[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Peracetic Acid Oxidation of Hydrazones. I. Aromatic Aldehyde Alkylhydrazones[1,2]

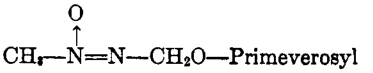
BERNARD T. GILLIS AND KARL F. SCHIMMEL

Received July 26, 1961

The oxidation of aromatic aldehyde alkylhydrazones by commercial 40% peracetic acid was shown to give good yields of *cis*-azoxy compounds of the type p-Z—$C_6H_4CH_2N{=}N(O)$—R, where Z = H, CH_3O, C_6H_5, NO_2; R = C_6H_5; and fair yields of the same type where Z = H, CH_3, Br, NO_2; R = CH_3. These compounds easily rearranged to the hydrazides, p-Z—C_6H_4—CO—NHNH—R, in the presence of acid and above room temperature. The mechanism of the rearrangement leading to hydrazide was shown to depend on stabilization by conjugation. When an azoxy compound was substituted by similar primary alkyl groups, the rearrangement proceeded by oxidation of the carbon attached to the quatervalent nitrogen. Thus, $C_6H_5—CH_2—N{=}N(O)—CH_2C_6H_4—CH_3(p)$ led to $C_6H_5—CH_2—NHNHCO—C_6H_4—CH_3(p)$ and p-$CH_3—C_6H_4—CH_2—N{=}N(O)—CH_2—C_6H_5$ gave p-$CH_3—C_6H_4—CH_2NHNHCO—C_6H_5$ by rearrangement.

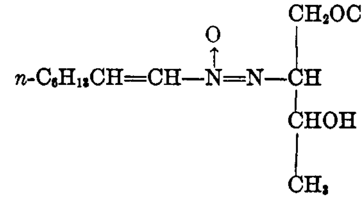
The purpose of this investigation was first, to prepare selectively azoxy compounds in which the site of the nitrogen to oxygen bond was known, and secondly, to develop a method for the determination of the position of the nitrogen to oxygen bond in azoxy compounds without resort to ultraviolet spectroscopy which necessitates a chromophore in conjugation with the azoxy group.

There are two compounds containing the azoxy group that occur naturally and they are Macrozamin (I)[3] and Elaiomycin (II).[4] The structures of these compounds have been determined; however, the position of the nitrogen to oxygen bond in I was not clearly established.



$CH_3—\overset{\overset{O}{\uparrow}}{N}{=}N—CH_2O—\text{Primeverosyl}$

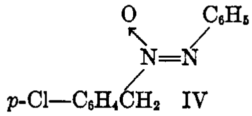
I



$n\text{-}C_6H_{11}CH{=}CH—\overset{\overset{O}{\uparrow}}{N}{=}N—\underset{\underset{\underset{CH_3}{|}}{\underset{CHOH}{|}}}{\overset{\overset{CH_2OCH_3}{|}}{CH}}$

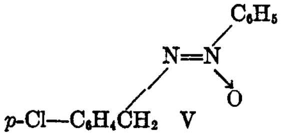
II

In 1923, Bergmann, Ulpts, and Witte[5] showed that the reaction of monoperphthalic acid with benzaldehyde phenylhydrazone gave a benzyl phenyl azoxy compound. The compound was then investigated by other groups[6] and finally was assigned the correct structure α-(phenyl-*NON*-azoxy)toluene[7] (III). By the use of both synthetic methods and ultraviolet spectral studies, J. N. Brough, et al.,[8] identified both the positional and geometric isomers formed by perbenzoic acid oxidations of a substituted benzaldehyde phenylhydrazone and the correspondingly substituted benzylazobenzene. The compounds that resulted from oxidation of the latter were *trans*-α-(phenyl-*NNO*-azoxy)-4-chlorotoluene (IV) and *trans*-α-(phenyl-*NON*-azoxy)-4-chlorotoluene (V), while the oxidation of p-chlorobenzaldehyde phenylhydrazone gave *cis*-α-(phenyl-*NON*-azoxy)-4-chlorotoluene (VI).



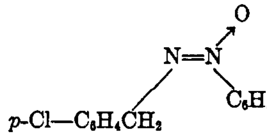
IV

λ 292 mμ



V

λ 249 mμ



VI

λ 254 mμ

In the present investigation, when 40% peracetic acid was used as the oxidizing agent on substituted benzaldehyde phenylhydrazones, only one isomer was also formed. The absorption maxima of the azoxy compounds ranged from 255.5 to 257 mμ and thus were assigned a *cis*-configuration with the

---

[1] This work was supported by a research grant (E-2923) from the National Institute of Allergy and Infectious Diseases, National Institutes of Health.

[2] Abstracted from the Doctoral thesis of Karl F. Schimmel, Duquesne University, 1961.

[3] B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

[4] C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *J. Am. Chem. Soc.*, **80**, 6088 (1958).

[5] M. Bergmann, R. Ulpts, and C. Witte, *Ber.*, **56**, 679 (1923).

[6](a) K. H. Pausacker, *J. Chem. Soc.*, 3478 (1950). (b) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 2517 (1953). (c) B. Witkop and H. M. Kissman, *J. Am. Chem. Soc.*, **75**, 1975 (1953). (d) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1131 (1954). (e) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 3340 (1954).

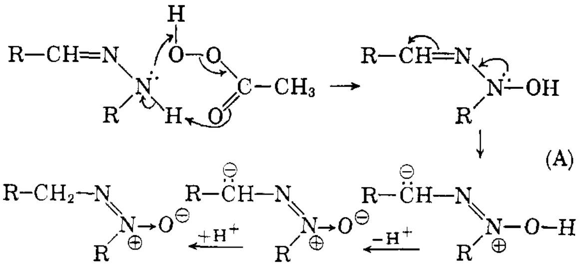
[7] This nomenclature is consistent with that given in footnote 18 of ref. 4; *cf.* the system adopted in ref. 8.

[8] J. N. Brough, B. Lythgoe, and P. Waterhouse, *J. Chem. Soc.*, 4069 (1954).

TABLE I

cis-Azoxy Compound	λ_{max} (C_2H_5OH)	log ε	M.P.°	Yield, %
C_6H_5—CH_2—N=N(O)—C_6H_5	257 mμ	4.057	187	54
p-NO_2—C_6H_4—CH_2—N=N(O)—C_6H_5	255.5 mμ	4.170	172	85
p-C_6H_5—C_6H_4—CH_2—N=N(O)—C_6H_5	256 mμ	4.117	188	87
p-CH_3O—C_6H_4—CH_2—N=N(O)—C_6H_5	257 mμ	4.079	162	74

nitrogen to oxygen bond adjacent to the phenyl ring. The compounds prepared are listed in Table I along with their absorption maxima, ε, melting point, and yield. The satisfactory formation of *cis*-azoxy compounds using commercial 40% peracetic acid obviated the use of the less available perbenzoic and monoperphthalic acids.[9] A possible mechanism to explain these results is shown below in scheme (A) where R = C_6H_5:


(A)

The infrared spectra of the azoxy compounds in Table I were all devoid of —OH and —NH— absorption and exhibited strong bands at 1460–1500 cm.$^{-1}$ and 1280–1320 cm.$^{-1}$ characteristic of the azoxy group.[6b,c;8]

When substituted benzaldehyde methylhydrazones were treated with peracetic acid at ice bath temperatures azoxy compounds were also formed. These aliphatic azoxy compounds were by analogy assigned the *cis*-configuration and are listed in Table II. Their ultraviolet spectra were determined in tetrahydrofuran. That of α-(methyl-*NON*-azoxy)-toluene (VII) was determined in both tetrahydrofuran and ethanol and exhibited a 12-mμ shift in the absorption maxima due to solvent. The infrared spectra of the compounds were all consistent with the assigned structures and showed no —OH or —NH— absorption but strong absorption characteristic of the azoxy group.

If the substituted benzaldehyde methylhydrazones were treated with peracetic acid at the reflux temperature of the solvent employed, the correspondingly substituted 1-benzoyl-2-methylhydrazines were the major products obtained. These alkyl hydrazides arose from rearrangement of the azoxy compounds in the presence of acetic acid. The rearrangement of III was previously noted[5,6e] to occur in hot acetic acid and a mechanism was proposed by Lynch and Pausacker.[6e] The azoxy compounds from the benzaldehyde methylhydrazones appear far more labile in the presence of acetic acid. Hydrolysis of these methylazoxy compounds in refluxing concentrated hydrochloric acid resulted in isolation of a 75–85% yield of the corresponding substituted benzoic acid. The hydrolysis undoubtedly proceeded through the alkyl hydrazide. While primary aliphatic nitro compounds hydrolyze in acid to the corresponding carboxylic acid[10] and hydrolysis of Elaiomycin[4] II, resulted in oxidation of the carbon attached to the quatervalent nitrogen by a path similar to (b) in scheme (B), stabilization by conjugation can be cited as a major factor in causing VII to hydrolyze by path (a). That this was indeed the case, was shown by the preparation and hydrolysis of primary azoxy compounds whose alkyl groups were closely similar.

TABLE II

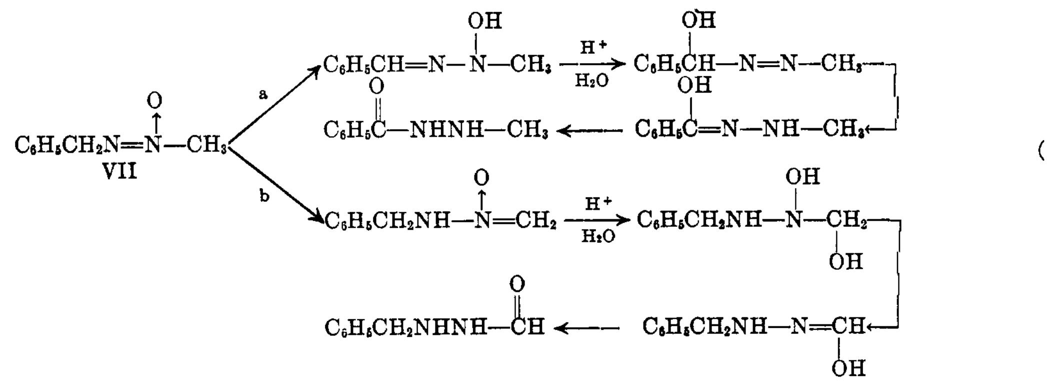
cis-Azoxy Compound	λ_{max} mμ (THF)	log ε	M.P.°	Yield %
C_6H_5—CH_2N=N(O)—CH_3(VII)	230	4.872	153	53
	218 (EtOH)	4.008		
p-CH_3—C_6H_4—CH_2N=N(O)—CH_3(XII)	229	4.898	116	61
p-NO_2—C_6H_4—CH_2N=N(O)—CH_3 (XIII)	229.5	4.894	205	72
p-Br—C_6H_4—CH_2N=N(O)—CH_3 (XIV)	230.5	4.893	185	61

Peracetic acid oxidation of *p*-tolualdehyde benzylhydrazone resulted in formation of two products, α-(benzyl-*NON*-azoxy)-*p*-xylene (VIII) and 1-benzoyl-2-(α-*p*-xylyl)hydrazine (IX). When VIII was refluxed with dilute acid IX was formed which indicated that it arose in the initial oxidation by rearrangement of the first formed azoxy compound. When benzaldehyde α-*p*-xylylhydrazone was treated with peracetic acid, α-(benzyl-*NNO*-azoxy)-*p*-xylene (X) and 1-*p*-toluyl-2-benzylhydrazine (XI) were obtained. Similarly, when X was refluxed with dilute acid XI was formed. The infrared spectra of both VIII and X were free of —OH and —NH— absorption and showed strong absorption characteristic of the azoxy group. Compounds IX and XI were independently synthesized for comparison purposes and were identical to those formed in the two oxidations.

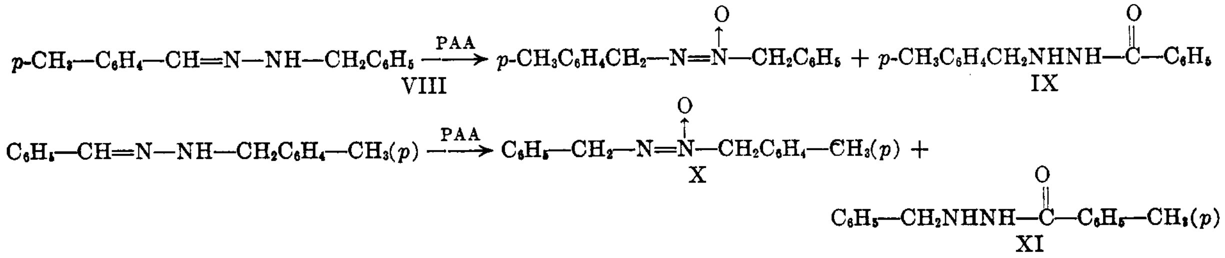
---

(9) While monoperphthalic and perbenzoic acid gave apparent azoxy compounds in refs. 6b, 6c, and 6d, the melting points do not correspond to those obtained in numerous runs by peracetic acid oxidation. Since the ultraviolet spectra were not obtained by the authors in ref. 6b and 6d and the melting points are not consistent from peracetic and monoperphthalic acid oxidations, no conclusion can be drawn as to what they had obtained. See Experimental for individual azoxy compounds.

(10) S. B. Lippincott and H. B. Hass, *Ind. Eng. Chem.*, 31, 118 (1939).



(B)



$p\text{-}CH_3\text{—}C_6H_4\text{—}CH{=}N\text{—}NH\text{—}CH_2C_6H_5 \xrightarrow{PAA} p\text{-}CH_3C_6H_4CH_2\text{—}N{=}\overset{O}{\overset{\uparrow}{N}}\text{—}CH_2C_6H_5 + p\text{-}CH_3C_6H_4CH_2NHNH\text{—}\overset{O}{\overset{\|}{C}}\text{—}C_6H_5$

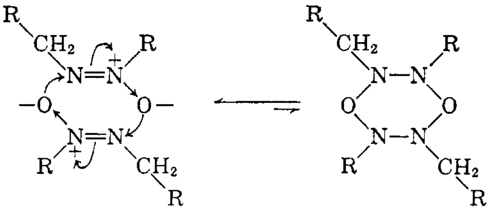
VIII IX

$C_6H_5\text{—}CH{=}N\text{—}NH\text{—}CH_2C_6H_4\text{—}CH_3(p) \xrightarrow{PAA} C_6H_5\text{—}CH_2\text{—}N{=}\overset{O}{\overset{\uparrow}{N}}\text{—}CH_2C_6H_4\text{—}CH_3(p) + C_6H_5\text{—}CH_2NHNH\text{—}\overset{O}{\overset{\|}{C}}\text{—}C_6H_4\text{—}CH_3(p)$

X XI

These results indicate that when the alkyl groups attached to the azoxy function are similar, oxidation occurs exclusively at the carbon atom adjacent to the quatervalent nitrogen upon acid hydrolysis.[11] Extension of our results to the acid hydrolysis of Macrozamin offers conclusive evidence for structure I since formic acid and no methylhydrazine was formed.[3,11]

It is noteworthy that the cis aliphatic azoxy compounds are all high melting in contrast to the known trans aliphatic azoxy compounds.[3] This may be due to their higher dipole moments or to partial dimeric association of the type shown below:



EXPERIMENTAL[12]

The peracetic acid oxidation of the benzaldehyde phenylhydrazones. To 0.10 mole of the phenylhydrazone in ether was slowly added with stirring 25.0 g. of a 40% peracetic acid solution in ether. After the addition was complete, the mixture was allowed to stir for 3 hr. The precipitated azoxy compound was filtered, washed with chloroform and ether, and dried. Recrystallization of the azoxy compounds required very large amounts of any solvent. The compounds are listed in Table I. The *cis*-α-(phenyl-*NON*-axoxy)-toluene[7] melted at 187° dec.[13]

Anal. Calcd. for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.39; H, 5.42; N, 13.72.

The *cis*-α-(phenyl-*NON*-azoxy)*p*-methoxytoluene[7] melted 161–162°.[14]

Anal. Calcd. for $C_{14}H_{14}N_2O$: C, 69.40; H, 5.82; N, 11.57. Found: C, 69.11; H, 5.55; N, 11.56.

The *cis*-α-(phenyl-*NON*-azoxy)-*p*-nitrotoluene[7] melted 171–172°.[15]

Anal. Calcd. for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.28; N, 16.35. Found: C, 60.37; H, 4.52; N, 16.51.

The *cis*-α-(phenyl-*NON*-azoxy)p-phenyltoluene[7] melted 188°.

Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 78.37; H, 5.85; N, 10.10. Found: C, 78.52; H, 5.53; N, 10.28.

The peracetic acid oxidation of the benzaldehyde methylhydrazones at low temperature. The benzaldehyde methylhydrazones were prepared according to the method of Wiley and Irick[16]: benzaldehyde methylhydrazone, b.p. 81–86° (0.8 mm.)[16]; *p*-tolualdehyde methylhydrazone (63%), b.p. 110° (5 mm.); *p*-bromobenzaldehyde methylhydrazone, (95%), b.p. 156–160° (5 mm.), m.p. 42–43°; and *p*-nitrobenzaldehyde methylhydrazone, (95%), m.p. 100–101°. The methylhydrazones were used the same day due to their instability.[15]

---

[11] Exactly how similar the alkyl groups attached to the azoxy function must be, to rely on the use of acid hydrolysis in structure determination has not been completely established. Toward increasing difference in the groups the hydrolysis mechanism becomes governed by stabilization as cited above.

[12] Melting and boiling points are uncorrected. Spectra of samples were determined on a Beckman DU ultraviolet spectrophotometer and a Perkin-Elmer model 137 double beam infrared spectrophotometer. Microanalyses were performed by A. Bernhardt, Mulheim, Germany; H. W. Galbraith, Knoxville, Tennessee; and Drs. Weiler and Strauss, Oxford, England.

[13] The melting point was found to depend on the rate of heating and on the temperature at insertion in the melting point bath. Insertion at 170° resulted in a very sharp dec. at 187°. Inserted lower, it darkens slightly but dec. at a higher temperature. Ref. 6b reports m.p. 201° (dec.) from monoperphthalic acid oxidation and ref. 6c reports m.p. 203–206° dec. from perbenzoic acid oxidation.

[14] Ref. 6b reported m.p. 176° from a monoperphthalic acid oxidation, and the authors in ref. 6c reported m.p. 176° from a perbenzoic acid oxidation.

[15] Ref. 6b reported m.p. 135° from monoperphthalic acid oxidation.

[16] R. H. Wiley and G. Irick, *J. Org. Chem.*, 24, 1925 (1959).

To 0.1 mole of methylhydrazone in ether was slowly added 20 g. of 40% peracetic acid in ether at 0°. After the addition was complete, the solution was allowed to stir for 3 hr. and warm to room temperature. The solution was washed twice with water, and then with a sodium bicarbonate solution sufficiently to remove all acid present. The ether solution was then dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The solid azoxy compounds were then recrystallized from ether and dried. The compounds are listed in Table II.

The *cis*-*α*-(methyl-*NON*-azoxy)toluene[7] (VII) melted at 153°.

Anal. Calcd. for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.08; H, 6.69; N, 18.79.

The *cis*-*α*-(methyl-*NON*-azoxy)-*p*-xylene[7] (XII) melted at 115-116°.

Anal. Calcd. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.73; H, 7.34; N, 17.11.

The *cis*-*α*-(methyl-*NON*-azoxy)-*p*-bromotoluene[7] (XIII) melted at 185°.

Anal. Calcd. for $C_8H_9BrN_2O$: C, 41.94; H, 3.96; N, 12.23. Found: C, 42.01; H, 3.72; N, 12.12.

The *cis*-*α*-(methyl-*NON*-azoxy)-*p*-nitrotoluene[7] (XIV) melted at 205°.

Anal. Calcd. for $C_8H_9N_3O_3$: C, 49.23; H, 4.65; N, 21.53. Found: C, 49.44; H, 4.84; N, 21.39.

Acid hydrolysis of the methylazoxy compounds. The compounds VII, XII, XIII, and XIV were individually refluxed with excess concentrated hydrochloric acid for a period of 24 hr. Work-up in the usual manner for acids resulted in isolation of the following with their melting points and yields: from VII, benzoic acid, m.p. 120°, (85%); from XII, *p*-toluic acid, m.p. 180°, (75%); from XIII, *p*-bromobenzoic acid, m.p. 254°, (85%); from XIV, *p*-nitrobenzoic acid, m.p. 242°, (78%). Mixed melting points of the obtained acids with authentic samples of the corresponding benzoic acids were undepressed.

The peracetic acid oxidation of the benzaldehyde methylhydrazones at reflux temperature. To 0.1 mole of the benzaldehyde methylhydrazone in ether was added 20 g. of 40% peracetic acid solution in ether at such a rate that a steady reflux was continued. After the addition was complete the solution was stirred 1 hr. and then the acid was removed by rinsing the ether solution twice with water followed by sufficient bicarbonate solution extractions. The ether phase was separated and dried over anhydrous sodium sulfate. After filtration the ether solution was cooled and the precipitated azoxy compound was removed by filtration. Upon concentration the more soluble hydrazide crystallized out of solution. Following this procedure, from benzaldehyde methylhydrazone, 2.0 g. (13.3%) of VII and 5.0 g. (33.3%) of 1-benzoyl-2-methylhydrazine, m.p. 87–88° [17] was obtained. From *p*-tolualdehydemethylhydrazone was obtained 1.5 g. (9.2%) of XII, and 7.2 g. (44%) of 1-*p*-toluoyl-2-methylhydrazine, m.p. 65°.

Anal. Calcd. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.74; H, 7.24; N, 17.00.

From *p*-bromobenzaldehyde methylhydrazone was obtained 4.0 g. (17.4%) of XIII, and 12 g. (52.4%) of 1-*p*-bromobenzoyl-2-methylhydrazine, m.p. 165°.

Anal. Calcd. for $C_8H_9N_2O$: C, 41.94; H, 3.96; N, 12.23. Found: C, 41.86; H, 3.99; N, 12.11.

From *p*-nitrobenzaldehyde methylhydrazone was obtained 3.6 g. (18.5%) of XIV, and 11.0 g. (56.5%) of 1-*p*-nitrobenzoyl-2-methylhydrazine, m.p. 198°.

Anal. Calcd. for $C_8H_9N_3O_3$: C, 49.23; H, 4.65; N, 21.53. Found: C, 49.11; H, 4.78; N, 21.38.

N-Benzoyl-p-tolualdehyde hydrazone. To 24 g. (0.176 mole) of benzoic acid hydrazide in ethanol was added 12 g. (0.1 mole) of *p*-tolualdehyde. The solution was warmed on a steam bath 1 hr., and then cooled. The crystallized product was filtered and dried to furnish 41 g. (91%) of *N*-benzoyl-*p*-tolualdehyde hydrazone, m.p. 156°.

Anal. Calcd. for $C_{15}H_{14}N_2O$: N, 11.76. Found: N, 11.61.

1-Benzoyl-2-(α-p-xylyl)hydrazine (IX). To 22.2 g. (0.1 mole) of *N*-benzoyl-*p*-tolualdehyde hydrazone in 95% ethanol was added 0.05 g. of palladium-on-charcoal catalyst. The mixture was placed in the Parr apparatus and allowed to absorb one molar equivalent of hydrogen, after which the solution was filtered and cooled. The solution yielded 17 g. (76%) of IX, m.p. 123°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.00; H, 6.80; N, 11.48.

p-Tolualdehyde benzylhydrazone. To 25 g. (0.15 mole) of 1-acetyl-2-benzylhydrazine, m.p. 81°,[18] in aqueous ethanol was added 50 g. of potassium hydroxide and the mixture was refluxed 18 hr. under a nitrogen atmosphere. The solution was then cooled and extracted with ether and the ether phase dried over anhydrous sodium sulfate. After filtration the ether was removed on a steam bath leaving 11.2 g. (61%) of crude benzylhydrazine. The crude hydrazine was placed in 50 ml. of 50% ethanol and 12 g. (0.1 mole) of *p*-tolualdehyde was added. A heavy precipitate formed which was filtered and recrystallized to yield 15 g. (67%) of *p*-tolualdehyde benzylhydrazone, m.p. 111–112°. The known instability of benzylhydrazones required the preparation of a stable derivative.

To a solution of 3.5 g. (0.025 mole) of benzoyl chloride in pyridine was added 4.4 g. of the *p*-tolualdehyde benzylhydrazone and the mixture was stirred 30 min. This mixture was then poured into water and extracted with ether. The ether phase was rinsed with dilute hydrochloric acid and with aqueous sodium bicarbonate solution. The ether phase was separated, dried over anhydrous sodium sulfate, filtered, and vacuum concentrated. The residue on recrystallization from aqueous ethanol yielded after drying, 5.1 g. (77%) of *N*-benzoyl-*p*-tolualdehyde benzylhydrazone, m.p. 131°.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 79.92; H, 6.71; N, 8.48. Found: C, 80.21; H, 6.72; N, 8.25.

The peracetic acid oxidation of p-tolualdehyde benzylhydrazone. To 11.2 g. (0.05 mole) of *p*-tolualdehyde benzylhydrazone in ether was slowly added 10 g. of 40% peracetic acid at ice bath temperature with stirring. After the addition was complete the solution was stirred for 3 hr. and allowed to warm to room temperature. The solution was rinsed twice with water followed by successive bicarbonate rinses to remove all acid. The ether solution was then separated and dried over anhydrous sodium sulfate. After filtration the ether was partially evaporated and 3.0 g. (25%) of *α*-(benzyl-*NON*-azoxy)-*p*-xylene (VIII), m.p. 204° was obtained.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.24; H, 6.77; N, 11.67.

On cooling the mother liquor from the above 5.0 g. (41.6%) of a white crystalline 1-benzoyl-2-(*α*-*p*-xylyl)hydrazine (IX), m.p. 123°, precipitated. A mixed melting point of this material with an authentic sample of IX showed no depression.

1-p-Toluyl-2-benzylidenehydrazine. To 15 g. (0.1 mole) of *p*-toluylhydrazine in ethanol was added 10 g. (0.1 mole) of benzaldehyde. The solution was warmed on a steam bath for 1 hr., cooled, and 18.0 g. (82%) of 1-*p*-toluyl-2-benzylidenehydrazine, m.p. 233° was obtained.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.72; H, 6.09; N, 11.77.

1-p-Toluyl-2-benzylhydrazine. To 22.2 g. (0.1 mole) of 1-*p*-toluyl-2-benzylidenehydrazine in ethanol was added 0.05 g. of palladium-on-charcoal catalyst and the mixture was allowed to absorb 0.1 mole of hydrogen on a Paar apparatus. Filtration of the catalyst and cooling the solution resulted

---

(17) R. Hinman and D. Fulton, *J. Am. Chem. Soc.*, 80, 1895 (1958) reported m.p. 86–88°.

(18) Prepared essentially by the method of A. N. Kurtz and C. Niemann, *J. Org. Chem.*, 26, 1843 (1961) who reported m.p. 81–82°.

in the crystallization of 16 g. (71.5%) of 1-*p*-toluyl-2-benzylhydrazine (XI), m.p. 127°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.04; H, 6.66; N, 11.92.

N-Acetyl-p-tolualdehyde hydrazone. To 14.8 g. (0.2 mole) of acetic acid hydrazide in ethanol was added 24 g. of *p*-tolualdehyde and the mixture was warmed on a steam bath for 1 hr. On cooling 16 g. of *N*-acetyl-*p*-tolualdehyde hydrazone, m.p. 132°, crystallized.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.21; H, 7.06; N, 16.09.

1-Acetyl-2-(α-p-xylyl)hydrazine. To 17.6 g. (0.10 mole) of *N*-acetyl-*p*-tolualdehyde hydrazone in ethanol was added 0.05 g. of 10% palladium-on-charcoal catalyst. The mixture was allowed to take up one molar equivalent of hydrogen on a Paar apparatus. After removal of the catalyst by filtration the solution was cooled and 12.8 g. (72%) of 1-acetyl-2-(α-*p*-xylyl)hydrazine, m.p. 120° was obtained.

Anal. Calcd. for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.52; H, 8.03; N, 15.90.

Benzaldehyde α-p-xylylhydrazone. To 26.7 g. (0.15 mole) of 1-acetyl-2-(α-*p*-xylyl)hydrazine in aqueous ethanol was added 50 g. of potassium hydroxide and the mixture refluxed for 18 hr. The mixture was then cooled and extracted with ether and the ether phase separated and dried over anhydrous sodium sulfate. After filtration the ether was removed on a steam bath to leave 11 g. (54%) of crude hydrazine. This was placed in 50 ml. of 50% ethanol and 11 g. (0.092 mole) of benzaldehyde was added. A total of 12 g. of crystalline benzaldehyde α-*p*-xylylhydrazone was obtained. A recrystallization of this material from ethanol resulted in a solid, m.p. 85–86°. The benzoyl derivative was prepared because of the known instability of benzyl hydrazones.

To a solution of 3.5 g. (0.025 mole) of benzoyl chloride in pyridine was added 4.4 g. (0.02 mole) of benzaldehyde α-*p*-xylylhydrazone and the resulting mixture was stirred for 30 min. The mixture was poured into water and extracted with ether. The ether phase was washed with dilute hydrochloric acid and several aqueous bicarbonate rinses. The ether solution was dried over anhydrous sodium sulfate. After filtration the solution was vacuum concentrated and the residue recrystallized from ethanol to yield 5.4 g. (81%) of *N*-benzoylbenzaldehyde α-*p*-xylylhydrazone, m.p. 92–93°.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 79.92; H, 6.71; N, 8.48. Found: C, 79.94; H, 6.57; N, 8.25.

The peracetic acid oxidation of benzaldehyde α-p-xylylhydrazone. To 11.2 g. (0.05 mole) of benzaldehyde α-*p*-xylylhydrazone in ether was slowly added with stirring at 0°, 10 g. of a 40% peracetic acid solution in ether. After the addition was complete the solution was stirred for 3 hr. and then allowed to warm to room temperature. The solution was washed twice with water and sufficient times with sodium bicarbonate to remove all acid. The ether solution was dried over sodium sulfate, filtered, and then concentrated to half volume. A total of 2.8 g. (23%) of α-(benzyl-*NNO*-azoxy)-*p*-xylene (X), m.p. 210–211° was isolated.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.86; H, 6.60; N, 11.69.

The mother liquor from above was cooled and yielded 6.0 g. (50%) of 1-*p*-toluyl-2-benzylhydrazine (XI), m.p. 127°. A mixed melting point of this material with an authentic sample of XI showed no depression.

Acknowledgment. The authors wish to acknowledge funds toward the purchase of a Perkin-Elmer Infracord I. R. spectrophotometer used in this work from the National Science Foundation. They also thank Becco Chemical Division, Buffalo, N. Y., for generous supplies of 40% peracetic acid.

PITTSBURGH 19, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

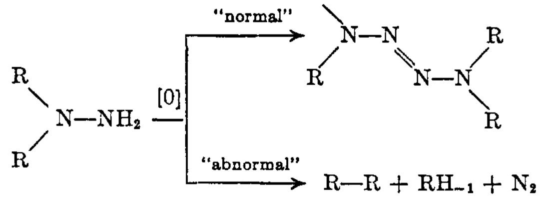
Azo Compounds. XXXVIII. The Mercuric Oxide Oxidation of 1-Amino-2-phenylpiperidine[1]

C. G. OVERBERGER AND LOUIS P. HERIN[2]

Received June 29, 1961

1-Amino-2-phenylpiperidine was synthesized and treated with yellow mercuric oxide to give, depending on the experimental procedure, partial evolution of nitrogen and varying yields of phenylcyclopentane, 1-phenylpentene-1,5-phenylpentene-1, and a tetrazene. These experimental data provide further evidence for the previously proposed mechanism of the reaction.

The so-called "abnormal" oxidation reaction of certain 1,1-disubstituted hydrazines proceeds to give evolution of nitrogen with the formation of coupled, and in some cases also olefinic, hydrocarbon products rather than the "normal" oxidation product, tetrazene.



In earlier papers[4] we have reported the preparation and oxidation of a number of such hydrazines: 1-amino-2,6-dicyano-2,6-dimethylpiperidine; *cis*- and *trans*-1-amino-2,6-diphenylpiperidine; 1-amino-2,6-dicyano-2,4,6-trimethylpiperidine; and *D,D*-*N*-amino-α,α′-dimethyldibenzylamine. Hinman and

---

[1] This is the thirty-seventh in a series of papers dealing with the preparation and reactions of azo and related compounds. For the previous paper in this series, see C. G. Overberger and J. R. Hall, *J. Org. Chem.*, 26, 4359 (1961).

[2] This paper comprises a portion of the Dissertation submitted by Louis P. Herin in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.