The residue was recrystallized twice from diisopropyl ether to give 175 mg. (78%) of product, m.p. 102–104°.

*Anal.* Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.79; H, 5.64; N, 12.31.

**Zinc Dust Reduction of 1-Hydroxy-2-phenylbenzimidazole (V).**—A mixture of 210 mg. (1.0 mmole) of V and 200 mg. (3.0 mg.-atoms) of zinc dust was heated at 240° for 2 hr. The mixture was allowed to cool and was extracted with warm ethanol. After the ethanol had been decanted, the residue was dissolved in dilute hydrochloric acid. The resulting solution was filtered, and the filtrate was made slightly basic. The basic filtrate then was extracted with three 15-ml. portions of warm chloroform. The chloroform was removed by distillation, and the residue was recrystallized from ethanol–benzene to yield 113 mg. of IV (58%), m.p. 292–294°, m.m.p. 293–294.5°.

**Conversion of N-Benzylidene-*o*-nitroaniline (II) to 1-Hydroxy-2-phenylbenzimidazole (V).**—A solution of 452 mg. (2.0 mmoles) of II and 212 mg. (2.0 mmoles) of benzaldehyde in 3 ml. of dry toluene was heated under reflux for 72 hr. The reaction mixture was allowed to stand in the freezer for 3 days, and the resulting crystalline precipitate was removed by filtration and purified by boiling toluene to give V in a 82-mg. yield (20%, m.p. 220° dec.). Identity was established by mixture melting point determination and infrared spectrum.

**Conversion of N,N-Benzylidenedi(*o*-nitroaniline) (III) to V.**—A solution of 364 mg. (1.0 mmole) of III and 318 mg. (3.0 mmoles) of benzaldehyde in 3 ml. of dry toluene was heated under reflux for 2 days. From the mixture was obtained 200 mg. of crude product which upon recrystallization from ethanol gave 117 mg. (56%) of V, m.p. 220° dec.

**Acknowledgment.**—We wish to express thanks to Varian Associates for assistance in determination and interpretation of n.m.r. spectra. This investigation was supported in part by a grant (G 1100) from the National Science Foundation.

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# Oxidation by Solids. III. Benzalanilines from N-Benzylanilines and Related Oxidations by Manganese Dioxide

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A variety of benzalanilines are readily obtained in excellent yield upon heating a suspension of manganese dioxide in a benzene solution of the corresponding N-benzylaniline in an apparatus equipped with a water trap. Close to theoretical yields of the by-product water collect at a rate which measures the rate of the oxidation. The effect of changes in structure of the reactants on the rate indicates that the process proceeds *via* free radicals. N-*t*-Alkyl benzylamines are also oxidized smoothly. Quinoline is obtained in good yield from 1,2,3,4-tetrahydroquinoline under the same conditions, and indole and acridine are readily prepared from 2,3-dihydroindole and acridane. The oxidation of a number of hydrazobenzenes to the azobenzenes proceeds rapidly in nearly quantitative yield, and, under modified conditions, azobenzenes are also obtained in good yield from a variety of anilines.

It has been found that, when a solution of an N-benzylaniline in benzene is heated under reflux with manganese dioxide in an apparatus equipped with a Bidwell–Sterling water trap, excellent yields of the corresponding benzalanilines and approximately theoretical yields of the by-product water are ordinarily obtained (Table I). These mild, anhydrous conditions prevent the further oxidation or hydrolysis of the product which often occurs when other methods of oxidation are used.[3,4]

$$p\text{-}RC_6H_4CH_2NHC_6H_4R'\text{-}p + MnO_2 \longrightarrow p\text{-}RC_6H_4CH = NC_6H_4R'\text{-}p + MnO + H_2O$$

A plot of the yield of water *vs.* time gives smooth curves of constantly decreasing slope which are closely reproducible and which show no tendency to cross one another as the reactant is varied. The times required for 50% of the theoretical yield of water to collect ($t_{50\%}$) are, therefore, valid measures of the relative reaction rates.

Data in the first and fourth sections of the table show that shifting a methoxyl group from the *para* to the *meta* to the *ortho* position or a methyl group from the *para* to the *ortho* position decreases the rate. The decrease in rate is reasonably ascribed to an increase in steric hindrance and as expected on this basis the shift of the methyl group has less effect than the shift of the larger methoxyl group.

It is of interest that dibenzylamine (fifth section) was oxidized at about the same rate as N-benzylaniline although only the latter compound gives a product in which the new double bond is conjugated with both aromatic rings. The oxidation also proceeded smoothly, although much more slowly, when the anilino ring of N-benzylaniline was replaced by tertiary alkyl groups.

No well-defined products were isolated when attempts were made to oxidize benzylamine, N-methylbenzylamine, N-isopropylbenzylamine, N-methylaniline, N-butylaniline, dibutylamine, or piperidine under the standard conditions. Apparently, unstable Schiff bases, which reacted further, were formed, since in all these cases water was collected in over 80% yield. Some of these amines have been oxidized by manganese dioxide under other conditions,[5,6] and, although in

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(1) From the Ph.D. thesis of T. P. McGovern, April, 1962.

(2) For the preceding paper in this series, see E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, **28**, 638 (1963).

(3) (a) P. Friedlander, "Fortschritte der Theerfarbenfabrikation," Vol. **4**, Julius Springer, Berlin, 1890, p. 129 (German Patent 91503); (b) p. 131 (German Patent 92084); (c) R. Hubner, *Ber.*, **35**, 731 (1902); (d) C. M. Rosser and J. J. Ritter, *J. Am. Chem. Soc.*, **59**, 2179 (1937); (e) F. W. Newman and C. W. Gould, *Anal. Chem.*, **25**, 751 (1953); (f) J. T. Edwards, *J. Chem. Soc.*, 1464 (1954); (g) A. A. Bolandin and N. A. Vasyunina, *Dokl. Akad. Nauk* SSSR, **103**, 831 (1955); *Chem. Abstr.*, **50**, 9283 (1956).

(4) E. A. Braude, A. G. Brook, and R. P. Linstead [*J. Chem. Soc.*, 3574 (1954)] describe a procedure employing diphenylpicrylhydrazyl for the conversion of N-benzylaniline to benzalaniline which is of considerable theoretical, but limited preparative, interest.

(5) (a) R. J. Highet and W. C. Wildman, *J. Am. Chem. Soc.*, **77**, 4399 (1955); (b) H. B. Henbest and A. Thomas, *J. Chem. Soc.*, 3032 (1957).

(6) M. Z. Barakat, M. F. Abdel-Wahab, and M. M. El Sadr, *ibid.*, 4605 (1956).

TABLE I

OXIDATION OF N-BENZYLANILINES, HYDRAZOBENZENES, AND RELATED COMPOUNDS[a]

| Reactant | $t_{50\%}$, min. | $H_2O$, % | Product, % |
|---|---|---|---|
| N-Benzyl-*p*-Substituted Anilines | | | |
| $C_6H_5CH_2NHC_6H_4OCH_3$-*p* | 48 | 113 | 80 |
| $C_6H_5CH_2NHC_6H_4CH_3$-*p* | 65 | 110 | 82 |
| $C_6H_5CH_2NHC_6H_4C_6H_5$-*p* | 68 | 110 | 91 |
| $C_6H_5CH_2NHC_6H_4Cl$-*p* | 96 | 105 | 83 |
| $C_6H_5CH_2NHC_6H_5$ | 98 | 101 | 84 |
| $C_6H_5CH_2NHC_6H_4NO_2$-*p* | 130 | 103 | 73 |
| N-(*p*-Substituted benzyl)anilines | | | |
| *p*-$O_2NC_6H_4CH_2NHC_6H_5$ | 59 | 109 | 82 |
| *p*-$CH_3OC_6H_4CH_2NHC_6H_5$ | 82 | 109 | 69[b] |
| $C_6H_5CH_2NHC_6H_5$ | 98 | 101 | 84 |
| *p*-$CH_3C_6H_4CH_2NHC_6H_5$ | 99 | 103 | 64[b] |
| *p*-$ClC_6H_4CH_2NHC_6H_5$ | 103 | 110 | 76 |
| *p,p'*-Disubstituted N-Benzylanilines | | | |
| *p*-$CH_3OC_6H_4CH_2NHC_6H_4OCH_3$-*p* | 50 | 101 | 77 |
| *p*-$ClC_6H_4CH_2NHC_6H_4Cl$-*p* | 85 | 111 | 86 |
| $C_6H_5CH_2NHC_6H_5$ | 98 | 101 | 84 |
| *p*-$O_2NC_6H_4CH_2NHC_6H_4NO_2$-*p* | 103[c] | 103 | 85 |
| Other Benzylanilines | | | |
| $C_6H_5CH_2NHC_6H_4OCH_3$-*m* | 136 | 102 | 70 |
| $C_6H_5CH_2NHC_6H_4CH_3$-*o* | 146 | 97 | 78 |
| $(C_6H_5)_2CHNHC_6H_5$ | 149 | 104 | 89 |
| $C_6H_5CH_2NHC_6H_4OCH_3$-*o* | 162 | 96 | 78 |
| N-Substituted Benzylamines | | | |
| $C_6H_5CH_2NHCH_2C_6H_5$ | 103 | 106 | 62 |
| $C_6H_5CH_2NHC(CH_3)_2CH_2C(CH_3)_3$ | 173 | 106 | 85 |
| $C_6H_5CH_2NHC(CH_3)_3$ | 250 | 97 | 80 |
| Heterocyclic Amines | | | |
| $o\text{-}\underbrace{C_6H_4CH_2CH_2N}H$ | 40 | 134 | 59[d] |
| $\underbrace{C_6H_4CH_2C_6H_4N}H$[e] | 46 | 117 | 93 |
| $o\text{-}\underbrace{C_6H_4CH_2CH_2CH_2N}H$ | 72[f] | 100[f] | 79[f] |
| *p*-Substituted Hydrazobenzenes | | | |
| *p*-$CH_3OC_6H_4NHNHC_6H_5$ | 34 | 111 | 96 |
| $C_6H_5NHNHC_6H_5$ | 40 | 100 | 97 |
| *p*-$ClC_6H_4NHNHC_6H_5$ | 46 | 109 | 96 |
| *p*-$CH_3C_6H_4NHNHC_6H_5$ | 55 | 107 | 96 |
| *p,p'*-Disubstituted Hydrazobenzenes | | | |
| *p*-$CH_3C_6H_4NHNHC_6H_4CH_3$-*p* | 39 | 116 | 99 |
| $C_6H_5NHNHC_6H_5$ | 40 | 100 | 97 |
| *p*-$ClC_6H_4NHNHC_6H_4Cl$-*p* | 44 | 101 | 91 |

[a] Standard conditions: 0.05 mole of amine, 0.40 mole of manganese dioxide, and 500 ml. of benzene stirred magnetically while distilling the by-product water at 81°. [b] The yield of these low melting products could probably be raised 10 to 15% if isolated by distillation instead of crystallization. [c] This value may be low since reactant was not completely soluble. [d] Yield could probably be raised by stopping reaction when yield of water reaches 100%. [e] Acridine. [f] Product is quinoline and yield of water and $t_{50\%}$ value are recorded on this basis.

certain cases evidence of the formation of Schiff bases was obtained, none were isolated.

Oxidation under the standard conditions proved to be an excellent way to convert 1,2,3,4-tetrahydroquinoline to quinoline; two molecules of water per molecule of reactant were rapidly evolved (sixth section). Indole and acridine were also readily obtained from their dihydro precursors.

Results in the last two sections of the table show that a variety of hydrazobenzenes are oxidized in 96% average yield to the azobenzenes. For a number of the hydrazobenzenes, the rate differences were too small to be significant. In all cases the reaction proceeded markedly faster than for the corresponding N-benzylanilines. On the other hand, starting material was recovered in 90% yield when the oxidation of dibenzyl was attempted.

In numerous cases correlation, on even a qualitative basis, of the rate data in the first three sections of Table I with the relative ability of the *para* substituents to attract electrons[7,8] is impossible. This lack of correlation and the relatively small changes in rate resulting from changes in these substituents indicate that the reaction proceeds *via* free-radical rather than ionic intermediates. It seems improbable that changes in the ease of absorption of the reactants on the manganese dioxide resulting from changes in the *para* substituents would interfere with correlations of rate with electron-attracting ability of these substituents to the extent found here. The evidence that this reaction proceeds *via* free radicals is re-enforced by the previously reported evidence that the oxidation of phenylcarbinols[9] and of diphenylmethanes,[2] under similar conditions, are homolytic processes; the effects of varying the *para* substituents found in these two earlier studies are not unlike those summarized in Table I. Although ionic reactions are often catalyzed by acids or bases, *p*-toluenesulfonic acid (0.001 mole) had no appreciable effect on the rate of oxidation of N-benzylaniline. Oxidations by diphenylpicrylhydrazyl are certainly homolytic processes[4] and the fact that both this hydrazyl and manganese dioxide oxidize hydrazobenzene more rapidly and dibenzyl more slowly than they oxidize N-benzylaniline suggests that these oxidations by manganese dioxide are also homolytic reactions. A mechanism analogous to those of the related preceding studies[2,9] is, therefore, proposed.

$$RCH_2NHR' + O{=}Mn^{+4}{=}O \longrightarrow RCH_2\dot{N}R' + HO{-}Mn^{+3}{=}O$$

$$RCH_2\dot{N}R' + HO{-}Mn^{+3}{=}O \longrightarrow RCH{=}NR' + HO{-}Mn^{+2}{-}OH$$

$$HO{-}Mn^{+2}{-}OH \longrightarrow H_2O + Mn^{+2}{=}O$$

Some of the product could result from disproportionation of the intermediate radical, as shown below,

$$2RCH_2\dot{N}R' \longrightarrow RCH{=}NR' + RCH_2NHR'$$

but the tendency for the concentration of active radicals to be low ordinarily minimizes their interaction.[10]

It is well-recognized that, when a radical can be formed by loss of a hydrogen atom from either nitrogen or carbon, loss from nitrogen ordinarily takes precedence, and the remaining steps tend to require less energy.[4,11] The interpretation that the odd electron first appears on the nitrogen is in agreement with the fact that N-benzylaniline is oxidized more rapidly than dibenzyl

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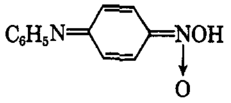
[7] The rate-decreasing effect of the nitro group would be a logical result of the existence of an appreciable proportion of the compound in the tautomeric form.



[8] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 188–197; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[9] E. F. Pratt and John F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

[10] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, New York, N. Y., 1959, p. 692.

[11] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 53.

and more slowly than hydrazobenzene, and also with the fact that a substituent tends to have a greater effect when on the anilino than when on the benzyl group of N-benzylaniline (Table I).

Attempts to oxidize aniline under the standard conditions for the experiments of Table I gave only a 47% yield of azobenzene; when, however, the manganese dioxide was not dried (by distilling the water from a suspension of it in benzene) before the aniline was added, a 91% yield of azobenzene was obtained. Since under these modified conditions the water evolved from the oxidation was accompanied by about three times as much water from the dehydration of the manganese dioxide, it was impractical to determine differences in rates of oxidation of various anilines.

Good yields of azobenzenes were obtained from a variety of anilines under the modified conditions. The compounds oxidized and the yields obtained were as follows: *p*-chloroaniline, 96%; aniline, 91%; *p*-phenylaniline, 76%; *p*-toluidine, 71%; *p*-anisidine, 60%; *p*-nitroaniline, 55%; *m*-nitroaniline, 50%; γ-aminopyridine, 49%; *o*-nitroaniline, 21%; and *p*-cyanoaniline, 18%. This method, because of its facility and generality, is in many cases an improvement upon previously described methods.[6,12,13]

## Experimental[14,15]

**Starting Materials.**—The manganese dioxide for the experiments of Table I was prepared by a modified Attenburrow[16] procedure. A solution of 281 g. of manganous sulfate monohydrate (Mallinckrodt, A.R.) in 500 ml. of water was added concurrently with 390 ml. of 40% aqueous sodium hydroxide to a mechanically stirred solution of 320 g. of potassium permanganate (Mallinckrodt, A.R.) in 2 l. of water. The permanganate solution was warmed to 80° at the start, and during the additions the temperature gradually rose to 90°; the mixture was stirred at this temperature for 1 hr. after the additions were completed. It was found that the precipitate could be washed much more rapidly if the manganese sulfate was added over a 60-min. period while the addition of the sodium hydroxide extended over only the first 45 min. of this period. After the hot mixture was filtered, the precipitate was washed in the filter with copious amounts of hot water until the filtrate was neutral to litmus. The manganese dioxide was dried at 125° for 24 hr. and ground to pass a 60-mesh sieve. A number of batches were thoroughly mixed to give a single large batch which was used for all experiments of Table I. The manganese dioxide was allowed to equilibrate with atmospheric moisture by exposing it in $^3/_8$-in.-thick layers to the room atmosphere for 5 days during which it was thoroughly mixed at about 5-hr. intervals; the gain in weight amounted to over 5%. The dioxide was then weighed into 0.4-mole (34.78-g.) portions and stored at −20° in tightly closed containers until used. It was found that this equilibration of the dioxide with the atmospheric moisture markedly improved the reproducibility of the reaction rates.

N-Benzyl-*m*-anisidine [b.p. 226–227° (27 mm.), $n^{20}\mathrm{D}$ 1.6080] and N-benzyl-*o*-anisidine [b.p. 211–212° (27 mm.), $n^{20}\mathrm{D}$ 1.6053] were prepared, in 90 and 60% yields, by a method described for the *para* isomer.[17] N-*p*-Chlorobenzylaniline, m.p. 60–61°, was obtained from N-*p*-chlorobenzalaniline upon reduction with sodium borohydride,[18] and *p*-methoxyhydrazobenzene, m.p. 74–75°, was obtained from the corresponding azobenzene.[19] *p*-Hydrazotoluene, m.p. 129.5–131°, was prepared from *p*-nitrotoluene.[19] Results of ultimate analyses were satisfactory in all cases.

All other components of the reaction mixtures were purchased or prepared by previously published procedures and purified by standard methods until their refractive index or melting point agreed closely with the literature values.

**Experiments of Table I.**—Except for readily apparent modifications, the previously described procedure was used.[9] During the 5 hr. of refluxing to dry the manganese dioxide, before the amine was added, 2.53 ± 0.05 ml. of water ordinarily collected. Frequent readings of water volume, time, and temperature were taken until the reaction was 80% complete. Heating was ordinarily continued overnight to complete the reaction.

With only a few minor exceptions, the temperature for the 10 to 80% portion of the relatively slow reactions in the fourth and fifth sections of Table I was 81.8 ± 0.2°, while for the reactions in the other sections it was 81.0 ± 0.2°. It was found that the $t_{50\%}$ values, which were read from the plots of the yield of water *vs.* time, were readily reproducible to within 5%.

The reaction mixture was filtered through a Celite mat and the mat was washed with benzene. Most of the solvent was removed from the combined filtrate and washings under reduced pressure and the residues were freed of the remainder of the solvent in an air stream. The products were purified by standard crystallization and distillation procedures until their melting points or refractive indices agreed satisfactorily with the literature values except for the following six products which had the indicated refractive indices: N-benzal-*p*-toluidine, $n^{21}\mathrm{D}$ 1.6432; N-benzal-*m*-anisidine, $n^{21}\mathrm{D}$ 1.6374; N-benzal-*o*-toluidine, $n^{21}\mathrm{D}$ 1.6272; N-benzal-*o*-anisidine, $n^{21}\mathrm{D}$ 1.6439; N-benzal-*t*-butylamine, $n^{20}\mathrm{D}$ 1.5156; and N-benzal-1,1,3,3-tetramethylbutylamine, $n^{20}\mathrm{D}$ 1.5130.

When, under conditions otherwise identical with those for the fifth experiment of the table, the amount of manganese dioxide was decreased from 0.4 to 0.3 to 0.2 mole, the yields of pure benzalaniline decreased from 84 to 66 to 0%; when the temperature was decreased from 111 to 81 to 52° (by changing the solvent) the yields were 70, 84, and 60%.

The oxidation of the hydrazobenzenes (last two sections of the table) was carried out with the standard 0.4 mole (34.78 g.) of manganese dioxide in order to facilitate comparison with the N-benzylanilines. Less manganese dioxide gave equally good yields of product, however, and the reaction tended to proceed even faster, probably because of increased efficiency of the stirring. Thus, when the amount of manganese dioxide was increased from 0.2 to 0.3 to 0.4 mole, the $t_{50\%}$ values were 24, 40, and 40 min., respectively. The total yields of water were 86, 96, and 100%, and the yields of product were 98, 97, and 97%.

**Azobenzenes from Anilines.**—When aniline and *p*-chloroaniline were oxidized under the standard conditions given for Table I, the yields of water were 100 and 112%, but the yields of the pure azobenzenes were only 47 and 72%; black tarry material was also produced. It was found that higher yields of product were obtained if the dehydration of the manganese dioxide (by refluxing for 5 hr. before the amine was added) was omitted. For the oxidation of anilines, the standard procedure was, therefore, modified by adding both the 0.05 mole of the aniline and the 0.4 mole of manganese dioxide after the 30 min. of refluxing to dry the apparatus. In all cases, heating was continued for 24 hr., at which time water evolution had virtually ceased. The total volume of water was ordinarily 3.25 to 3.50 ml. When the yield of the azobenzene was less than 60%, starting material was ordinarily recovered in 20 to 35% yield. The manganese dioxide employed for oxidation of the anilines was prepared as previously described[9] except that, after the final heating of the oxide, it was allowed to come into equilibrium with the moisture in the air as described above.

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(12) (a) G. B. Barlin, K. H. Pausacker, and N. V. Riggs, *J. Chem. Soc.*, 3122 (1954); (b) K. H. Pausacker and J. G. Scroggie, *ibid.*, 4003 (1954); (c) E. Baer and A. L. Tosoni, *J. Am. Chem. Soc.*, **78**, 2857 (1956); (d) A. P. Terent'ev and Ya. D. Magilyanski, *Dokl. Akad. Nauk SSSR*, **103**, 91 (1955); *Chem. Abstr.*, **50**, 4807 (1956); (e) P. S. Raman, *Proc. Indian Acad. Sci.*, **45A**, 65 (1957); *Chem. Abstr.*, **51**, 13,795 (1957).

(13) K. H. Pausacker [*J. Chem. Soc.*, 1989 (1953)] proposes a free-radical mechanism for the oxidation of aniline to azobenzene by phenyliodosoacetate in benzene; hydrazobenzene is assumed to be an intermediate.

(14) All melting points are corrected.

(15) We wish to thank Dr. Franz Kasler for the microanalyses reported here.

(16) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(17) Y. Sprinzak, *J. Am. Chem. Soc.*, **78**, 3207 (1956).

(18) J. H. Billman and A. C. Riesing, *J. Org. Chem.*, **22**, 1068 (1957).

(19) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1961, pp. 631, 632.

When the amount of manganese dioxide employed for the oxidation of aniline was decreased from 0.4 to 0.3 to 0.2 mole, the yield of azobenzene decreased from 91 to 75 to 48%. When the temperature was decreased from 111 to 81 to 52°, by changing the solvent, the corresponding yields of azobenzene were 85, 91, and 76%.

**Acknowledgment**—It is a pleasure to acknowledge financial support by the National Science Foundation, the Union Carbide Corporation, and the National Institutes of Health which greatly aided the progress of this work.

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# Ring Closure of Ylidenemalononitriles. III.[1] Formation of Six-Membered Rings and Related Chemistry[2]

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Several $\gamma$-aryl ylidenemalononitriles, including that of a phenylacetaldehyde derivative, were cyclized in concentrated sulfuric or polyphosphoric acid to 1-naphthylamine derivatives. Surprisingly, ylidenemalononitriles derived from $\alpha$-acetonaphthalene did not form six-membered rings *via* cyclization to the 8-position. Hydration to the *trans*-cyanoamide was the principal reaction in these cases. The ring closure was shown to proceed by attack of a protonated nitrile group, rather than an amido group, on the aromatic ring, by cyclizing *cis*-2-cyano-3-methyl-4-phenyl-2-butenamide, a reaction which failed for the *trans* isomer. The configuration of the isomers was established by n.m.r. studies. The ultraviolet absorption spectra of the hindered and unhindered 2-cyano- and 2-carboxamido-1-naphthylamines produced by these cyclizations are discussed.

Substituted indenones and indanones can be produced by strong acid treatment of the appropriate ylidenemalononitriles.[1,4] From the ring closure of these dinitriles, compounds containing newly formed five-membered rings were obtained. The study of this facile ring closure has now been extended to ylidenemalononitriles leading to six-membered rings.

Cyclizations of aromatic derivatives of nitriles to form six-membered cyclic ketones and aromatic amines are well known. Atkinson and Thorpe[5] prepared a series of 1,3-diaminonaphthalene derivatives by ring closing various derivatives of ethyl $\beta$-imino-$\alpha$-phenylbutyrate in sulfuric acid. *o*-Biphenylacetonitrile and its derivatives have been converted to phenanthrylamines or phenanthrones by an intramolecular cyclization in sulfuric acid.[6] Howell and Taylor[7] prepared 1,2,3,4-tetrahydrofluoren-1-one from $\gamma$-3-indenylbutyronitrile in the presence of anhydrous zinc chloride and hydrogen chloride. Several other papers[8] report cyclizations involving nitrile groups to form six-membered heterocyclic compounds. The conversion of $\gamma$-(1-cyclohexenyl)butyronitrile to $\Delta^9$-1-octalone in polyphosphoric acid[9] showed that ring closure of a nitrile can also occur by electrophilic attack on an olefinic double bond.

Only two reports have been found describing the cyclization of an ylidenemalononitrile to form a six-membered ring. Dufraisse and Etienne[10] accomplished the bicyclization of 1,3-diphenylisopropylidenemalononitrile to 11,12-diaminonaphthacene in a phosphoric acid–sulfuric acid–phosphorus pentoxide mixture. Jaeger[11] describes the ring closure of 2-(cyclohexylidene)cyclohexylidenemalononitrile to 10-amino-9-cyano-1,2,3,4,5,-6,7,8-octahydrophenanthrene in sulfuric acid.

As shown by earlier results,[4] good yields of $\alpha$-carboxamido-$\alpha,\beta$-unsaturated ketones were obtained from the ring closure of certain $\alpha$-cyano-$\beta$-substituted cinnamonitriles. In most instances, the second nitrile was hydrated during cyclization. It was of interest to investigate cyclizations of ylidenemalononitriles which could lead to six-membered cyclic compounds having the partial structure **1**, especially since this structure is present in certain antibiotics.

It was found that treatment of several ylidenemalononitriles (**2**) with sulfuric acid gave good yields of newly formed six-membered rings. The ring closure of ylidenemalononitrile **2a** to 2-cyano-3,4,4-trimethyl-1-keto-1,4-dihydronaphthalene (**4**) has already been reported.[4b] Ylidenemalononitriles (**2**), with $R^1 = H$, were prepared (Table I) and were all ring closed to derivatives of 1-naphthylamine (Table II).

A good yield of 2-cyano-3-methyl-1-naphthylamine (**3a**, $Z = CN$) was obtained when phenylisopropylidenemalononitrile (**2b**) was allowed to stand in concentrated sulfuric acid at room temperature for 1 hr. It was interesting to note that the amine was isolated from the acid solution after the reaction mixture was poured over ice. No further product was isolated when the mother liquor was made basic. The second nitrile group resisted hydration similar to that of **4** mentioned above. However, when the sulfuric acid solution was heated for 1 hr. at 90°, only the hydrated product **3a**

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(3) Taken in part from the (a) Ph.D. thesis of D. Maulding, June, 1962, Bristol Predoctoral Fellow, 1960–1962; (b) Ph.D. thesis to be submitted by W. Roelofs, National Institute of Health Predoctoral Fellow, 1962–1964.

(4) (a) E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, *J. Org. Chem.*, **27**, 4428 (1962); (b) E. Campaigne and D. R. Maulding, *ibid.*, **28**, 1391 (1963).

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