amino-4,6-diamino-*s*-triazine (21.5 g.) in an equal amount of dimethylformamide was heated under nitrogen in a citrate bottle in the presence of dimethyl α,α'-azodiisobutyrate (0.32 g.) at 75° for 16 hr. The polymer was precipitated from the viscous solution on the addition of acetone, and filtered. It was washed with hot acetone and hot isopropyl alcohol to remove monomer. The dry polymer weighed 20 g. (93%). It was insoluble in common solvents, but dissolved in formic or acetic acid and in dilute aqueous mineral acids, using at least equivalent amounts of acid.

Similar polymers were also obtained from *N*-methyl-*N*-2-vinoxypropyl-melamine, *N*-1,1-dimethyl-2-vinoxyethyl-melamine, *N*-cyclohexyl-*N*-vinoxyethylmelamine, and methacrylamidoisobutyroguanamine in 40, 74, 52, and 90% yields, respectively.

Hydroxymethylation of polymer from N-methyl-N-vinoxyethylmelamine. The polymelamine (2.1 g., 0.01 mole) was heated with a solution of 36% aqueous formaldehyde (8.2 g., 0.1 mole) and water (10 ml.) made slightly basic with sodium carbonate. After 10 min. at 80–90° and 10 min. at 60°, the clear solution was cooled and carefully acidified with 10 ml. of 0.5*N* hydrochloric acid (0.005 mole). The resulting solution could be diluted further without separation of insoluble material.

Reaction of hydroxymethylated polymer with alcohols. A solution was prepared as before from the polymelamine (2.1 g.) and 37% aqueous formaldehyde solution (5 g., 0.06 mole). Methanol (about 5 ml.) was added until turbidity appeared and the *p*H was adjusted to 5.0 with formic acid. After heating at 60° for 10 min., more methanol was added and the heating repeated. Evaporation to dryness gave a clear, viscous oil soluble in alcohols.

The resin, when repeatedly evaporated with 13-g. portions of *n*-butanol to remove water and methanol, gave a clear, viscous oil soluble in xylene. The original polymer and its hydroxymethylated derivative are insoluble in xylene.

Copolymer of methyl methacrylate and methacrylamidoisobutyroguanamine. A solution of methyl methacrylate (95 g., 0.95 mole) and methacrylamidoisobutyroguanamine (11.8 g., 0.05 mole) in 2-ethoxyethyl acetate (131 g.) was heated at 100° in a nitrogen atmosphere, using benzoyl peroxide (2 g.) as initiator. Additional initiator (0.4 g. total) in the same solvent (15 g.) was added during the heating period of 4.5 hr. A portion of the final, very viscous solution was treated with excess hot methanol to precipitate polymer. A dry, brittle solid, soluble in ethoxyethyl acetate, was obtained. Analysis indicated that a true copolymer had been produced; N, calcd. 3.9; found, 3.3. A portion of the copolymer solution was mixed with a 40% solution of formaldehyde in butanol (20% by weight of polymer solids) and para-toluenesulfonic acid (1% based on polymer solids). The resultant mixture was filmed and baked at 150° for 30 min. to give films of extreme hardness (8H-Koh-i-noor pencil) and exceptional resistance to lacquer solvents.

Copolymers containing 10 mole per cent of the guanamine were also prepared and possessed similar properties.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA]

Reaction of Aromatic Ketoximes with Carbon Monoxide and Hydrogen[1]

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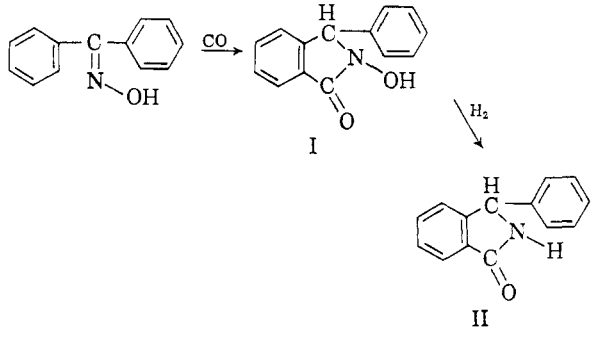
A new synthesis of 3-phenyl, 3-methyl, and 3-benzylphthalimidine as well as of 3-phenyl-3,4-dihydroisocarbostyril has been achieved by application of the oxo reaction to aromatic ketoximes. Carbon monoxide and hydrogen also reacted with methyl phenyl ketoxime to give a dimer described tentatively as 3,4-dimethyl-3,4-diphenyl-2-azetidinone. The infrared spectra of the phthalimidines, isocarbostyril, and the dimer product are described.

The oxo reaction[2] is an established procedure for converting olefins to aldehydes or alcohols. The application of this reaction to several aromatic ketoximes is here described.

Benzophenone oxime reacted with carbon monoxide and hydrogen (98.5:1.5) at 4100 p.s.i. and at 250° in the presence of preformed dicobalt octacarbonyl as catalyst to yield 3-phenylphthalimidine (II) in about 80% yield. The structure of II was established by direct comparison with an authentic sample of 3-phenylphthalimidine.[3] Presumably 3-phenylphthalimidine was produced from the expected *N*-hydroxyphthalimidine (I) by reduction



of the latter with hydrogen. The infrared absorption data of 3-phenylphthalimidine are recorded in the experimental. Our observations (absorption at 1675 and 1600 cm.$^{-1}$) agree with the bands for an α-β-unsaturated lactam reported by Edwards and Singh.[4] *o*-Benzoylbenzoic acid oxime also gave 3-phenylphthalimidine in almost quantitative yield.

When methyl phenyl ketoxime reacted with

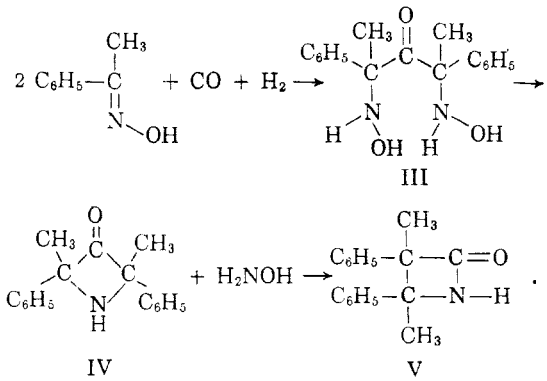
(1) The author (A.R.) is grateful to the National Research Council for the 1956 and 1957 Summer Research Associateships under which part of this work was performed. This investigation was supported in part by a research grant from the National Research Council, Ottawa, Canada.

(2) I. Wender, H. W. Sternberg, and M. Orchin, *Catalysis*, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, Vol. 5, p. 73.

(3) R. E. Rose, *J. Am. Chem. Soc.*, **33**, 388 (1911).

(4) O. E. Edwards and Tara Singh, *Can. J. Chem.*, **32**, 683 (1954).

carbon monoxide and hydrogen a sirup was obtained from which three fractions were isolated by alumina chromatography. As the first fraction (about 10%) contained no carbonyl group, no further work was done on it. Chemical analyses of fraction C indicated that two moles of methyl phenyl ketoxime had condensed with one mole of carbon monoxide and of hydrogen to yield the dimer (III) which then cyclized by splitting out one mole of hydroxylamine. If this is true, the product obtained is either 2,4-dimethyl-2,4-diphenyl-3-azetidinone (IV) or 3,4-dimethyl-3,4-diphenyl-2-azetidinone (V). The rearrangement of



III

IV V

IV to V is typical of the 3-azetidinones.[5] Compound C does not give positive 2,4-dinitrophenylhydrazine and oxime tests but does show strong infrared absorption at 1700 cm.$^{-1}$ which is attributed to the β-lactam structure.[6] Nitrosation of fraction C afforded a bright yellow crystalline *N*-nitroso derivative. It is tentatively suggested, therefore, that the compound's structure is that represented by V. The third fraction (D) was identified as 3-methylphthalimidine[7] by comparison with an authentic sample.

Similarly desoxybenzoin oxime yielded a mixture of two products which were separated by fractional crystallization from ethanol followed by chromatographic purification on alumina. On the bases of chemical and infrared analyses[4] (bands at 3250, 1670 and 1600 cm.$^{-1}$), the minor crystalline component was assumed to be 3,4-dihydro-3-phenylisocarbostyril. The major component was compared with an authentic sample of 3-benzylphthalimidine[8] and shown to be the same.

Two other instances of effecting ring closure with carbon monoxide catalyzed with dicobalt octacarbonyl have recently been reported by Murahashi and Horiie.[9]

We are presently working on the synthesis of *N*-hydroxyphthalimidines by carbonylating aromatic ketoximes.

EXPERIMENTAL[10]

General considerations. The high pressure reactions were carried out in an Aminco Superpressure rocker reaction vessel having a void of 280 ml. The preformed dicobalt octacarbonyl was prepared from cobalt (II) carbonate.[11] The carbon monoxide, obtained from The Matheson Co., East Rutherford, N. J., contained 1.5% hydrogen. The aluminum oxide (calcined) "Analar" was procured from the British Drug Houses (Canada) Ltd., Toronto 14.

Reaction of benzophenone oxime with carbon monoxide and hydrogen to yield 3-phenylphthalimidine. To a solution of benzophenone oxime (14.1 g., 0.07 mole) and dicobalt octacarbonyl (7 g., 0.02 mole) in 25 ml. of purified thiophene-free benzene contained in a glass liner in the bomb was added a mixture of carbon monoxide and hydrogen, (98.5:1.5) at 2070 p.s.i. The bomb was rocked and heated at 250° and 4070 p.s.i. for 6 hr. After the vessel was cooled the pressure was 1915 p.s.i. After the dicobalt octacarbonyl was decomcomposed at 70–80°, the benzene was removed under reduced pressure. Extraction of the solid residue with three 100 ml. portions of ether gave a green solution which upon evaporation gave 2 g. of green colored sirup melting at about −10°. The remaining residue was extracted with hot chloroform to yield 11.6 g. (80%) of material. Recrystallization from ethanol gave 3-phenylphthalimidine, m.p., 218–220°, mixed melting point with an authentic sample of 3-phenylphthalimidine,[3] 218–220°.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.37; H, 5.30; N, 6.70; O, 7.64; mol. wt., 209. Found: C, 80.65; H, 5.41; N, 6.86; O, 7.40; mol. wt. (Rast), 233.

Infrared spectrum of 3-phenylphthalimidine in Nujol (cm.$^{-1}$): 3180 (W), 2900 (S), 1675 (S), 1600 (W), 1458 (S), 1375 (S), 1310 (W), 1210 (W), 1040 (W), 953 (W), 918 (W), 783 (M), 730 (S), 695 (M). S, strong; M, medium; W, weak.

The compound was acetylated with acetic anhydride and sodium acetate; m.p., 153–154°; mixed melting point with an authentic sample of 3-phenylphthalimidine acetate,[3] 153–155°.

3-Phenylphthalimidine from o-benzoylbenzoic acid oxime. In a similar way *o*-benzoylbenzoic acid oxime (6.2 g.) was treated with carbon monoxide and hydrogen (4400 p.s.i.) at about 250° with preformed dicobalt octacarbonyl (about 5 g.) in 40 ml. of benzene. After the bomb was cooled to 23°, the observed increase in pressure was about 150 p.s.i. The white crystalline compound (4.6 g.) was extracted from the metallic cobalt present in the product with boiling chloroform, and then thrice recrystallized from ethanol; m.p. 218–220°, mixed melting point with an authentic sample of 3-phenylphthalimidine,[3] 218–220°.

3-Methylphthalimidine and 3,4-dimethyl-3,4-diphenyl-2-azetidinone from methyl phenyl ketoxime. Methyl phenyl ketoxime (13.5 g.) was similarly allowed to react with carbon monoxide and hydrogen (98.5:1.5) at 3800 p.s.i. and at 220° for 4.5 hr. After removal of the catalyst and solvent, a portion of the sirup (1.43 g.) in 5 ml. benzene was added to the top of a glass column containing a 120 × 38 mm. (diam.) adsorbent column of alumina which had been prewashed

(5) H. Staudinger, *Ber.*, **50**, 1035 (1917).
(6) J. C. Sheehan and A. K. Bose, *J. Am. Chem. Soc.*, **72**, 5158 (1950).
(7) S. Gabriel and A. Neumann, *Ber.*, **26**, 705 (1893).
(8) S. Gabriel, *Ber.*, **18**, 1251, 2433 (1885).
(9) S. Murahashi and S. Horiie, *J. Am. Chem. Soc.*, **77**, 6403 (1955); **78**, 4816 (1956).

(10) All melting points were obtained on a Leitz heating stage and are corrected. The infrared analyses were done on a Perkin-Elmer Intracord Spectrophotometer, Model 137, using a sodium chloride crystal. Microanalyses were done by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, im Max-Planck-Institut fur Kohlenforschung, Mülheim (Ruhr), Germany.
(11) I. Wender, H. Greenfield, and M. Orchin, *J. Am. Chem. Soc.*, **73**, 2656 (1951).

with 100 ml. of benzene. The following mixtures of developer were then added consecutively:

(1) 100 ml. benzene which gave 0.14 g. of a colorless sirup A. (A showed no carbonyl band in the infrared.)

(2) 400 ml. benzene-ether (50:50 by vol.) which yielded 0.05 g. of sirup B.

(3) 200 ml. benzene-ethanol (98:2) which gave 0.53 g. of a light yellow sirup C.

(4) 300 ml. benzene-ethanol (90:10) which gave 0.45 g. of solid D.

Fraction D was recrystallized from chloroform-light petroleum ether or from ligroin (b.p. 95–110°), m.p. 110–111°; mixed m.p. of D with an authentic sample of 3-methylphthalimidine,[7] 109–111°.

Fraction C, b.p. 130–140° at 0.01 mm., failed to crystallize from various solvents. After standing at room temperature for 2 months it solidified to a glass. Fraction C did not give a derivative with 2,4-dinitrophenylhydrazine nor with hydroxylamine. Chemical and infrared analyses indicated that C was probably 3,4-dimethyl-3,4-diphenyl-2-azetidinone (V).

Anal. Calcd. for $C_{17}H_{17}NO$; C, 81.30; H, 6.78; N, 5.57; active H, 0.40; mol. wt., 251. Found: C, 81.31; H, 7.10; N, 5.36; active H, 0.44; mol. wt., (Rast) 273.

Infrared spectrum of C in Nujol: 3280 (W), 2920 (S), 1700 (S), 1515 (W), 1460 (S), 1370 (S), 1315 (W), 1215 (M), 1140 (S), 1018 (W), 758 (S), 745 (M), 697 (S).

Treatment of 0.25 g. of fraction C in 6 ml. of glacial acetic acid with excess nitrous acid for 1 hr. according to the procedure of Haworth and Hey[12] gave a bright yellow sirup which crystallized from ether–light petroleum ether; yield, 0.05 g., m.p., 120–122°. This compound was probably 3,4-dimethyl-3,4-diphenyl-1-nitroso-2-azetidinone.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; mol. wt., 280. Found: C, 72.38; H, 5.31, mol. wt. (Rast), 243.

3,4-Dihydro-3-phenylisocarbostyril and 3-benzylphthalimidine from desoxybenzoin oxime. Desoxybenzoin oxime (15 g.) was allowed to react with carbon monoxide and hydrogen (98.5:1.5) in the presence of dicobalt octacarbonyl (7 g.) in 55 ml. benzene at 3600 p.s.i. and 250° for 2 hr. (pressure drop of 200 p.s.i. at room temperature). The (15.9 g.) sirup (Norite) obtained on removal of solvent from the catalyst-free solution was crystallized from 600 ml. of anhydrous ethanol at 0° for 3 hr.; yield 2.5 g. (16%). Pure 3,4-dihydro-3-phenylisocarbostyril was obtained after three recrystallizations from the same solvent; m.p., 202–203°.

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; O, 7.17; N, 6.28. Found: C, 80.32; H, 6.01; O, 7.54; N, 6.19.

Infrared spectrum of 3,4-dihydro-3-phenylisocarbostyril in Nujol ($cm.^{-1}$) 3250 (W), 2920 (S), 1670 (S), 1600 (W), 1528 (W), 1450 (S), 1375 (S), 1245 (W), 1150 (W), 1070 (W), 1028 (W), 755 (M), 720 (M), 695 (M).

After removal of the ethanol from the filtrate, the sirup was triturated with 500 ml. of ether. A crystalline solid (0.2 g.) was removed by filtration.

The residual sirup obtained after removal of the ether was purified by chromatography on alumina using benzene-anhydrous ethanol (99:1 by vol.) as developer. After removal of the solvent from the eluent the sirup was crystallized from ether-light petroleum ether. Recrystallization from the same solvent pair or aqueous alcohol gave 3-benzylphthalimidine; m.p., 135–136°; mixed m.p. with an authentic sample,[8] 134–136°.

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(12) J. W. Haworth and D. H. Hey, *J. Chem. Soc.*, 361 (1940).