before to afford a crude solid product, m.p. 134.5–138°. The solid was crystallized from hexane, m.p. 136–138°, yield 44 mg. (72.6%). The analytical sample was obtained as colorless dense crystals after two more crystallizations from hexane, m.p. 136–137.5°; $[\alpha]_D$ +89° (1% dioxane); $\Delta[M]_D^{OAc-OH}$ +69°.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9 15. Found: C, 76.22; H, 8.99.

CHICAGO 80, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Hydrogen Transfers from 1-Substituted Dihydropyridines. I. Reduction of Nitro Groups[1-3]

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1-Benzyl-1,4-dihydronicotinamide reduces nitrobenzene at 139° in the absence of added solvent. The intermediate, nitrosobenzene, is trapped, presumably as a nitrone which is identified by its hydrolysis to benzaldehyde. The reaction products, after hydrolysis of the reaction mixture, are aniline, nicotinamide, benzaldehyde, phenylhydroxylamine, and hydrazobenzene. Hydroquinone had no effect on the yields of products. A *p*-nitro group facilitates the reduction; a *p*-dimethylamino group hinders it. *o*-Nitrophenol and *o*-nitroanisole are reduced in comparable yields. 2,6-Dimethylnitrobenzene was reduced with difficulty. Other compounds reduced were nitrosobenzene, *p*-nitroso-*N*,*N*-dimethylaniline, phenylhydroxylamine, azoxybenzene, and azobenzene. Aliphatic nitro compounds were not reduced.

Dihydropyridines play an important role in biological reductions, and the study of model reactions which may simulate an enzymic reaction may lead to an understanding of the catalytic action of enzymes. Dihydropyridine derivatives have been reported to reduce a variety of substances nonenzymically: thio ketones,[5] keto acids,[6] quinones,[7] dyes,[7c,8] benzil,[9] derivatives of maleic and fumaric acids,[9] and bromotrichloromethane.[10]

Enzymic reductions of nitro groups may directly or indirectly involve dihydrodiphosphopyridine nucleotide (dihydronicotinamide-adenine-dinucleotide).[11]

Nitrobenzene has been used frequently as an oxidizing agent for organic compounds.[12] Several reductions of nitro groups by dihydropyridines have been reported. There is a photochemically induced intramolecular reduction of 4-(2′-nitrophenyl)-1,4-dihydropyridine.[13] *trans*-4-Nitrostilbene is reduced to 4-aminostilbene (16% yield) and nitrobenzene is reduced to aniline (yield greater than 8%) by the Hantzsch dihydropyridine (1,4-dihydro - 2,6 - dimethyl - 3,5 - dicarbethoxypyridine).[9] There have been no published reports of the nonenzymic reduction of nitro groups by a dihydronicotinamide.[14]

Reduction of nitrobenzene. When nitrobenzene and 1-benzyl-1,4-dihydronicotinamide were heated at 139° under nitrogen the following products were identified after hydrolysis of the reaction mixture by dilute aqueous acid: nicotinamide (30%), aniline (60–68%), benzaldehyde (11%), phenylhydroxylamine and hydrazobenzene. Aniline was shown to be present before hydrolysis, whereas benzaldehyde was not. Small amounts of carbon dioxide and ammonia were produced also.

The carbon dioxide and ammonia are formed presumably by opening of the pyridinium ring,[15] hydrolysis of the amide group and decarboxylation

(1) We wish to acknowledge the support of the National Science Foundation (Grant 7582) for part of this work.

(2) For complete experimental details see John M. Kolyer, Ph.D. Thesis, University of Pennsylvania, 1960.

(3) Reported in part at 136th Meeting, American Chemical Society, Atlantic City, N. J., September 1959.

(4) Walter T. Taggart Memorial Fellow, 1959–60.

(5) R. H. Abeles, R. F. Hutton, and F. H. Westheimer, *J. Am. Chem. Soc.*, **79**, 712 (1957).

(6) R. Abeles and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5459 (1958); K. Wallenfels and D. Hofmann, *Tetrahedron Letters*, No. 15, 10 (1959).

(7)(a) H. Kühnis, W. Traber, and P. Karrer, *Helv. Chim. Acta*, **40**, 757 (1957); (b) E. A. Braude, J. Hannah, and R. Linstead, *J. Chem. Soc.*, 3249 (1960); (c) K. Wallenfels and M. Gellrich, *Ann.*, **621**, 149 (1959).

(8) D. Mauzerall and F. H. Westheimer, *J. Am. Chem. Soc.*, **77**, 226 (1955); P. Karrer, G. Schwarzenbach, F. Benz, and U. Solmssen, *Helv. Chim. Acta*, **19**, 824 (1936); S. J. Leach, J. H. Baxendale, and M. G. Evans, *Australian J. Chem.*, **6**, 395 (1953).

(9) E. A. Braude, J. Hannah, and R. Linstead, *J. Chem. Soc.*, 3257 (1960).

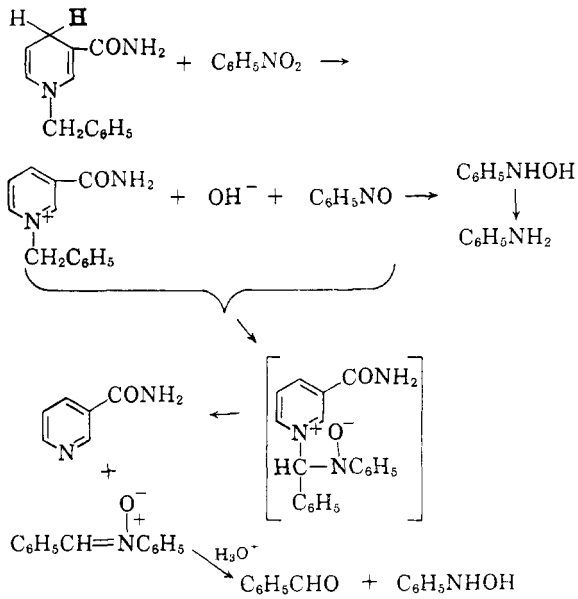
(10) J. L. Kurz, R. Hutton, and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 584 (1961).

(11) W. A. Müller, *Z. physiol. Chem.*, **311**, 155 (1958); A. Saz and R. B. Slie, *J. Biol. Chem.*, **210**, 407 (1954).

(12) There are many examples in the literature of which may be mentioned the oxidation of dihydroquinolines (Skraup reaction) [R. H. F. Manske and M. Kulka, *Org. Reactions*, **7**, 59 (1953); H. Gilman, J. Eisch, and T. S. Soddy, *J. Am. Chem. Soc.*, **81**, 4000 (1959)], the acid-catalyzed dehydrogenation of 9,10-dihydroanthracene and the dihydro adducts formed in the Scholl reaction [C. D. Nenitzescu and A. Balaban, *Chem. Ber.*, **91**, 2109 (1958); R. Scholl and C. Seer, *Ber.*, **55**, 330 (1922)], the oxidation of benzyl alcohol in alkaline solution [L. T. Smith and R. E. Lyons, *J. Am. Chem. Soc.*, **48**, 3165 (1926)] and the oxidation of eugenol to vanillin [E. Mayer, *Österr. Chemiker-Ztg.*, **50**, 40 (1949); *Chem. Abstr.*, **44**, 1451 (1950)].

(13) J. A. Berson and E. Brown, *J. Am. Chem. Soc.*, **77**, 447 (1955).

(14) Professor F. H. Westheimer has informed us that his co-workers have observed an apparent reduction of the nitro group in *p*-nitrothiobenzophenone by 1-benzyl-1,4-dihydronicotinamide.



of the β-aldehydic acid so formed. Nitrosobenzene and phenylhydroxylamine are intermediates in the reduction of nitrobenzene by other methods.[16] The formation of nitrones by condensation of an aromatic nitroso compound with 1-substituted pyridinium salts is well known and the subject has been reviewed.[17]

Condensation of nitrosobenzene and aniline gives azobenzene[18] which is reduced by 1-benzyl-1,4-dihydronicotinamide to hydrazobenzene. Azoxybenzene, which may be produced by disproportionation of phenylhydroxylamine[19] or by condensation of nitrosobenzene and phenylhydroxylamine,[20] may also be the precursor of hydrazobenzene.

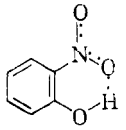
Hydroquinone had no effect on the yields of products. Irradiation by ultraviolet light of nitrobenzene and 1-benzyl-1,4-dihydronicotinamide in benzene in a quartz flask, either with or without the addition of benzoyl peroxide, produced only traces of aniline, although there was considerable decomposition of the dihydro compound.

Nitrobenzene also was reduced by 1-benzyl-3-acetyl-1,4-dihydropyridine and by 1-(2,6-dichlorobenzyl)-1,4-dihydronicotinamide. The latter gave only 1% of 2,6-dichlorobenzaldehyde upon hydrolysis of the reaction mixture. The *ortho* chlorine atoms probably hinder sterically the formation of the nitrone.

It was not possible to reduce nitrobenzene by refluxing it with 1-benzyl-1,4-dihydronicotinamide in acetic acid, in ethanol, or in ethanolic hydrochloric acid. However, addition of sodium cyanide or sodium ethoxide to the reactants in ethanol afforded small amounts of reduction. Sodium cyanide or sodium ethoxide alone did not reduce nitrobenzene under the same reaction conditions.

Reduction of substituted nitrobenzenes. The order of the ease of reduction of *p*-substituted nitrobenzenes is $NO_2>H>N(CH_3)_2$, $-NH_2$. The reduction of *p*-dinitrobenzene occurs readily in refluxing ethanol whereas nitrobenzene does not. The same order of reactivity has been observed in the polarographic reduction and catalytic hydrogenation of nitrobenzene,[21] although in the latter case *p*-dinitrobenzene was hydrogenated a little slower than nitrobenzene. This order of reactivity reflects the relative instabilities of the initial states. It may be noted that *p*-dinitrobenzene is inert to reduction by cyclohexene and palladium.[22]

The reduction of *o*-nitrophenol under nitrogen at 139° yields about 30% *o*-aminophenol; under the same conditions, *p*-nitrophenol gave less than 3% *p*-aminophenol. Hydrogen-bonding between the hydroxyl group and the nitro group may catalyze the reduction by making the nitrogen more positive and more likely to accept a hydride ion. An *ortho* hydroxyl group facilitates the reduction of



thiobenzophenone by 1-benzyl-1,4-dihydronicotinamide.[5] On the other hand, *o*-nitroanisole is reduced in nearly as good a yield as *o*-nitrophenol. The *ortho* methoxy group may destabilize the initial state by steric inhibition of resonance. The absorption of *o*-nitroanisidine in the ultraviolet is at lower wave lengths and generally lower intensities than *p*-nitroanisidine, *m*-nitroanisidine, or *o*-nitrophenol.[23]

No reduction of 2,6-dimethylnitrobenzene was observed at 139°, but reduction did proceed at 210°. Very little benzaldehyde was formed. These results imply that the hydrogen transfer (as well as nitrone formation) is sterically hindered.

When 1-benzyl-1,4-dihydronicotinamide is heated under nitrogen at 210° for one hour, a 28% yield of nicotinamide is obtained. This may be the result of a homolytic cleavage of the C—N bond to yield a benzyl radical. The dihydro compound does not decompose at 139°.

Reduction of nitroso groups and related functional groups. Aromatic nitroso compounds are more

(15) See, for example, the formation of glutaconic aldehyde from 1-(2,4-dinitrophenyl)pyridinium chloride and hydroxide ion [T. Zincke, G. Heuser, and W. Möller, *Ann.*, **333**, 296 (1904)].

(16) F. Haber, *Z. physik. Chem.*, **32**, 202 (1900); A. Sugimori, *Bull. Chem. Soc. Japan*, **33**, 1599 (1960).

(17) F. Kröhnke, *Argew. Chem.*, **65**, 605 (1953).

(18) A. Baeyer, *Ber.*, **7**, 1638 (1874); C. Mills, *J. Chem. Soc.*, **67**, 928 (1895).

(19) E. Bamberger and F. Brady, *Ber.*, **33**, 271 (1900).

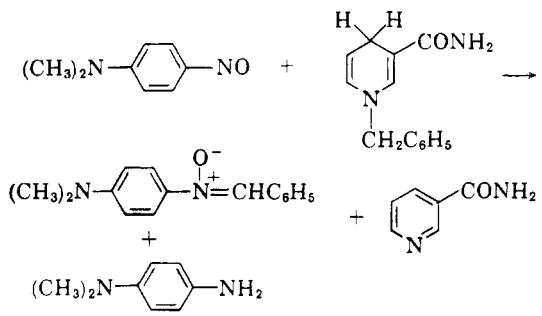
(20) E. Bamberger and E. Renauld, *Ber.*, **30**, 2278 (1897).

(21) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961); W. P. Dunworth and F. F. Nord, *J. Am. Chem. Soc.*, **72**, 4197 (1950).

(22) E. A. Braude, R. P. Linstead, and K. R. H. Wooldridge, *J. Chem. Soc.*, 3586 (1954).

(23) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952).

easily reduced by 1-benzyl-1,4-dihydronicotinamide than are the corresponding nitro compounds. Nitrosobenzene and *p*-nitroso-*N*,*N*-dimethylaniline are reduced in refluxing ethanol, conditions under which the nitro compounds are not reduced. The nitrone (89%) could be isolated in the reduction of *p*-nitroso-*N*,*N*-dimethylaniline in refluxing ethanol.



Nitrosobenzene gave some phenylhydroxylamine and hydrazobenzene along with aniline. The isolation of the nitrone may tend to support the assumption of the nitrone intermediate in the reduction of nitrobenzene.

Reduction of phenylhydroxylamine at 139° gave aniline and a small amount of benzaldehyde. This reduction could proceed *via* the disproportionation of phenylhydroxylamine to aniline and nitrosobenzene.[19] The reduction of azoxybenzene at 139° yields aniline (18%), hydrazobenzene, and a small amount of benzaldehyde; azobenzene yields hydrazobenzene and a small amount of benzaldehyde. Azoxybenzene and azobenzene were, by themselves, stable under the reaction conditions.

Copper(II) sulfate is reduced by the dihydro compound to copper(I) oxide.

Attempted reductions. Treatment of nitrocyclohexane with 1-benzyl-1,4-dihydronicotinamide at 210° gave carbon dioxide and nicotinamide, but these compounds are produced from the dihydro compound alone at this temperature. There was no evidence for the formation of cyclohexylamine. Similar results were obtained with 1-benzyl-3-acetyl-1,4-dihydronicotinamide. No reduction by 1 - benzyl - 1,4 - dihydronicotinamide was observed with any of the following: nitromethane (reflux, 1.5 hr.), *t*-nitrobutane (190°, 7 hr.), 1-nitropropane (100°, 48 hr.), dimethyl sulfoxide (refluxing ethanol, 2 hr.), benzal *p*-*N*,*N*-dimethylaminoaniline (139°, 2 hr.), cyclohexanone oxime (139°, 1 hr.), acetaldehyde phenylhydrazone (139°, 1.5 hr.), benzaldehyde phenylhydrazone (139°, 1 hr.), lithium nitrate (refluxing bis-2-methoxyethyl ether, 3 hr.), and sodium nitrite (melt).

EXPERIMENTAL

1-Benzyl-1,4-dihydronicotinamide was prepared according to Mauzerall and Westheimer.[8] 1-(2,6-Dichlorobenzyl)-1,4-dihydronicotinamide was prepared by the method of Wallenfels and Schüly.[24]

Reduction of nitrobenzene. Nitrobenzene (0.480 ml., 0.00468 mole) and 1-benzyl-1,4-dihydronicotinamide (1.00 g., 0.00468 mole) were heated at 139° (over refluxing xylene). Vigorous effervescence was noted. Nitrogen was passed over the reaction during the heating and into ether saturated with hydrogen chloride. Ammonium chloride (1%) precipitated. In other runs, the nitrogen was passed through concentrated barium hydroxide solution, and carbon dioxide (*ca.* 3%) was identified as barium carbonate. A solution of the reaction mixture in 1*N* hydrochloric acid was heated in steam for 30 min. (to convert phenylhydroxylamine to *p*-aminophenol and hydrazobenzene to benzidine). The solution was chromatographed on Whatman No. 1 paper, (*n*-butyl alcohol–water) and *p*-aminophenol and benzidine were identified by spraying with 0.2% sodium nitrite in 0.1*N* hydrochloric acid followed by 0.5% 2-naphthol in 5% sodium hydroxide solution. In another run, the reaction mixture was taken up in 10 ml. of ethanol and distilled with 5 ml. of phosphoric acid and 5 ml. of water. Addition of 2,4-dinitrophenylhydrazine reagent[25] to the distillate gave benzaldehyde 2,4-dinitrophenylhydrazone (11%), identified by mixed melting point with an authentic sample, m.p. 240°. In another run, nitrobenzene (4.80 ml., 0.0468 mole) and 1-benzyl-1,4-dihydronicotinamide (10.0 g., 0.0468 mole) were heated under nitrogen at 139° for 1 hr. The reaction mixture was extracted with 200 ml. of water in a Soxhlet apparatus for 7 hr. Evaporation of the water left nicotinamide, identified as the picrate (4.84 g., 30%) by mixed melting point with an authentic sample, m.p. 197°.

In other runs, the reaction mixture was examined by gas chromatography. Aniline (60–68%) was identified. Aniline was also identified as diphenylthiourea by mixed melting point with an authentic sample, m.p. 156°. The infrared spectrum of the derivative was identical to that of a known sample. In another run, hydroquinone (0.124 g., 0.00113 mole) was added to the reactants (0.00468 mole). The yield of aniline was not altered.

A $1.6 \times 10^{-3}M$ solution of 1-benzyl-1,4-dihydronicotinamide in nitrobenzene was clear orange and displayed a broad absorption (λ_{max} 428 mμ, ϵ 3.5×10^2) from about 425 to 460 mμ. When 50% (by volume) of the nitrobenzene was replaced by benzene, chloroform, or methanol, the absorption maximum was unchanged.

Effect of ultraviolet light on the reduction of nitrobenzene. A solution of nitrobenzene (0.480 ml., 0.00468 mole), 1-benzyl-1,4-dihydronicotinamide (1.00 g., 0.00468 mole), and benzoyl peroxide (0.014 g.) in 20 ml. of benzene was stirred magnetically in a stoppered quartz flask and irradiated by an ultraviolet lamp for 20 hr. Considerable tar separated. Paper chromatography indicated a faint trace of aniline. The reaction mixture was extracted with dilute hydrochloric acid. The extract was made basic and extracted with ether. Evaporation of the ether left no appreciable aniline.

Reduction of nitrobenzene by 1-benzyl-3-acetyl-1,4-dihydropyridine. 1-Benzyl-3-acetyl-1,4-dihydropyridine, m.p. 68° (lit.[26] m.p. 61–67°), was prepared by the method of Anderson and Berkelhammer.[26] Nitrobenzene (0.485 ml., 0.00473 mole) and 1-benzyl-3-acetyl-1,4-dihydropyridine (1.00 g., 0.00472 mole) were heated at 139° under nitrogen for 1 hr. Phenylhydroxylamine and hydrazobenzene were identified by paper chromatography. The reaction mixture was extracted with 30 ml. of 1:5 sulfuric acid. The extract was washed with two 15-ml. portions of ether, made basic with 10% sodium hydroxide solution, and extracted with two 20-ml. portions of ether. Evaporation of the ether left aniline, identified as the phenylthiourea (0.218 g., 61%) by mixed

(24) K. Wallenfels, H. Schüly, and D. Hofmann, *Ann.*, **621**, 128 (1959).

(25) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, 4th ed., p. 219.

(26) A. G. Anderson and G. Berkelhammer, *J. Am. Chem. Soc.*, **80**, 992 (1958).

melting point with an authentic sample. In another run, extraction of the reaction mixture with water gave 3-acetylpyridine, identified as the picrate by mixed melting point with an authentic sample, m.p. 134.5°.

Reduction of nitrobenzene by 1-(2,6-dichlorobenzyl)1,4-dihydronicotinamide. Nitrobenzene (0.13 ml., 0.0013 mole) and 1-(2,6-dichlorobenzyl)-1,4-dihydronicotinamide (0.367 g., 0.00130 mole) were heated under nitrogen at 165–175° for 30 min. The reaction mixture was taken up in 5 ml. of ethanol, 4 ml. of 1:1 sulfuric acid was added, and the mixture allowed to stand for 10 min. Water (5 ml.) was added, and the mixture was extracted with four 5-ml. portions of ether. Evaporation of the ether left 2,6-dichlorobenzaldehyde, identified as the 2,4-dinitrophenylhydrazone by mixed melting point with an authentic sample, m.p. 251°. The yield of 2,6-dichlorobenzaldehyde was only 1%.

Effect of sodium cyanide and sodium ethoxide. A solution of 1-benzyl-1,4-dihydronicotinamide (0.255 g., 0.0012 mole), nitrobenzene (0.120 ml.), and sodium cyanide (0.019 g.) in 5 ml. of absolute alcohol was refluxed for 5 hr. Paper chromatography indicated the presence of hydrazobenzene and a trace of aniline. The reaction mixture was distilled with 2.5 ml. of phosphoric acid and 2.5 ml. of water. Addition of 2,4-dinitrophenylhydrazine reagent to the distillate gave 2.3% benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 238°, identified by a mixed melting point (239°) with an authentic sample. In a blank run, a solution of nitrobenzene (0.12 ml.) and sodium cyanide (0.021 g.) in 5 ml. of absolute ethanol was refluxed for 5 hr. No reduction products could be identified by paper chromatography.

A solution of 1-benzyl-1,4-dihydronicotinamide (0.512 g.), nitrobenzene (.24 ml.) and 4.4×10^{-4} *M* sodium ethoxide in 10 ml. of absolute ethanol was refluxed for 5 hr. Paper chromatography indicated the presence of hydrazobenzene and a trace of aniline. On distillation of the reaction mixture from dilute phosphoric acid, 4% benzaldehyde was obtained which was determined as its 2,4-dinitrophenylhydrazone, m.p. 239°. In a blank run, a solution of 0.24 ml. of nitrobenzene in 10 ml. of the sodium ethoxide solution was refluxed for 5 hr. No reduction products could be identified by paper chromatography.

Reduction of p-dinitrobenzene. *p*-Dinitrobenzene (0.396 g., 0.00235 mole) and 1-benzyl-1,4-dihydronicotinamide (0.504 g., 0.00235 mole) were heated under nitrogen at 139° for 30 min. Carbon dioxide (2%) was identified as barium carbonate. Paper chromatography indicated *p*-nitroaniline and a trace of *p*-phenylenediamine. In another run with twice the above quantities, the reaction mixture was extracted with dilute hydrochloric acid. The extract was made basic and extracted with ether. Evaporation of the ether left *p*-nitroaniline (1%), identified by mixed melting point with an authentic sample, m.p. 150°. The infrared spectra of the two samples were identical.

A solution of *p*-dinitrobenzene (0.395 g., 0.00235 mole) and 1-benzyl-1,4-dihydronicotinamide (0.504 g., 0.00236 mole) in 10 ml. of ethanol was refluxed for 1.25 hr. Paper chromatography indicated *p*-nitroaniline and a faint trace of *p*-phenylenediamine. The solution was distilled with 5 ml. of phosphoric acid and 5 ml. of water. Addition of 2,4-dinitrophenylhydrazine reagent to the distillate gave benzaldehyde 2,4-dinitrophenylhydrazone (0.320 g., 48%), identified by mixed melting point with an authentic sample. In another run, the ethanol was evaporated from the reaction solution, and the residue was stirred with 30 ml. of hot water for 3 hr. The extract was washed with 15 ml. of ether and treated with charcoal. Evaporation of the water left nicotinamide, identified as the picrate (0.839 g., 51%) by mixed melting point with an authentic sample.

Reduction of p-nitrodimethylaniline and p-nitroaniline. *p*-Nitro-*N,N*-dimethylaniline (0.393 g., 0.00237 mole) and 1-benzyl-1,4-dihydronicotinamide (0.522 g., 0.00244 mole) were heated under nitrogen at 139° for 30 min. Paper chromatography showed no *p*-*N,N*-dimethylaminoaniline. The reaction mixture was then heated under nitrogen at 210° for 15 min. No appreciable carbon dioxide was evolved; paper chromatography indicated a trace of *p*-*N,N*-dimethylaminoaniline. The mixture was then heated with a flame for 5 min. and was extracted with 6 ml. of 1:5 sulfuric acid. The extract was made basic and extracted with two 20-ml. portions of ether. Evaporation of the ether left a slight residue; the addition of phenyl isothiocyanate gave no solid derivative. Apparently, the yield of *p*-*N,N*-dimethylaminoaniline was extremely low.

p-Nitroaniline (0.323 g.) and 1-benzyl-1,4-dihydronicotinamide were heated at 139° under nitrogen for 1 hr. Paper chromatography indicated a trace of *p*-phenylenediamine.

Reduction of o- and p-nitrophenol and o-nitroanisole. *o*-Nitrophenol (0.164 g.) and 1-benzyl-1,4-dihydronicotinamide were heated under nitrogen at 139° for 1 hr. Then the reaction mixture was triturated with dilute hydrochloric acid, filtered and a 0.01-ml. aliquot chromatographed on Whatman No. 1 paper along with standard solutions of 2-aminophenol (R_f 0.42). The chromatograms were developed as described under the section on the reduction of nitrobenzene. The yield of 2-aminophenol was estimated to be *ca.* 30%. In another run, the same quantities of reactants were refluxed in absolute alcohol for 28 hr. Paper chromatography showed a trace of *o*-aminophenol.

The reduction of *p*-nitrophenol was carried out under the same conditions as for *o*-nitrophenol and an aliquot of the reaction mixture chromatographed on paper with standard amounts of *p*-aminophenol (R_f 0.29). The yield of *p*-aminophenol was estimated to be less than 3%.

o-Nitroanisole (0.143 ml.) and 1-benzyl-1,4-dihydronicotinamide (0.251 g.) were heated under nitrogen at 139° for 1 hr. The reaction mixture was diluted with hydrochloric acid, filtered and chromatographed on paper as above with standard amounts of *o*-anisidine (R_f 0.47). The yield was estimated at between 20–30%.

Reduction of 2,6-dimethylnitrobenzene. 2,6-Dimethylnitrobenzene (0.318 ml., 0.00234 mole) and 1-benzyl-1,4-dihydronicotinamide (0.503 g., 0.00235 mole) were heated under nitrogen at 139° for 1 hr. Paper chromatography showed no 2,6-dimethylaniline. When the temperature was raised to 200° for 15 min., 2,6-dimethylaniline was identified. In another run, 2,6-dimethylnitrobenzene (0.636 ml., 0.00468 mole) and 1-benzyl-1,4-dihydronicotinamide (1.02 g., 0.00476 mole) were heated under nitrogen at 210° (over refluxing nitrobenzene) for 1 hr. Carbon dioxide (1.4%) was identified as barium carbonate. 2,6-Dimethylaniline (36–51%) was identified by gas chromatography and as its phenylthiourea by mixed melting point with an authentic sample, m.p. 193°. In another run, the reaction mixture was taken up in 13 ml. of ethanol and distilled with 5 ml. of phosphoric acid and 5 ml. of water. Addition of 2,4-dinitrophenylhydrazine reagent to the distillate gave benzaldehyde 2,4-dinitrophenylhydrazone (0.0029 g., 0.2%), identified by mixed melting point with an authentic sample.

Decomposition of 1-benzyl-1,4-dihydronicotinamide at 210°. 1-Benzyl-1,4-dihydronicotinamide (.251 g.) was heated at 210° under nitrogen for 1 hr. Water was added and the mixture was heated on a steam bath for 3 hr. The water extract was washed with 3 ml. of ether, treated with charcoal and evaporated on a steam bath to a yellow sirup. This was taken up in 2 ml. of ethanol, and 2 ml. of alcohol saturated with picric acid was added. Nicotinamide picrate (.117 g., 28%) precipitated. It was recrystallized from benzene and identified by its mixed melting point (198°) with an authentic sample. No nicotinamide was observed when the dihydro compound was heated at 139° for 1 hr.

Reduction of p-nitroso-N,N-dimethylaniline and nitrosobenzene. *p*-Nitroso-*N,N*-dimethylaniline (0.684 g., 0.00456 mole) and 1-benzyl-1,4-dihydronicotinamide (1.00 g., 0.00468 mole) were heated under nitrogen at 139° for 1 hr. The reaction mixture was extracted with 12 ml. of 1:6 sulfuric acid. The extract was washed with 15 ml. of ether, made basic with 10% sodium hydroxide solution, saturated with salt, and extracted with two 20-ml. portions of ether. Evap-

oration of the ether left *p*-*N*,*N*-dimethylaminoaniline, identified as the phenylthiourea (0.304 g., 49%) by mixed melting point with an authentic sample, m.p. 147.5°. The infrared spectra of the samples were identical.

p-Nitroso-*N*,*N*-dimethylaniline (1.40 g., 0.00934 mole) and 1-benzyl-1,4-dihydronicotinamide (1.00 g., 0.00468 mole) were dissolved in 15 ml. of ethanol, and the solution was boiled for 10 min. Water was added to bring the total volume to 50 ml. The mixture was chilled in an ice bath, and 50 ml. of water was added. Filtration gave a red-brown crystalline solid (1.27 g.). One recrystallization from alcohol and two recrystallizations from 50% acetone gave fine yellow plates (0.086 g., 8%) m.p. 137–140.5°, identified as the nitrone from nicotinamide-1-benzylochloride by the identity of the infrared spectrum with that of an authentic sample. In another run, 2,4-dinitrophenylhydrazine reagent was added directly to the reaction solution after 10 min. of reflux to give benzaldehyde 2,4-dinitrophenylhydrazone (89%), identified by mixed melting point with an authentic sample. In another run, the ethanol was removed from the reaction mixture, and the residue was extracted with 20 ml. of warm water. The extract was washed with ether, treated with charcoal, and evaporated to dryness, leaving nicotinamide, which was identified as the picrate (0.696 g., 42%) by mixed melting point with an authentic sample.

A solution of nitrosobenzene (0.503 g.) and 1-benzyl-1,4-dihydronicotinamide (1.01 g.) in 20 ml. absolute ethanol was refluxed for 1 hr. The alcohol was evaporated and the residue was extracted with 20 ml. of water. The extract was washed with two 20-ml. portions of ether, treated with charcoal, and evaporated to dryness. The residue was taken up in 5 ml. of ethanol. Addition of alcohol saturated with picric acid gave no precipitate of nicotinamide picrate. The residue remaining from the water extraction was dissolved in 10 ml. of ethanol and distilled with 5 ml. of phosphoric acid and 5 ml. of water. Addition of 2,4-dinitrophenylhydrazine reagent to the distillate gave benzaldehyde 2,4-dinitrophenylhydrazone (3%), identified by mixed melting point (235°) with an authentic sample. In other runs, hydrazobenzene, phenylhydroxylamine and aniline were identified by paper chromatography.

Reaction of nicotinamide-1-benzylochloride and p-nitrosodimethylaniline. Nicotinamide-1-benzylochloride (2.51 g., 0.0101 mole), *p*-nitrosodimethylaniline (1.51 g., 0.0101 mole) and piperidine (1 ml., 0.01 mole) in 50 ml. of ethanol were refluxed for 25 min. Enough water was added to bring the total volume to 100 ml. A brown solid (0.961 g., 40%) precipitated on chilling. Two recrystallizations from 50% acetone gave yellow crystals (0.145 g.), m.p. 137–139°. An analytical sample of this nitrone melted at 141–143°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.82, 75.10; H, 6.73, 6.81; N, 11.63, 11.73.

Reduction of phenylhydroxylamine. Phenylhydroxylamine (0.500 g.) and 1-benzyl-1,4-dihydronicotinamide (1.00 g.) were heated at 139° under nitrogen for 30 min. The reaction mixture was extracted with 30 ml. of 1:5 sulfuric acid. The extract was washed with two 15-ml. portions of ether, made basic with 10% sodium hydroxide, saturated with sodium chloride, and extracted with two 20-ml. portions of ether. Evaporation of the ether left aniline (14%) identified as phenylthiourea by mixed melting point (155°) with an authentic sample. In another run, 1% benzaldehyde was identified as its 2,4-dinitrophenylhydrazone.

In a blank run, phenylhydroxylamine (0.632 g.) was heated at 139° under nitrogen for 63 min. Aniline was identified as the phenylthiourea (0.120 g., 9%) by mixed melting point (155.5°) with an authentic sample.

Reduction of azoxybenzene. Azoxybenzene (0.927 g.) and 1-benzyl-1,4-dihydronicotinamide (1.01 g.) were heated under nitrogen at 139° for 43 min. Benzaldehyde (1%) was isolated when the reaction mixture was hydrolyzed. In another run with twice the above quantities, the reaction mixture was extracted with 30 ml. of 1:5 sulfuric acid. The extract was washed with three 15-ml. portions of ether, made basic with sodium hydroxide solution, saturated with salt, and extracted with two 20-ml. portions of ether. Evaporation of the ether left aniline, identified as diphenylthiourea (0.384 g., 18%) by mixed melting point with an authentic sample. The infrared spectra of the samples were identical. Paper chromatography indicated a trace of hydrazobenzene.

Reduction of azobenzene. Azobenzene (0.431 g.) and 1-benzyl-1,4-dihydronicotinamide (0.502 g.) were heated at 139° under nitrogen for 1 hr. Paper chromatography showed the presence of hydrazobenzene. Distillation of the acidified reaction mixture gave benzaldehyde identified as its 2,4-dinitrophenylhydrazone (0.022 g., 3%).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

The Chemistry of Dimethylketene Dimer. IV. The Polyester and β-Lactone Dimer of Dimethylketene[1]

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The polymerization of dimethylketene catalyzed by sodium methoxide yields a polyester which decomposes on heating to the β-lactone dimer of dimethylketene. Mechanisms for formation and pyrolysis of the polyester are offered. The β-lactone dimer can also be prepared by the aluminum chloride-catalyzed dimerization of dimethylketene or rearrangement of the normal dimer, tetramethyl-1,3-cyclobutanedione.

In the last paper of a series of publications on ketenes, Staudinger described the polymeric products obtained by treatment of monomeric dimethylketene with catalytic amounts of triethylamine.[2] These polymers had properties of both polyketones (I) and polyacetals (II); ozonization gave some acetone, but degradation by acids and bases also gave isobutyric acid, dimethylmalonic acid, and diisopropyl ketone. Thermal decomposition regenerated 50–60% of the monomeric dimethylketene. Staudinger suggested that the polymer

(1) Paper III: R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).

(2) H. Staudinger, F. Felix, P. Meyer, H. Harder, and E. Stirnemann, *Helv. Chim. Acta*, **8**, 322 (1925).