diphenyl-2H-imidazol-2-ylidene)-1-methylpyridine (IX) as small golden red crystals. Compound IX was somewhat sensitive to light and air. It behaved as an anhydro base and was decolorized in acid solution and regenerated when the acid solution was basified. Its spectral properties were consistent with the structure proposed. The infrared spectrum in $CHCl_3$ had no N-H absorption but showed absorption at 3.39 (=CH), 6.14, and 6.28 μ (C=C or C=N). Maxima at 451 mμ (log ϵ 4.377) in ethanol and at 501 mμ (log ϵ 4.534) in benzene were observed. The nmr spectrum in $CDCl_3$ had a singlet at τ 5.9 ($>NCH_3$, 3 H) and a complex multiplet from τ 1.95 to 3.1 (about 14 H) which was due to both the aromatic and 1,4-dihydropyridine protons. Compound VIII was also prepared by alkylation of pyridine-4-carboxaldehyde with methyl benzenesulfonate and reaction of the crude product with benzil and ammonium acetate in refluxing acetic acid. This showed that VII was alkylated on the pyridine and not the imidazole ring.

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[1] Part I: J. H. M. Hill, *J. Org. Chem.*, **28**, 1931 (1963).

[2] U. Mayer, H. Baumgärtel, and H. Zimmermann, *Tetrahedron Letters*, 5221 (1966).

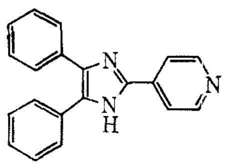
[3] U. Mayer, H. Baumgärtel, and H. Zimmermann, *Angew. Chem.*, **78**, 303 (1966).

[4] D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).

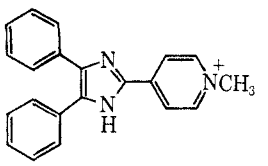
[5] H. Behringer and U. Turck, *Chem. Ber.*, **99**, 1815 (1966).

[6] Some compounds of this type have been reported: E. F. Silversmith, French Patent 1,395,112 (1965).

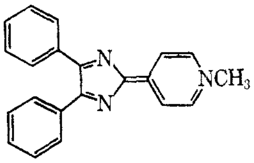
While II and VI were stable to light and air at room temperature indefinitely, IX was not and slowly decomposed to a material which showed infrared absorption at about 5.8 μ. This is reminiscent of the previously observed lack of stability of some cyclopentadienylidene dihydropyridines.[7,8]



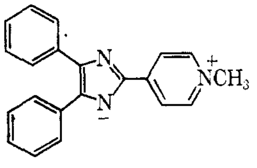
VII



VIII



IX



X

The electronic spectra of the 1,4-diazafulvenes all showed solvent dependent long wavelength maxima in the visible range. In the cases of II and VI, small bathochromic shifts (4 and 11 mμ, respectively) were observed with increased solvent polarity, suggesting that the excited state is more polar than the ground state[9] or that hydrogen bonding between solute and solvent is greater in the excited states of these molecules than in their ground states.[10] For IX, a somewhat larger hypsochromic shift (50 mμ) was observed under the same conditions. Similar large shifts have been observed for N-pyridinium cyclopentadienide[11] and N-pyridinium-2-benzimidazolide[12] and these have been interpreted as being due to a decreased charge separation between the pyridinium ring and the remainder of the molecule in the excited state compared with the ground state. If such an explanation pertains to the 1,4-diazafulvenes, it suggests that while II and VI are best represented by the structures given, IX might be best represented by the dipolar structure N-methylpyridinium-2-(4,5-diphenylimidazolide) (X).

Because IX is an anhydro base, an alternative explanation for its large hypsochromic shift in protic solvents is available.[13] While II and VI are not reversibly protonated in 0.1 *N* HCl, IX is converted into its conjugate acid, presumably VIII, which has a long wavelength maximum at 394 mμ (log ε 3.877). Therefore if IX is protonated in polar protic solvents such as ethanol, it will be in equilibrium with VIII and a hypsochromic shift will result.[14]

Experimental Section

Infrared spectra were determined on a Beckman IR-8 spectrophotometer. Electronic spectra were obtained with a Beckman DB spectrophotometer and recorded on a Photovolt Model 43 recorder. Nmr spectra were determined on a Vari A-60 spectrometer.

2-Benzhydryl-4,5-diphenylimidazole (I).—A mixture of benzil (21.1 g, 0.1 mole), freshly distilled diphenylacetaldehyde (19.6 g, 0.1 mole), and ammonium acetate (40.0 g, 0.52 mole) in glacial acetic acid (250 ml) was refluxed for 12 hr and then poured into aqueous ammonia (3 l. of 2 *M*). The cream precipitate was recrystallized twice from aqueous ethanol to yield I as white needles (31.2 g, 81%), mp 229°.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.77; N, 7.25. Found: C, 87.14; H, 5.71; N, 7.04.

2-Benzhydrylidene-4,5-diphenyl-2H-imidazole (II). Method A.—A suspension of I (3.86 g, 0.01 mole) in dry benzene (200 ml) was stirred with freshly prepared lead peroxide (25 g). After 48 hr at 35°, the resulting deep yellow solution was filtered and concentrated *in vacuo* to a yellow glass which was dissolved in dry acetone. Concentration and cooling of this solution yielded several crops of crystals which were combined and recrystallized from acetone to yield orange crystals of II (1.23 g, 32%), mp 177°.

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.36; H, 5.30; N, 7.11.

Method B.—A solution of I (3.86 g, 0.01 mole) in $CHCl_3$ (50 ml) was treated with N-bromosuccinimide (1.78 g, 0.01 mole). The mixture was refluxed and irradiated through Pyrex with a 500-w tungsten lamp. After 4 hr the mixture was cooled and filtered and the filtrate was treated with triethylamine (1.2 g, 0.011 mole). After stirring at 0° for 24 hr, the solution was evaporated *in vacuo* and the gummy residue was chromatographed on neutral alumina. Benzene eluted five components the second of which, after recrystallization from acetone, yielded II (0.47 g, 12%). The physical and spectroscopic properties of this product were identical with those of the previous preparation. The other four components were not identified.

4,5-Diphenylimidazolyldiphenyl Carbinol (IV).—Concentrated sulfuric acid (15 ml) was chilled in ice and stirred while II (0.384 g, 0.001 mole) was added in small portions. The dark green solution was poured onto crushed ice (50 g) and the resulting suspension was made basic with ammonia. The white solid was crystallized from aqueous ethanol to yield II as a white powder (0.17 g, 41%): mp 194–196°; infrared spectrum ($CHCl_3$) 2.78 (OH) and 2.97 μ (NH).

Anal. Calcd for $C_{25}H_{22}N_2O$: C, 83.56; H, 5.51; N, 6.96. Found: C, 83.41; H, 5.80; N, 7.14.

4-(4,5-Diphenyl-2H-imidazol-2-ylidene)-2,5-cyclohexadien-1-one (VI) was prepared by a previously described method[3] using $CHCl_3$ as solvent and was isolated as deep red-brown needles which darkened above 120° but did not melt until 290–300° when heated rapidly. The decomposition point has been reported to be 155°.[3]

Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03; mol wt, 310.4. Found: C, 81.41; H, 4.47; N, 9.24; mol wt, 305 (cryoscopic in benzene).

2-(4-Pyridyl)-4,5-diphenylimidazole (VII).—A solution of benzil (21.1 g, 0.1 mole) and pyridine-4-carboxaldehyde (10.7 g, 0.1 mole) in glacial acetic acid (100 ml) was added dropwise to a refluxing solution of ammonium acetate (40 g, 0.52 mole) in glacial acetic acid (150 ml) under nitrogen. After addition was complete, the reflux was continued for 10 hr and the resulting red solution was poured into aqueous ammonia (2 l. of 2 *M*). The resulting precipitate was crystallized twice from aqueous pyridine and once from methanol to yield VII (15.4 g, 52%), mp 235–236°.

Anal. Calcd for $C_{20}H_{15}N_3$: C, 80.78; H, 5.10; N, 14.13. Found: C, 80.64; H, 4.78; N, 14.41.

4-(4,5-Diphenylimidazolyl)-1-methylpyridinium Benzenesulfonate (VIII).—A mixture of VII (2.97 g, 0.01 mole) and methyl benzenesulfonate (1.72 g, 0.01 mole) in anhydrous methanol (50 ml) was refluxed under nitrogen for 72 hr. The yellow fluorescent solution was evaporated *in vacuo* and the residue was triturated with dry ether. The solid product was purified by repeated precipitation from anhydrous methanol with dry ether and was isolated as a yellow powder (2.44 g, 52%), mp 242–244°, with shrinking at 225–230°.

Anal. Calcd for $C_{27}H_{23}N_3SO_3$: N, 8.95. Found: N, 8.77.

1,4-Dihydro-4-(4,5-diphenyl-2H-imidazol-2-ylidene)-1-methylpyridine (IX).—A solution of VIII (2.35 g, 0.005 mole) in anhydrous methanol (25 ml) was treated dropwise with a solution of sodium methoxide in methanol (12.4 ml of 0.405 *M*) under nitrogen. The solution became deep red immediately. After 2 hr it was concentrated to dryness at ice temperature *in vacuo* and the

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[7] G. V. Boyd, *Proc. Chem. Soc.*, 253 (1960).

[8] G. V. Boyd and L. M. Jackman, *J. Chem. Soc.*, 548 (1963); however, J. A. Berson, E. M. Evleth, and Z. Hamlet, *J. Am. Chem. Soc.*, **87**, 2887 (1965), report otherwise.

[9] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[10] G. S. Hammond and F. J. Modic, *J. Am. Chem. Soc.*, **75**, 1385 (1953).

[11] D. Lloyd and J. S. Sneezum, *Tetrahedron*, **3**, 334 (1958); E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.*, **81**, 856 (1959).

[12] G. V. Boyd, *Tetrahedron Letters*, 3369 (1966).

[13] Thanks are due to a referee for suggesting this explanation.

[14] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 192.

resulting brown solid residue was extracted into dry ether (100 ml). This solution was concentrated to dryness and extracted into warm benzene (100 ml), which was cooled and concentrated to a small volume, whereupon small golden red crystals of product were deposited. Recrystallization from benzene afforded bronze crystals of IX (0.23 g, 15%) which charred above 130° and did not melt. The product was stable only when stored under nitrogen in the dark.

Anal. Calcd for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.49; mol wt, 311.4. Found: C, 80.77; H, 5.71; N, 13.27; mol wt, 306 (cryoscopic in benzene).

Alternatively, pyridine-4-carboxaldehyde (0.54 g, 0.005 mole) and methyl benzenesulfonate (0.86 g, 0.005 mole) were heated together in refluxing acetonitrile (20 ml) for 72 hr under nitrogen. The solvent was removed *in vacuo* and the resulting syrup, dissolved in glacial acetic acid (50 ml), was heated with benzil (1.06 g, 0.005 mole) and ammonium acetate (10 g, 0.13 mole) under nitrogen for 12 hr. The solution, initially deep green, became orange. It was poured into ice water (200 ml) and neutralized with solid sodium carbonate. The orange solution was immediately extracted with four 15-ml portions of $CHCl_3$ and the extract was dried with sodium sulfate and evaporated *in vacuo*. The brown solid was crystallized from benzene to yield IX as bronze crystals (0.19 g, 12%). Its spectral properties were identical with those of the product from the previous preparation. Tlc on buffered Kieselguhr-G with pyridine elution showed only one spot from both preparations (R_f 0.87).

Registry No.—I, 13341-64-5; II, 13341-65-6; IV, 13341-66-7; VI, 1970-91-8; VII, 13319-97-6; VIII, 13341-68-9; IX, 13341-69-0.

Acknowledgments.—The nmr spectra of II and VI were determined by Dr. R. E. K. Winter at the Polytechnic Institute of Brooklyn. Support for this work by a Frederick Gardner Cottrell Grant from Research Corp. is gratefully acknowledged.

Elimination During the Reduction of Pyridinium Salts

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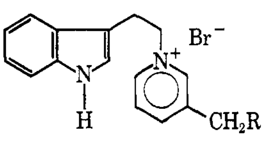
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520

Received May 3, 1967

The reduction of N-[β-(3-indolyl)ethyl]pyridinium salts with metal hydrides has been studied by a number of investigators[2-5] in an attempt to prepare compounds amenable to the construction of indole alkaloids. Wenkert and co-workers[4] have reported that treatment of the pyridinium salt **1a** with lithium aluminum tri-*t*-butoxyhydride in dry tetrahydrofuran followed by exposure to aqueous acid afforded the tetracyclic **2a** whereas reduction with sodium borohydride or lithium aluminum hydride gave tricyclic **3a**. With the latter reagent, small amounts of tetracyclic **2a** were also obtained.

In an attempt to prepare the allylic alcohol **2b**, the pyridinium salt **1b** was subjected to the conditions[6] for cyclization, affording two crystalline products which were readily separated by chromatography on acid-washed alumina. The more polar of the two substances was identified as the allylic alcohol **3b** (*m/e* 256), whose nmr spectrum displayed a broad two-proton singlet at δ 3.85 (CH_2O) and a broad one proton singlet at 5.65 (vinyl). The less polar component (*m/e* 238) was assigned structure **4** based upon the following data.



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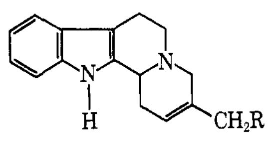
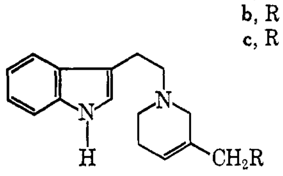


2a, R = CH_3
b, R = OH
c, R = OAc



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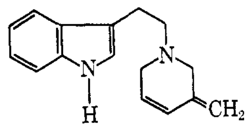

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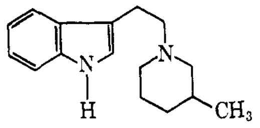

5

Catalytic hydrogenation in ethanol over 10% palladium on charcoal proceeded with the uptake of 2 equiv of hydrogen, affording a compound which was identical (undepressed mixture melting point and superimposable infrared spectrum) with the amine **5** prepared from tryptophyl bromide and 3-methyl piperidine. The presence of a diene chromophore was evident in the ultraviolet spectrum of **4**. The absorption band in the region of 220 mμ had an extinction coefficient greater by about 10,000 than the corresponding reduced product **5**. The substitution pattern of the diene was revealed by its nmr spectrum, showing a broad two-proton singlet at 5.0 (methylene vinyl) and a two-hydrogen multiplet at 5.8–6.7 (vicinal vinyl).

The diene can be thought to arise by Scheme I. It was felt that the diene could be derived from that amount of salt **1b** which was present as the aluminate of the alcohol function, whereas any uncoordinated alcohol would give rise to the allylic alcohol. Consequently, reduction with lithium aluminum hydride would be expected to give predominately the diene, and sodium borohydride, in turn, the allylic alcohol. Reduction of salt **1b** with lithium aluminum hydride in tetrahydrofuran yielded the diene in 50% yield as the only reduction product, whereas sodium borohydride in ethanol afforded the allylic alcohol **3b** in 73% yield, exclusive of the diene.[7]

Reduction of the pyridinium salt **1c** with either sodium borohydride, lithium aluminum tri-*t*-butoxyhydride, or lithium aluminum hydride gave the diene in 29, 30, and 45% yields, respectively, exclusive of the

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[1] National Institutes of Health Predoctoral Fellow, 1966–1967.

[2] For a general review, see R. E. Lyle and P. S. Anderson, *Advan. Heterocyclic Chem.*, **6**, 46 (1966).

[3] R. C. Elderfield, B. C. Fischer, and J. M. Lagowski, *J. Org. Chem.*, **22**, 1376 (1957).

[4] E. Wenkert, R. A. Massy-Westropp, and R. G. Lewis, *J. Am. Chem. Soc.*, **84**, 3732 (1962).

[5] K. T. Potts and I. D. Nasri, *J. Org. Chem.*, **29**, 3407 (1964).

[6] The nature of the products in all the reactions studied was unaltered when the aqueous acid treatment was omitted.

[7] The crude reaction mixtures were examined by thin layer chromatography to determine their composition.