by heating with an infrared lamp for several hours while maintaining a high vacuum. This degassing procedure was adopted after several experiments showed evidence for the evolution of gases from the glass, even at the relatively low temperatures employed in this measurement. The sample break seal was then opened and evacuation was continued for several minutes to removes any gases desorbed from the sample chamber itself. The sample chamber was then cooled in liquid nitrogen, and the sample arm of the apparatus was sealed off.

Pressure measurements were carried out by carefully admitting air to the gauge envelope until the pointer returned to its 0 point as read by a wall-mounted telescope fitted with a scaled reticule. The balancing pressure was then read from a dibutylphthalate manometer using a cathetometer graduated to 0.05 mm. The vacuum are of the manometer was maintained at less than 0.1 μ by continuous pumping. The pressure gauge was immersed in a thermostat bath regulated to 0.5° by a bimetallic regulator. The temperature deviations actually observed during a pressure reading did not exceed 0.1°.

Registry No.—I, 281-23-2.

Acknowledgment.—Our grateful thanks to Professor F. A. Cotton of Massachusetts Institute of Technology, without whose support and encouragement this work would have been impossible, and to Professor E. F. Westrum, Jr., of the University of Michigan, for his valuable advice.

Reduction of Nitrobenzene with Crabon Monoxide and Copper Salt–Amine Complexes

Herbert R. Appell[1]

Koppers Research Center, Monroeville, Pennsylvania 15146

Received December 27, 1966

Copper compounds are known to be effective in activating hydrogen in homogeneous solution[2] and carbon monoxide has recently been reported to reduce aromatic nitro compounds to the corresponding azo derivatives using iron pentacarbonyl as catalyst.[3] The author wishes to report that copper salt–amine complexes in conjunction with carbon monoxide can be used for the reduction of aromatic nitro compounds to the corresponding amines.

Cupric salts dissolve readily in an aqueous solution of ammonia or a variety of primary amines[4] to give deep blue solutions which are reduced to the corresponding cuprous compound or to metallic copper by carbon monoxide in the absence of oxidizing agents. The work now reported shows that if nitrobenzene, or other easily reducible nitro compound, is present it is reduced to the amine, usually in quantitative yield. This technique is, therefore, a convenient laboratory method for the selective reduction of nitro groups, especially in compounds containing other reducible groups such as double bonds or carbonyl groups. If the carbon monoxide is replaced by hydrogen the reaction is too slow to be of preparative value.

The pH of the copper salt–amine solution should be greater than 10 and the rate of reaction increases significantly as the pH is increased. In order to obtain high reaction rates the copper should be added as the hydroxide or as a salt of a weak acid and the amine should be highly basic and present in high concentration. Inasmuch as the amine reacts with the carbon dioxide formed in the reaction it is necessary to use an excess or, as an alternative, add sufficient sodium hydroxide to combine with the carbon dioxide. Tables I–III illustrate the effect of the variables on the rate of reduction of nitrobenzene to aniline at partial conversions. Complete conversions are readily obtained at conditions described in the Experimental Section.

Table I

Effectiveness of Amines on Nitrobenzene Reduction Rate

Amine[a]	Hr	Aniline yield, %
Ethylenediamine	5	50
1,2-Propanediamine	8	20
1,3-Propanediamine	7	Trace
3,3′-Diaminodipropylamine	5	85
1,6-Hexanediamine	7	11
Triethylenetetramine	5	16
Ammonia[b]	6	33

[a] Aqueous amine (50 ml of 50%) containing 2% by weight of copper acetate and 2 ml of nitrobenzene were used in these tests. See Experimental Section. [b] The ammonia was blended 1:1 with carbon monoxide and fed to the reactants in a Parr shaker at 2 atm of pressure.

Table II

Effect of Copper Concentration on Reduction Rate

Copper acetate concn[a]	Hr	Aniline, %
0.0	5	None
0.4	5	Trace
1.2	7	3
4.0	3	33

[a] Weight per cent in 10% aqueous ethylenediamine at 85°, conducted as in Table I.

Table III

Effect of Ethylenediamine Concentration on Reduction Rate[a]

Ethylenediamine, wt %	Hr	Aniline, %
1.4	6	Trace
4.0	6	10
10	6	20
50	5	50
90	6	90

[a] Containing 2 wt % of copper acetate.

The reducibility of a compound by this technique can be readily ascertained by passing carbon monoxide through the copper salt–amine solution until the reduction of cupric to cuprous is complete as indicated by disappearance of the deep blue color and then adding a drop of the compound to be reduced. A return of the deep blue cupric complex indicates reduction of the compound in question has occurred. Completion of the reduction can be determined by periodic gas–liquid partition chromatography (glpc) analysis or by passing carbon monoxide until the blue color characteristic of copper(II) has disappeared.

Nitromethane, *o*-nitroanisole, *o*-chloronitrobenzene, *p*-nitrobenzoic acid, and cumene hydroperoxide were all

---

[1] Bureau of Mines, Pittsburgh, Pa. 15213.

[2] J. Halpern, in Proceeding of the 3rd International Congress on Catalysis, John Wiley and Sons, Inc., 1965, p 146; *Advan. Catalysis*, **9**, 302 (1957).

[3] J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

[4] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p 156.

easily reduced. β-Nitrostyrene, azoxybenzene, and azobenzene were not reduced at 90°.

Experimental Section

The data in the tables were obtained by placing 50 ml of a solution of the copper salt in the aqueous amine in a vertical, hard, glass tube (4 × 30 cm) fitted with a gas dispersion tube leading to the bottom for the introduction of carbon monoxide, an outlet near the top and stopcock at the top and bottom for adding or removing liquid samples. This vessel was placed in a hot water bath at 85° during the reaction period. Nitrobenzene (2 ml) was added and a stream of carbon monoxide passed into the reactor at atmospheric pressure at about 10 l./hr. The product was separated from the aqueous solution in a separatory funnel and analyzed by glpc.

Preparative runs with larger amounts of nitro compound were conducted in flasks fitted with good stirring or in a Parr low-pressure shaker. At these conditions all of the carbon monoxide was utilized. Essentially quantitative conversions can be obtained in less than 4 hr at 90° using 5 g each of copper carbonate, sodium hydroxide, and nitroaromatic in 50 ml of 50% ethylenediamine in a shaking apparatus at 15 psig.

Registry No.—Nitrobenzene, 98-95-3.

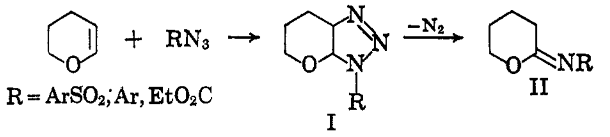
Evidence against Aziridine Intermediates in the Reaction of Azides with Dihydropyran

P. SCHEINER

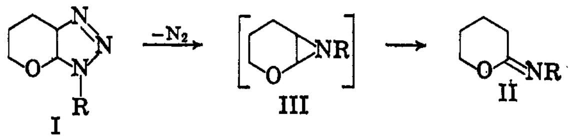
Central Research Division Laboratory, Mobil Oil Corporation, Princeton, New Jersey 08540

Received January 25, 1967

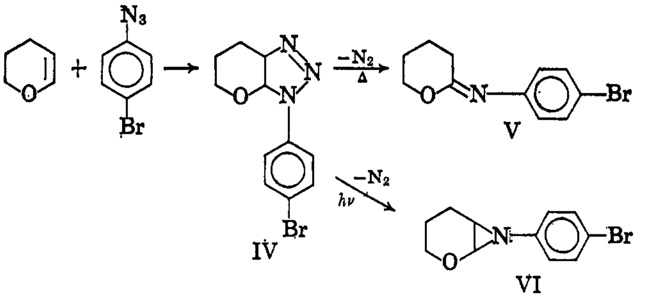
Recent reports have dealt with the thermal reaction of organic azides and 3,4-dihydro-2H-pyran. Benzenesulfonyl azides,[1,2] aryl azides,[3,4] and ethyl azidoformate[5] give imino lactones (II) with dihydropyran; analogous products are obtained with dihydrofuran.[3] Although the initially formed triazoline adduct (I) is not always isolable, kinetic evidence indicates its intermediacy.[5,6]



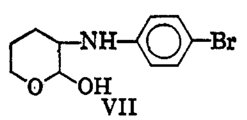
The pyrolytic conversion of triazolines to imines is a well-known reaction. In certain instances, however, triazolines give rise to aziridines, or mixtures of aziridines and isomeric imines.[7] Therefore, the possibility that triazolines of type I first decompose to aziridines (III) which subsequently rearrange to the observed products (II) has been suggested.[1,2] To examine this possibility, an independent preparation of III was attempted.



After 2 weeks at 40°, dihydropyran and *p*-bromophenyl azide gave adduct IV in 24% yield. The orientation of the addition accords with related azide additions to enol ethers[3] and enamines;[8] it is also in agreement with mechanistic information concerning this cycloaddition process.[9] Consistent with IV, the nmr spectrum showed a doublet at τ 4.57 (1 H, $J = 6.3$ cps), a multiplet at 5.90 (1 H), and a multiplet at 6.57 (2 H), as well as four aromatic and four "normal" aliphatic hydrogens. As reported for similar triazolines,[1–5] thermal decomposition of IV in toluene solution produced the imino lactone V, characterized by hydrolysis to *p*-bromoaniline and δ-valerolactone.



In contrast to thermolysis, the photodecomposition of triazolines has been shown to give aziridines in high yield.[10] Accordingly, the photolysis of IV was investigated. Irradiation of IV (27°, benzene, >300 mμ) resulted in a quantitative evolution of nitrogen and a crystalline solid in 67% yield. The photoproduct analyzed for $C_{11}H_{12}BrNO$ and its infrared spectrum showed no absorption in the C=N region, 1690–1640 cm^{-1}.[11] The nmr spectrum revealed a doublet at τ 5.87 (1 H, $J = 5.0$ cps), a multiplet centered at 6.30 (2 H), and four aromatic and five aliphatic (7.6–8.7) hydrogens. Structure VI was therefore assigned to the photoproduct. Although the compound appears to be indefinitely stable in a dry atmosphere, it rapidly deteriorates on exposure to moist air. Hydrolysis of VI at room temperature produced the hemiacetal (VII). Similar observations have been reported by others.[5]



VII

Aziridine VI was quantitatively recovered after being heated in toluene, under the conditions employed to bring about the thermal decomposition of triazoline IV. It is therefore apparent that the conversion of triazoline IV to imino lactone V does not occur *via* an aziridine intermediate. Furthermore, the result suggests that aziridines in general are not involved in the thermal reactions of azides with dihydropyran. The

---

[1] J. E. Franz, M. W. Dietrich, A. Henshall, and C. Osuch, *J. Org. Chem.*, **31**, 2847 (1966).

[2] D. L. Rector and R. H. Harmon, *ibid.*, **31**, 2837 (1966).

[3] R. Huisgen, L. Möbius, and G. Szeimies, *Ber.*, **98**, 1138 (1965).

[4] A. S. Bailey and J. E. White, *J. Chem. Soc., Sect. B*, 819 (1966); A. S. Bailey and J. J. Merer, *ibid., Sect. C*, 1345 (1966).

[5] I. Brown and O. E. Edwards, *Can. J. Chem.*, **43**, 1266 (1965).

[6] A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965).

[7] K. Alder and G. Stein, *Ann.*, **501**, 1 (1933); A. Mustafa, S. M. A. D. Zayed, and S. Khattab, *J. Am. Chem. Soc.*, **78**, 145 (1956); F. D. Marsh and M. E. Hermes, *ibid.*, **86**, 4506 (1964); G. Szeimies and R. Huisgen, *Ber.*, **99**, 491 (1966).

[8] M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).

[9] P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *ibid.*, **87**, 306 (1965).

[10] P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p 268.