If **3** is formed but decarboxylates rapidly to **4** through its carbanion,[7] carrying out the reaction in stronger acid concentration should inhibit the conversion of **3** into **4** and permit the isolation of **3**. Nmr studies of the reaction in various acid concentrations aided in establishing the best conditions for obtaining **3**. When the reaction was performed in 6 *N* aqueous HCl, **3** was isolated in high yield.

Experimental Section

The nmr spectral data were obtained on a Varian A-60 nmr spectrophotometer using dimethyl sulfoxide-d_6 as solvent. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS).

5-Chloro-1-methylimidazole[5] had the following nmr analysis: δ 3.60 ppm (CH_3, 1 position, 3 H, doublet, J = 0.9 Hz), 7.76 ppm (H, 2 position, 1 H), 7.00 ppm (H, 4 position, 1 H, doublet, J = 1.0 Hz).

5-Chloro-1-methyl-4-nitroimidazole (1)[2] had the following nmr analysis: δ 3.76 ppm (CH_3, 1 position, 3 H, doublet, J = 0.4 Hz), 8.02 ppm (H, 2 position, 1 H, unresolved multiplet).

Diethyl 1-Methyl-4-nitro-5-imidazolylmalonate (2).—Diethyl malonate (144 g, 0.9 mol) was added dropwise with stirring to a solution of sodium metal (17.4 g, 0.75 g-atom) in 750 ml of absolute ethanol. A Soxhlet extractor, containing 48.3 g (0.3 mol) of **1** in its thimble, was attached to the reaction flask, and the reaction mixture was refluxed for 12 hr after all of **1** had dissolved. The ethanol was removed under reduced pressure (steam bath). The residue was dissolved in 750 ml of water extracted with ether, and acidified with dilute hydrochloric acid. The aqueous layer was separated from the orange oil, and extracted with chloroform. The oil and chloroform extract were combined and filtered. After stripping of the chloroform, the oil solidified on cooling. The product was recrystallized from diisopropyl ether–ethanol (3:1): yield, 70.5 g (82.4%); mp 67°.

Anal. Calcd for $C_{11}H_{15}N_3O_6$: C, 46.31; H, 5.30; N, 14.73. Found: C, 46.60; H, 5.19; N, 14.65.

Nmr analysis showed δ 3.84 ppm (CH_3, 1 position, 3 H, doublet, J = 0.3 Hz), 7.93 ppm (H, 2 position, 1 H, unresolved multiplet), 5.94 ppm (CH, 5 position, 1 H, singlet), 4.28 ppm (CH_2, ester, 4 H, quartet), 1.22 ppm (CH_3, ester, 6 H, triplet).

1,5-Dimethyl-4-nitroimidazole (4).—Compound **2** (17.1 g, 0.06 mol) and 250 ml of 1.2 *N* aqueous HCl were refluxed (100°) for 12 hr. The solution was cooled to 25° and made basic with solid sodium carbonate. The precipitated product was filtered, and the aqueous filtrate extracted with chloroform. The solid obtained by evaporation of the chloroform extract was combined with the rest of the product, and recrystallized from water: yield, 6.8 g (80%); mp 162° (lit.[6] mp 160–161°).

Anal. Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.92; H, 5.18; N, 29.60.

Nmr analysis showed δ 3.68 ppm (CH_3, 1 position, 3 H, doublet, J = ~0.3 Hz), 7.74 ppm (H, 2 position, 1 H, unresolved multiplet), 2.57 ppm (CH_3, 5 position, 3 H, singlet).

Following the course of the above reaction in refluxing 1.2 *N* aqueous HCl by nmr,[8] **3** had formed in large amounts within 30 min. Also **4** was present in significant amounts by this time. After 12 hr, essentially complete conversion into **4** had occurred.

1-Methyl-4-nitro-5-imidazolylacetic Acid (3).—A solution of **2** (8.5 g, 0.03 mol) in 85 ml of 6 *N* aqueous HCl was refluxed (104°) for 25 min. The reaction mixture was cooled to 0° and neutralized to pH of 2.5 (pH meter) using solid sodium carbonate. The product **3** precipitated and was filtered. Purification was achieved by dissolving in 10% sodium carbonate solution at 10°, filtering, and precipitating the product with 6 *N* aqueous HCl. The product was filtered, washed with water, and dried: yield, 4.8 g (87.3%); mp 144° dec.

Anal. Calcd for $C_6H_7N_3O_4$: C, 38.92; H, 3.81; N, 22.70; neut equiv, 185.1. Found: C, 38.65; H, 3.87; N, 22.73; neut equiv, 185.3.

Nmr analysis showed δ 3.70 ppm (CH_3, 1 position, 3 H), 4.13 ppm (CH_2, 5 position, 2 H), 7.69 ppm (H, 2 position, 1 H). Neither spin coupling nor carboxyl hydrogen was observed.

The course of the above reaction in refluxing 6 *N* aqueous HCl was followed by nmr. Compound **3** was present in greatest amount within 30 min after reflux had begun with no **2** or **4** evident. Only after 5 hr at reflux did **4** become apparent. By this time, the nmr spectrum showed evidence of competing reactions taking place with only a small buildup of **4**. After 12 hr at reflux, only 5.9% **4** was isolated from the reaction mixture. The nmr spectrum still indicated the presence of a significant amount of **3**.

Registry No.—II, 7464-80-4.

Acknowledgment.—The authors thank Drs. M. W. Dietrich and M. D. Wolfinger for assistance with the nmr spectral data.

(7) Several other nitrogen-containing heterocyclic-substituted carboxylic and acetic acids are known to undergo decarboxylations with relative ease. For a review with references and mechanistic considerations, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 348–351.

(8) Aqueous HCl (6 *N*) was added to the initial aliquots, after cooling, to clarify the solutions.

Oxidation of Some Cyclic Benzylic Hydrazines Derived from Naphthalene, Acenaphthene, and Diphenylmethane

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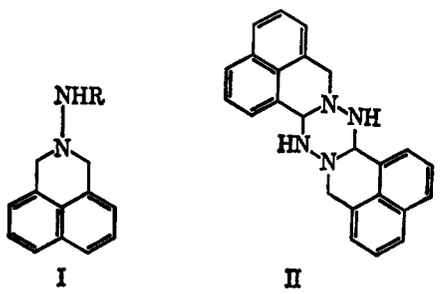
Although the oxidation of 1,1-dibenzylhydrazines with the formation of hydrocarbon products appears to be a general reaction, oxidation of cyclic benzylic hydrazine I (R = H) by means of mercuric oxide or other oxidants gave none of the expected acenaphthene.[1] Instead only the corresponding tetrazene was isolated.



I II

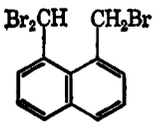
It has now been found that treatment of the *p*-toluenesulfonyl derivative (I, R = $SO_2C_6H_4CH_3$-*p*) with sodium ethoxide in ethanol, or simply by warming in ethanol alone, yields neither acenaphthene nor the tetrazene but rather the high melting compound II.[2] Structure II was established by an alternate synthesis involving treatment of tribromide III with hydrazine according to the method used by Schmitz[3] to obtain the analogous hexahydro-*s*-tetrazine IV from 2-(2-bromo-

(1) L. A. Carpino, *J. Amer. Chem. Soc.*, **85**, 2144 (1963).

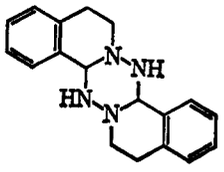
(2) Depending on the specific case there may or may not be a correspondence between the products obtained by direct oxidation of a 1,1-disubstituted hydrazine and those obtained by alkaline degradation of the *p*-toluenesulfonyl derivative. See also D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Amer. Chem. Soc.*, **85**, 1944 (1963).

(3) E. Schmitz, Ber., **91**, 1495 (1958). Several attempts to obtain an 8-halomethyl-1-naphthaldehyde having been unsuccessful, tribromodimethylnaphthalene was used as a convenient substitute.

ethyl)benzaldehyde. Tetrazine IV is also formed by oxidation[4] of N-aminotetrahydroisoquinoline and alkaline degradation of its *p*-toluenesulfonyl derivarive.

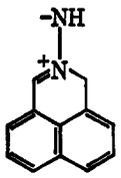


III

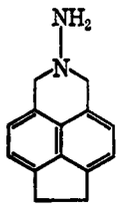


IV

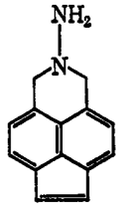
Formation of II from III presumably involves the dipolar intermediate V or some closely related species.[5]



V



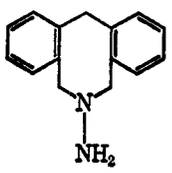
VI



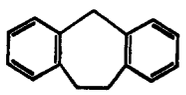
VII

Ionization[6] of I (R = $SO_2C_6H_4CH_3$-*p*) followed by deprotonation at carbon rather than nitrogen would lead to the same intermediate.

The results of an examination of three additional benzylic hydrazines (VI–VIII) provide a rationale for



VIII



IX

the supposedly anomalous lack of conversion of I into acenaphthene. Whereas oxidation of VI[7] by means of activated manganese dioxide gave none of the expected hydrocarbon, pyracene, similar treatment of VII[7] gave 1,2-dihydropyracylene, albeit in very low yield (8–15%). This suggests that in the latter case reaction can occur, at least to a limited extent, through a pathway involving fragmentation of the intermediate azamine to the 1,8-quinodimethane.[7] In the case of I and VI such a pathway is not available. Nevertheless it has been difficult to understand why reaction in these two cases could not proceed through a transition state similar to that which is involved in the case of simple acyclic benzylic hydrazines. An interesting case is provided by VIII which cannot undergo fragmentation to a quinodimethane but is far more flexible than I. In fact alkaline degradation of the *p*-toluenesulfonyl derivative of VIII has been found to give the corresponding hydrocarbon (IX) in good yield. One possible explanation for the lack of conversion of I into asenaphthene can therefore be given in terms of the compression involved in the transition state for collapse of the intermediate azamine to the strained[8] acenaphthene system.[9] Since this strain should be even greater in the conversion of VII into 1,2-dihydropyracylene the importance of an alternate fragmentation pathway to hydrocarbon products is clearly indicated. For the same reason N-aminodihydroisoindoles are readily converted into the still more highly strained benzocyclobutenes and in this case the fragmentation pathway is confirmed by the stereochemistry of the reaction.[10]

(4) E. Höft and A. Rieche, *Angew. Chem.*, **73**, 807 (1961).

(5) Compare D. M. Lemal and T. W. Rave, *J. Amer. Chem. Soc.*, **87**, 393 (1965); D. M. Lemal, F. Menger, and E. Coats, *ibid.*, **86**, 2395 (1964).

(6) D. M. Lemal, C. D. Underbrink, and T. W. Rave, *Tetrahedron Lett.*, 1955 (1964).

(7) L. A. Carpino and S. Göwecke, *J. Org. Chem.*, **29**, 2824 (1964).

Experimental Section[11]

Thermal Decomposition of 2-*p*-Toluenesulfonylamino-2,3-dihydro-1H-benz[*d*,*e*]isoquinoline.—A solution of 0.5 g of I (R = *p*-$CH_3C_6H_4SO_2$) in 55 ml of commercial absolute ethanol was refluxed for 9 hr. Filtration gave 0.2 g (74.5%) of II, mp 255–257° dec (sintering at 235°). Because of its insolubility no solvent could be found for recrystallization. The crude material was found to be analytically pure.

Anal. Calcd for $C_{24}H_{20}N_4$: C, 79.09; H, 5.53; N, 15.38. Found: C, 78.84; H, 5.87; N, 15.10.

Treatment of α,α,α'-Tribromo-1,8-dimethylnaphthalene with Hydrazine.—To a solution of 0.6 g of III[12] (mp 105–108°) in 15 ml of ethanol was added 0.4 ml of 64% hydrazine. Addition of 20 ml of water and filtration gave 0.13 g (47%) of II, identified by infrared comparison with the sample obtained by thermal decomposition of I (R = *p*-$CH_3C_6H_4SO_2$).

2-*p*-Toluenesulfonylamino-1,2,3,4-tetrahydroisoquinoline.—Treatment of the hydrochloride of 2-amino-1,2,3,4-tetrahydroisoquinoline with *p*-toluenesulfonyl chloride and triethylamine in DMF solution gave the tosyl derivative (60%) which after recrystallization from nitromethane and benzene had mp 129–131°.

Anal. Calcd for $C_{16}H_{18}N_2SO_2$: C, 63.57; H, 6.00; N, 9.27. Found: C, 63.90; H, 6.30; N, 9.01.

Treatment of the tosyl derivative with aqueous sodium hydroxide for a few minutes resulted in the precipitation of 97% IV, mp 249–251° dec, identified by comparison with authentic samples prepared by oxidation[4,13] of the free hydrazine and reaction of 2-(2-bromoethyl)benzaldehyde with hydrazine.[3]

Oxidation of VII.—Under a stream of nitrogen a solution of 0.5004 g of VII in 100 ml of methylene dichloride was treated over 5 min with 2 g of activated manganese dioxide with magnetic stirring. The mixture was stirred for an additional 5 min, allowed to settle and poured onto a column of basic alumina (Schuchardt, activity No. 1, Brockmann). Elution with methylene dichloride and evaporation of the solvent under a stream of nitrogen gave a residue which after recrystallization from ligroin (bp 60–70°) gave 0.0336 g (7.7%) of 1,2-dihydropyracylene, mp 154–156° (lit.[14] mp 155–156°). The compound was identified by comparison of its infrared spectrum with that of an authentic sample.[14] In other runs under the same conditions the yield varied from 8 to 15%. A similar attempt to oxidize VI gave no pyracene. In neither case did treatment of the corresponding *p*-toluenesulfonyl derivative with alkali give any hydrocarbon products.

Benzophenone-2,2'-dicarboxylic Acid.—A mixture of 92.6 g of

(8) A. G. Anderson, Jr., and R. H. Wada, *J. Amer. Chem. Soc.*, **74**, 2274 (1952).

(9) We are indebted to a referee for the suggestion that the loss of nitrogen from the azamine derived from I or VI might be hindered relative to the case of VIII because of severe steric hindrance to coplanarity in the developing biradicals assumed to be involved. Evaluation of this interesting suggestion must await further data on the extent to which radical (or ionic) character is important in the transition state for conversion of an azamine (acyclic as well as cyclic) into hydrocarbon products.

(10) L. A. Carpino, *Chem. Commun.*, 494 (1966).

(11) Melting points are uncorrected. Nmr spectra were recorded on a Varian A-60 instrument using TMS as internal standard. Infrared spectra were recorded on Perkin-Elmer 21 237B and Beckman IR-5 instruments. Elemental analyses are by Galbraith Laboratories, Knoxville, Tenn., and Alfred Bernhardt, Mülheim (Ruhr), Germany.

(12) W. Ried, H. Boden, U. Ludwig, and H. Neidhart, *Ber.*, **91**, 2479 (1958).

(13) We are indebted to Dr. Höft who kindly supplied an infrared spectrum of IV for comparison purposes.

(14) A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **23**, 517 (1958).

2-(2-methylbenzoyl)benzoic acid[15] in 1700 ml of water and 0.2 g of NaOH was heated on a steam bath with stirring and then carefully treated with solid $KMnO_4$ in small portions over 0.5 hr, after which time the vigorous foaming had subsided. Over the following 8 hr a total of 230 g of $KMnO_4$ was added portionwise. After an additional 15 hr of heating the mixture was cooled, treated with excess $NaHSO_3$ and filtered through Celite. The MnO_2 was washed with two 1-l. portions of hot water and the combined decolorized filtrates were acidified with hydrochloric acid to give 80.3 g (77%) of the acid, mp 185°, resolidification and final mp 212–213.5° [lit.[16] mp 210° (final)].

6-(*t*-Butyloxycarbonylamino)-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine.—A solution of 26.3 g of 2,2′-bis(bromomethyl)diphenylmethane (obtained from benzophenone-2,2′-dicarboxylic acid by the method of Bergmann and Pelchowicz[16]) and 9.9 g of *t*-butyl carbazate in 150 ml of DMF was warmed to 50° and 15.2 g of triethylamine added dropwise with stirring at a rate to keep the temperature < 60°. After the mixture was allowed to stir overnight 400 ml of water was added and the gummy solid extracted with CH_2Cl_2. Evaporation of the solvent followed by recrystallization from cyclohexane gave 13 g (53%) of the azocine: mp 104–105°; nmr δ (CCl_4) 1.38 s (*t*-Bu, 9 H), 4.3 m (CH_2, 6 H), 7.1 m (phenyl, 8 H).

Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.99; H, 7.41; N, 8.50.

6-Amino-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine.—A solution of 1.3 g of the carbo-*t*-butoxy derivative above in 25 ml of methanol was added to 75 ml of methanol which had been saturated with hydrogen chloride in an ice bath. The solution was allowed to stir overnight and evaporated to dryness and the residue recrystallized from methanol–ether to give 0.6 g (58%) of the hydrochloride, mp 210–214° dec (softening at 209°).

Anal. Calcd for $C_{15}H_{17}N_2Cl$: C, 69.08; H, 6.57; N, 10.74; Cl, 13.59. Found: C, 69.01; H, 6.62; N, 10.56; Cl, 13.66.

Conversion to the **free base** was effected by shaking with CH_2Cl_2 and $NaHCO_3$ solution. Recrystallization of the crude product from petroleum ether gave 72% of the hydrazine, mp 114–116°.

Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.10; H, 7.34; N, 12.27.

The **benzal** derivative, recrystallized from ethanol, had mp 165–166.5°.

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.57; H, 6.33; N, 9.01.

The ***p*-toluenesulfonyl** derivative, recrystallized from benzene–hexane had mp 146–148.5° dec.

Anal. Calcd for $C_{22}H_{22}N_2SO_2$: C, 69.82; H, 5.87; N, 7.40; S, 8.46. Found: C, 70.04; H, 6.01; N, 7.58; S, 8.42.

10,11-Dihydro-5H-dibenzo[*a*,*d*]cycloheptene.—A mixture of 20 ml of 20% NaOH and 2.5 g of the *p*-toluenesulfonyl derivative of VIII was heated for 10 min on a steam bath and cooled to room temperature and the oil extracted with CH_2Cl_2. Evaporation and recrystallization from methanol gave 1.1 g (85%) of the hydrocarbon, mp 74–76.5° (lit.[17] mp 78–79°), which was identified by comparison with an authentic sample.

Registry No.—II, 19406-76-9; 2-*p*-toluenesulfonylamino-1,2,3,4-tetrahydroisoquinoline, 19350-92-6; 6-(*t*-butyloxycarbonylamino)-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine, 19350-93-7; 6-amino-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine, 19350-94-8; 6-amino-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine hydrochloride, 19350-95-9; 6-amino-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine benzal derivative, 19350-96-0; 6-amino-5,6,7,12-tetrahydrodibenz[*c*,*f*]azocine *p*-toluenesulfonyl derivative, 19350-97-1.

Acknowledgment.—This work was supported by a grant (NSF GP-4283) from the National Science Foundation. We are indebted to Mr. Robert Kirkley for checking the oxidation of VII.

(15) M. S. Newman and C. D. McCleary, *J. Amer. Chem. Soc.*, **63**, 1537 (1941).
(16) E. D. Bergmann and Z. Pelchowicz, *ibid.*, **75**, 4281 (1953).
(17) W. Treibs and H. J. Klinkhammer, *Ber.*, **83**, 367 (1950).

Reaction of 6-Hydroxy-2-pyridone with Diazomethane. Isolation of a Novel Product

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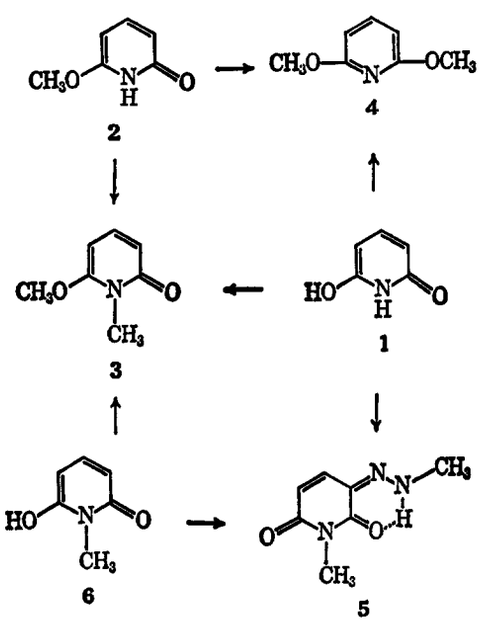
Received October 17, 1968

Alkylation reactions of nitrogenous heterocycles have been investigated extensively because of the biological importance of such reactions.[3] In the course of a study of the tautomerism and reactivity of 2,6-disubstituted pyridines, we investigated the reaction of 6-hydroxy-2-pyridone (**1**) (glutaconimide) with diazomethane. In addition to the expected N- and O-methylated products [6-methoxy-2-pyridone (**2**), 6-methoxy-1-methyl-2-pyridone (**3**), and 2,6-dimethoxypyridine (**4**)], an additional substance was observed upon thin layer chromatography. When a large ratio of diazomethane to 6-hydroxy-2-pyridone (**1**) was used (100:1), this product was the one isolated in largest yield. It has been assigned the structure of 1-methyl-1,2,3,6-tetrahydropyridine-2,3,6-trione 3-methylhydrazone (**5**) on the basis of the evidence discussed below. To our knowledge, the isolation of **5** represents the first reported example of substitution of a methylazo group on an aromatic or heterocyclic ring with diazomethane. We feel that this report is not a unique example of this type of substitution but that it may have occurred in methylations of phenols[4] and pyridones[5] with diazomethane and that the corresponding products have been overlooked as minor impurities.

Products **2**, **3**, and **4** were identified by comparison of their ir spectra and/or melting points with those of authentic samples.[6]



(1) New York University special Predoctoral Fellow, 1966–1967.
(2) Inquiries should be addressed to this author.
(3) A. Loveless, "Genetic and Allied Effects of Alkylating Agents," The Pennsylvania State University Press, University Park, Pa., 1966.
(4) H. von Pechmann, *Chem. Ber.*, **28**, 857 (1895).
(5) N. Kornblum and G. P. Coffey, *J. Org. Chem.*, **31**, 3447 (1966).
(6) A. R. Katritzky, F. D. Popp, and J. D. Rowe, *J. Chem. Soc., B*, 562 (1966).