MoO_3–Al_2O_3.—Al_2O_3–K (1% K) was impregnated with aqueous ammonium molybdate to give 10 wt % MoO_3.

Cr_2O_3–Al_2O_3.—Al_2O_3–K (0.1% K) was impregnated with chromic acid solution to give 13 wt % Cr.

Al_2O_3–B.—Alcoa aluminum was hydrolyzed by forming the mercury amalgam using mercuric chloride.

Al_2O_3–C.—Ammonium hydroxide was added to aluminum chloride (2 *M*) to form the hydroxide; the precipitate was washed with water until a negative test for chloride in the wash was obtained with $AgNO_3$.

Thoria.—25-Z was prepared by the thermal decomposition of thorium nitrate hydrate; the heating program was similar to 25-H in reference 12. ThO_2 (1.8 *M*): thorium hydroxide was precipitated from a 1.8 *M* thorium nitrate solution (or other concentration if given) and washed to give high surface area thoria.[13] ThO_2–Cl: the hydroxide was precipitated from 1 *M* thorium chloride solution with ammonium hydroxide and washed to a negative Cl test.[12] ThO_2–C: thorium carbonate was heated to 600° in air.

Dehydration Procedure.—The catalyst was heated in hydrogen or oxygen *in situ* for 4 hr at 600°. 2-Octanol was fed by a displacement pump (LHSV 0.3) and the liquid products were collected after passing through a water-cooled condensor. The 2-octanol contained about 1.8% 2-octanone. The samples were analyzed for conversion by temperature-programmed gc using a Carbowax 20M column. The octene isomers and heptene isomers (1-, *trans*-2-, and *cis*-2-olefin) were analyzed using the same column isothermally at 60°. These three isomers could be determined quantitatively in the *absence* of the 3 and 4 isomers. For several runs, the octene isomer peaks were trapped and no 3 or 4 isomers were detected by ir. The presence of large amounts of the 3- and 4-octene isomers could be detected by gc because of peak broadening and retention time changes, even though a complete separation of all octene isomers were not possible.

Registry No.—2-Octanol, 123-96-6; 1-heptene, 592 76-7; 1-heptanol, 111-70-6; 1-octene, 111-66-0; Al_2O_3, 1344-28-1; ThO_2, 1314-20-1.

[12] B. H. Davis, Dissertation, University of Florida, Gainesville, Fla., 1965.

[13] W. S. Brey, Jr., B. H. Davis, P. G. Schmidt, and C. G. Moreland, *J. Catal.*, **3**, 303 (1964).

Metal Nitrides in Organic Reactions. II. Reactions of Lithium Nitride with Aromatic Aldehydes[1a-c]

J. M. MORRIS,[1d] R. B. DUNMIRE,[1e] PAUL E. KOENIG, AND GEORGE R. NEWKOME*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received September 16, 1971

Aromatic aldehydes react with lithium nitride (Li_3N) in refluxing carbon tetrachloride to give numerous products, which have resulted from a combination of diverse reactions. Benzaldehyde gives primarily Tishchenko or Cannizzaro reaction products, as well as 2,4,5-triphenylimidazole, *cis*-*N*-(2-benzamido-1,2-diphenylethenyl)benzamide, and *threo*-1,2-diphenyl-2-benzamidoethanol. The isolation and structure determination of the various products will be discussed.

Early reports indicated that nitride (N^{-3}) failed to react with alkyl halides,[2] acid chlorides,[3] and other compounds.[2-4] However, nitrides with acid anhydrides have been reported to give nitriles[2] or imides,[5] and more recently nitrides with acid chlorides afforded amides[1a,b] and cyclic imides.[6] Various other diverse reactions of ionic nitrides have been observed.[1b] In this paper, we describe the assorted reactions of aromatic aldehydes with lithium nitride.

Results and Discussion

When benzaldehyde was allowed to react with lithium nitride in refluxing carbon tetrachloride under nitrogen, the following products were isolated (Table I): benzyl benzoate (**2a**), benzoic acid (**3a**), benzyl alcohol (**4a**), benzamide (**5a**), benzonitrile (**6a**), *cis*-*N*-(2-benzamido-1,2-diphenylethenyl)benzamide (**7a**), 2,4,5-triphenylimidazole (**8a**), and *threo*-1,2-diphenyl-2-benzamidoethanol (**9a**).

Non-nitrogen-Containing Products.—Benzyl benzoate (**2a**) is the major product (60%) of the reaction arising by either a Cannizzaro or Tishchenko reaction. It has been well established that benzaldehyde gives exclusively the Cannizzaro reaction products (benzyl alcohol and benzoic acid) when treated with either strong sodium hydroxide or other strong bases,[7] while under aprotic basic reaction conditions, using most commonly aluminum ethoxide[8] or sodium in tetrahydrofuran,[9] the Tishchenko reaction product (benzyl benzoate) is formed.[10] However, either reaction mechanism involves an oxidation–reduction sequence, which produces an adduct that transfers a hydride ion to another molecule of aldehyde. Since both hydride

[1] (a) Paper I: F. P. Baldwin, E. J. Blanchard, and P. E. Koenig, *J. Org. Chem.*, **30**, 671 (1965). (b) Preliminary communication: P. E. Koenig, J. M. Morris, E. J. Blanchard, and P. S. Mason, *ibid.*, **26**, 4777 (1961). (c) We gratefully acknowledge the support of the National Science Foundation through Grant No. G 22021 for partial support of this research. (d) Abstracted in part from the Ph.D. Dissertation submitted to Louisiana State University, Aug 1969. (e) National Science Foundation College Teacher Research Participant, Louisiana State University, summers, 1962–1964.

[2] F. Briegleb and A. Geuther, *Justus Liebigs Ann. Chem.*, **123**, 237 (1862).

[3] O. Emmerling, *Chem. Ber.*, **29**, 1634 (1896).

[4] M. A. Smits, *Recl. Trav. Chim. Pays-Bas*, **12**, 202 (1893).

[5] G. Beck, *Z. Anorg. Allg. Chem.*, **233**, 155 (1937).

[6] A. J. Gordon and R. L. E. Ehrenkaufer, *J. Org. Chem.*, **36**, 44 (1971).

[7] T. A. Geissman, *Org. React.*, **2**, 94 (1944).

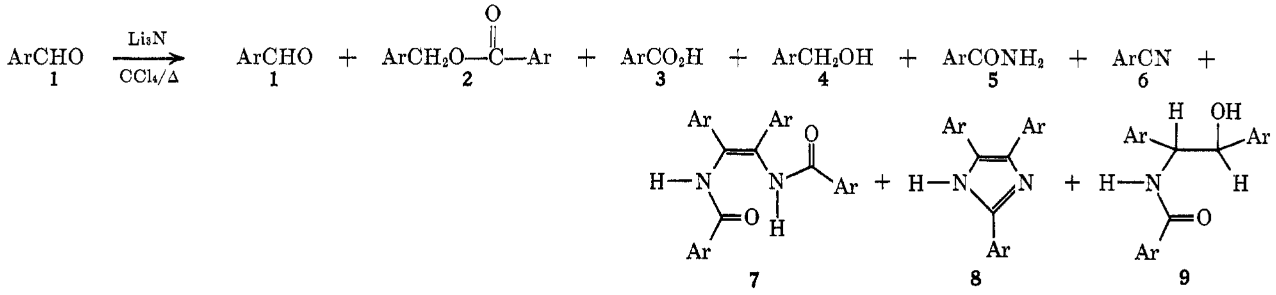
[8] Y. Ogata and A. Kawasaki, *Tetrahedron*, **25**, 929, 2845 (1969).

[9] C. E. Handlovits and J. B. Louch, U. S. Patent 3,387,020; *Chem. Abstr.*, **69**, 27052e (1968).

[10] See J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structures," McGraw-Hill, New York, N. Y., 1968, pp 908–910.

Table I

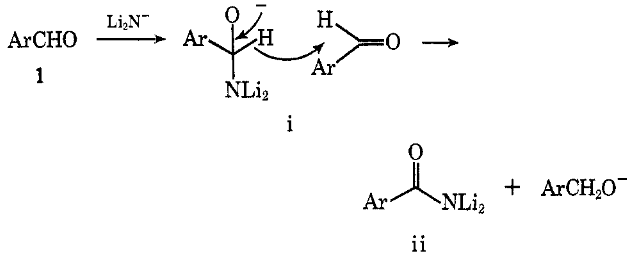
Structure and Yields of Products Derived from the Reaction of Arylaldehydes with Lithium Nitride

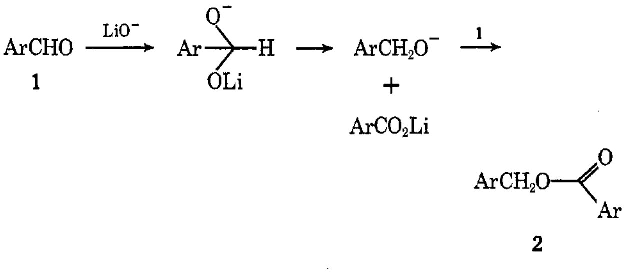


	Mol %[a]								
	1	2	3	4	5	6	7	8	9
1a, Ar = C_6H_5–	2.9	56	9.3	10.0	Traces	Traces	5.5	6.3	9.5
b, Ar = p-$CH_3C_6H_4$–	1.4	55	16.8	10.5	Traces	Traces	1.3	3.6	0[b]

[a] Yields are based on moles of isolated products per mole of aldehyde. [b] *N*-*p*-Xylyl-*p*-toluamide (**10**) was isolated (4.4%); **9b** was not detected in the reaction mixture.

ion[11] and the generated benzylate ion[12] are known to catalyze the formation of benzyl benzoate from benzaldehyde, the formulation of i seems reasonable. However, the subsequent formation of *N*,*N*-dilithiobenzamide (ii) would be expected to give at least some secondary or tertiary amides; no such products were detected in our reaction mixtures. Although trace quantities of benzamide are formed, an alternate scheme suggests that oxygen-containing impurities on the surface of the nitride, formed from atmospheric oxygen and/or moisture, react with adsorbed aldehyde by a Cannizzaro mechanism[13] to produce lithium benzoate and lithium benzylate. It is the latter which then proceeds to generate the benzyl benzoate *via* the Tishchenko reaction.





In addition to the ester, the Cannizzaro products were isolated in substantial quantities (see Table I). The somewhat unexpected isolation of the alcohol indicates that the Cannizzaro reaction proceeds, at least in part, after all the nitride has been consumed or poisoned in other reactions. Slow hydrolysis of the esters by lithium hydroxide could yield the alcohol and acid salts observed; such a slow organic-phase hydrolysis has been proposed[14] as one of the mechanisms by which heterogeneous Cannizzaro reactions proceed. The mole ratio of benzoate salts to benzyl alcohol observed with benzaldehyde is consistent with this possibility, while the higher ratio of acid to alcohol observed with *p*-tolualdehyde (**1b**) could result from oxidation of the alcohol (or aldehyde) to the acid.

Nitrogen-Containing Products.—*threo*-1,2-Diphenyl-2-benzamidoethanol (**9a**) was obtained (*ca.* 4%) from the reaction of benzaldehyde with lithium nitride. The structure follows from the nmr spectrum which shows a structural sequence [$NH^xCH^aCH^bOH^y$]; $\delta^x = 8.6$, $J_{ax} = 8$ Hz; $\delta^a = 5.35$, $J_{ax} = 8$ Hz, $J_{ab} = 7$ Hz; $\delta^b = 5.05$, $J_{ab} = 7$ Hz, $J_{by} = 6$ Hz; and $\delta^y = 5.7$, $J_{by} = 6$ Hz. Also consistent with this structure is the lack of a molecular ion in the mass spectrum with the prominent *m/e* 299 and 212 which corresponds to loss of H_2O and $C_6H_5CO^+$, respectively. Hydrolysis of **9a** afforded equal quantities of benzoic acid and *threo*-1,2-diphenyl-2-aminoethanol;[15] therefore, the synthesis of **9a** from the authentic *threo*-amino alcohol confirmed both its structure and stereochemistry. From all indications, the threo isomer is the predominant stereoisomer with little or no erythro isomer being detected.

Along with amide **9a**, *cis*-*N*-(2-benzamido-1,2-diphenylethenyl)benzamide (**7a**) and 2,4,5-triphenylimidazole (**8a**) were isolated. Amide **7a** was degraded by (1) ozonolysis in formic acid[16] affording only benzil and benzamide in a 1:2 mole ratio, (2) potassium dichromate oxidation in glacial acetic acid giving only dibenzamide (**11**), and (3) hydrolysis in aqueous sulfuric acid[17] quantitatively affording 2,4,5-triphenyloxazole (**12a**) *via* partial hydrolysis followed by rapid cyclization of the resultant α-acylamino ketone. The mass spectrum of **7a** indicates no parent ion but rather *m/e* 400, which suggests the pyrolytic loss of water.

---

[11] T. W. Swamer and C. R. Hauser, *J. Amer. Chem. Soc.*, **68**, 2647 (1946).

[12] H. Gilman and A. H. Blatt, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 104.

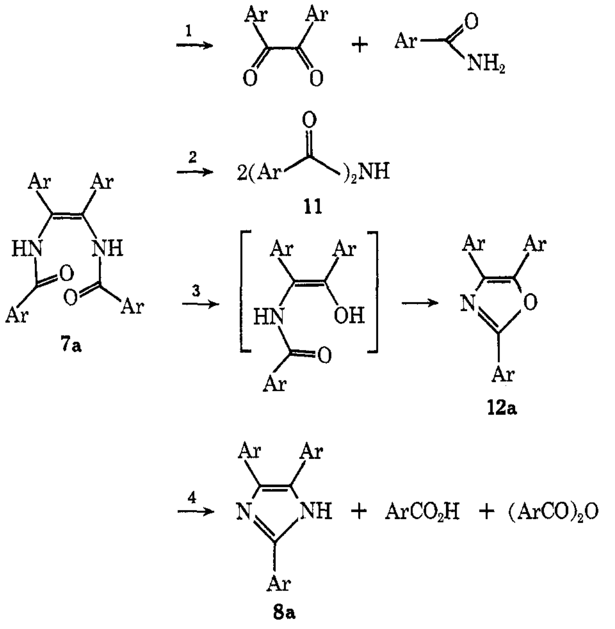
[13] G. E. Lewis [*J. Org. Chem.*, **30**, 2433 (1965)] proposes a similar explanation for the formation of Cannizzaro products in the reaction of *p*-nitrobenzaldehyde with sodium hydride.

[14] E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1954, p 718.

[15] A. McKenzie and D. J. C. Pirie, *Chem. Ber.*, **69B**, 876 (1936).

[16] W. Krabbe, H. Bohlk, and K. Schmidt [*ibid.*, **71**, 644 (1938)] used excess ozone in 97% formic acid for the degradation of the related *N*-(2,2-diphenylethenyl)benzamide.

[17] M. N. K. Irving and R. M. Parkins, *J. Inorg. Nucl. Chem.*, **27**, 270 (1965).



For an attempted mass spectral comparison, both *cis*- and *trans*-*N*-(2-benzamidoethenyl)benzamides (**13**) were synthesized; the mass spectrum of both *cis*- and *trans*-**13** indicated a comparable strong parent ion (m/e 266) and the lack of the $M^+ - 18$ ($-H_2O$) species. Since *trans*-**13** was initially synthesized by thermal isomerization of the cis isomer, *cis*-**13** under our mass spectral conditions (probe temperature >200°) must have isomerized to the more stable *trans*-**13** prior to fragmentation. The tetrasubstituted olefin **7** shows no signs of thermal isomerization at elevated temperatures which would correspond to the approximate probe temperature (refluxing phenyl ether), but under these conditions does slowly eliminate water to form a trisubstituted imidazole. In light of the concomitant elimination of water under mass spectral conditions as well as exclusive formation of 2,4,5-triphenylimidazole (**8a**),[18] both when **7a** was treated with benzoyl chloride at 100° and upon pyrolysis at 300° under nitrogen, **7** probably possesses the cis configuration.

The mechanism of formation of the amides and imidazoles is not easily visualized. Since we could obtain no such products by heating benzyl benzoate with lithium nitride, the nitrogen-containing compounds are apparently produced by a distinct path and are not secondary products of the Tishchenko reaction. Although the diamide products have not been reported previously, the formation of triarylimidazoles from substituted benzaldehydes has been observed under a variety of conditions.[19] Very little, however, has been published concerning the mechanisms by which imidazoles are formed. Since (1) the amides and imidazoles have apparent structural similarities (ArC=CAr), (2) amides **7** are converted thermally or chemically to imidazoles **8**, and (3) amides **7** could not be obtained from imidazoles (**8**) under varied rigorous conditions, we conclude that the imidazoles **8** arise from **7** or an immediate precursor of **7** containing the proper cis stereochemistry.

Attempts were made to isolate various proposed intermediates by interrupting the reaction at various times before completion; however, none of the envisioned intermediates nor the trans isomer of **7** could be isolated. Although the lingering possibility that **7** is the trans isomer cannot be readily dispelled by these data, we are attempting to elucidate a definitive stereochemistry of **7** by synthesis, and are conducting solvent studies of this reaction.

Experimental Section[20]

Reagents.—Benzaldehydes, free of trace acid contaminants, were purified by extraction with a 5% sodium carbonate solution, dried over anhydrous sodium carbonate and distilled at reduced pressures under an inert atmosphere.

The lithium nitride was generously supplied gratis by Foote Mineral Co., Exton, Pa., but could be prepared by the method of E. Masdupuy and F. Gallais.[21]

Reaction of Benzaldehyde with Lithium Nitride.—Benzaldehyde (171.2 g, 1.62 mol) was slowly added under nitrogen to a mechanically stirred suspension of Li_3N (12.25 g, 0.248 mol) in 700 ml of CCl_4 at 75°. The mixture was refluxed for 19 hr maintaining a slow nitrogen flow, which removed any ammonia produced. After cooling, the resultant precipitate (59.2 g) was filtered, washed successively with 100-ml portions of CCl_4, acetone, water, and ethanol, then dried *in vacuo*, affording crude *cis*-*N*-(2-benzamido-1,2-diphenylethenyl)benzamide (**7a**), mp 270–272°. Recrystallization from DMSO gave 9.2 g of pure **7a**: mp 292–294°; ir (Nujol) 3310, 1950, 1900, 1820, 1620 cm^{-1}; mass spectrum m/e (rel intensity) 418 (M^+, 9.7), 400 (8), 324 (4), 310, 297 (22), 210 (12), 105 (C_6H_5CO, 100), 89 (C_7H_5, 7.5), 77 (C_6H_5, 35).

Anal. Calcd for $C_{28}H_{22}N_2O_2$: C, 80.34; H, 5.31; N, 6.70; mol wt, 418.1688. Found: C, 80.22; H, 5.40; N, 6.68; mol wt, 418.1587 (mass spectrum).

Evaporation *in vacuo* of the aqueous washing of the crude precipitate gave a white solid, which upon acidification yielded 18.5 g of pure benzoic acid, mp 121–122°.

The reaction filtrate (*ca.* 1 l.) was concentrated *in vacuo*, giving a red viscous oil (125.2 g), which comprised about 80% of volatile components. The oil was fractionally distilled: fraction 1, bp 45–55° (10 mm), contained unreacted benzaldehyde (5 g); fraction 2, bp 60–75° (10 mm), contained benzyl alcohol (17.3 g) contaminated with traces of benzaldehyde and benzonitrile; fraction 3, bp 120° (1 mm), contained benzyl benzoate (94.5 g); and fraction 4, bp 130–140° (1 mm), contained last traces of benzyl benzoate and *threo*-1,2-diphenyl-2-benzamidoethanol (**9a**, 16 g), which solidified in the condenser. Recrystallization from ethanol afforded analytically pure **9a**: mp 223–224° (lit.[22] mp 225°); ir (Nujol) 3310, 3220 (w), 1630 cm^{-1} (C=O); nmr (DMSO-d_6) δ 5.05 (t, J = 7.0 and 6.0 Hz), 5.35 (t, J = 7.0 and 8 Hz), 7.4 (m, C_{arom} H), 7.6 (m, 2 H), and 8.6 (c, J = 8 Hz); mass spectrum m/e (rel intensity) 299 ($M^+ - 18$, 2), 213 (10), 212 (95), 211 (50), 194 (28), 180 (4.5), 179 (4), 164 (8), 106 (70), 105 (C_6H_5CO, 99), 104 (26), 90 (8), 79 (26), 78 (25), 77 (C_6H_5, 100).

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.5; H, 6.00; H, 4.42. Found: C, 79.6; H, 5.92; N, 4.28.

Column chromatography [alumina (Alcoa F-20), benzene–ethanol (70:30)] of the concentrate from the combined mother liquors of **9a** afforded 10 mg of crystalline benzamide, mp 123–124°, which was identical with an authentic sample.

The residue from the vacuum distillation was recrystallized several times from ethanol, giving 10 g of pure 2,4,5-triphenylimidazole (**8a**), mp 268–272° (lit.[18] mp 274°).

---

[18] D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).

[19] See K. Hofmann in "Imidazole and its Derivatives. Part I. The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience, New York, N. Y., 1953, and R. C. Elderfield in "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1957, Chapter 3.

[20] Melting points were recorded on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer 137B spectrophotometer. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer; chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectral data were determined in this laboratory using a Varian Associates Model M-66 mass spectrometer. Analyses were performed either by Mr. R. Seab in these laboratories or by Galbraith Laboratory, Inc., Knoxville, Tenn.

[21] E. Masdupuy and F. Gallais, *Inorg. Syn.*, **4**, 1 (1953).

[22] F. R. Japp and J. Moir, *J. Chem. Soc.*, **77**, 608 (1900); (b) T. Ishimaru, *Nippon Kagaku Zasshi*, **81**, 769 (1960); *Chem. Abstr.*, **56**, 369a (1962).

Hydrolysis of *cis*-*N*-(2-Benzamido-1,2-diphenylethenyl)benzamide (7a).—Amide **7a** (6.0 g, 14 mmol) suspended in 15 *M* aqueous sulfuric acid was steam distilled. Although undissolved amide rapidly disappeared, the distillation was continued until 230 ml of distillate had been collected. The distillate was made basic with sodium carbonate, concentrated, and acidified, affording 1.3 g (79%) of benzoic acid, mp 120–122°.

After the reaction vessel was cooled, the residue was carefully diluted with ice water (850 ml), causing a precipitation. Recrystallization of this dried solid from ethanol–acetone (99:1) gave 4.07 g (98%) of pure 2,4,5-triphenyloxazole (**12a**), mp 113–115° (lit.[23] mp 114–115°). A mixture melting point gave no depression and spectral data were identical with those of an authentic sample prepared by the method of Schonberg.[23]

Pyrolysis of *cis*-*N*-(2-Benzamido-1,2-diphenylethenyl)benzamide.—Amide **7a** (750 mg, 1.8 mmol) was heated at 300° for 15 min under a slow stream of dry nitrogen. During pyrolysis, a white solid and a colorless liquid were collected in a cooled trap; this pyrolysate was shown by glc and spectral data to be a mixture of benzonitrile (42 mg), benzoic acid (148 mg), and benzoic anhydride (20 mg). The residue (530 mg, 98%), free of **7a**, was decolorized with Norite and recrystallized from ethanol–water, affording 400 mg of pure 2,4,5-triphenylimidazole (**8a**), mp 273–274° (lit.[18] mp 274°).

Reaction of 7a with Benzoyl Chloride.[24]—A mixture of **7a** (1.0 g, 2.4 mmol) and benzoyl chloride (5 ml) was heated to 100° under nitrogen for 30 min. After cooling, the solution was treated with cold aqueous sodium hydroxide solution (10 ml, 20%) and then extracted with ether, dried over $MgSO_4$, and concentrated, affording 400 mg (50%) of 2,4,5-triphenylimidazole.

Recrystallization from pyridine–water gave pure **8a**, mp 273–274°.

Degradation of 7a. A. Ozonolysis in Formic Acid.—Amide **7a** (1.0 g, 2.4 mmol) was suspended in 97% formic acid (50 ml) and subjected at room temperature for 6 hr to excess ozone, which was produced by a Welsbach generator. The formic acid was removed *in vacuo*, giving a residue, which was dissolved in petroleum ether (400 ml, bp 30–60°). Upon concentration to 40 ml, benzamide (188 mg) crystallized, mp 125–127°. Further concentration to about 10 ml gave 212 mg of benzil, mp 94.5–95.5°. Mixture melting points with authentic samples of benzamide and benzil gave no depression.

Evaporation of the remaining solvent gave a yellow mixture, which contained only benzamide and benzil.

B. Oxidation of 7a.—To a stirred suspension of amide **7a** (1.0 g, 2.4 mmol) in glacial acetic acid (100 ml) was added potassium dichromate (1.0 g, 3.4 mmol) over 5 hr under nitrogen. The mixture was stirred at room temperature until the solution became green. Addition of water (400 ml) precipitated an unidentified solid (80 mg),[25] mp 200–230°.

The green filtrate was extracted with ether (two 100-ml portions). The ether extract was washed with water, dried over Drierite, and concentrated to *ca.* 10 ml. Addition of water (40 ml) and cooling gave a suspension, which slowly crystallized, mp 130–142°. Washing with ether and recrystallization from benzene gave 510 mg (48%) of pure dibenzamide: mp 148–149° (lit.[26] mp 148–150°); ir (KBr) 3180 (NH), 1695, 1665 cm^{-1} (C═O). A mixture melting point with an authentic sample produced by the method of Titherley[26] gave no depression.

The ether washings and the mother liquors were combined and concentrated. Column chromatography on silica gel (2 ft × 1 in). with ether–petroleum ether gave 113 mg of pure benzil: mp 94–95°; ir (KBr) 1680, 1600 cm^{-1} (C═O). This sample was identical in all respects with an authentic sample.

Hydrolysis of *threo*-1,2-Diphenyl-2-benzamidoethanol.—Amide **9a** (93.8 mg, 0.296 mmol, mp 223–224°) and potassium hydroxide (9.0 g) in ethanol (25 ml) were refluxed under nitrogen for 18 hr. After cooling, water (70 ml) was added. The solution was extracted with methylene chloride, dried, and concentrated *in vacuo*, giving 52 mg (83%) of crude *threo*-2-amino-1,2-diphenylethanol, mp 108–118°.[27] Recrystallization from chloroform gave threo isomer: mp 122–123° (lit.[15,22a] mp 129–130°); ir ($CHCl_3$) 3670 (–OH), 3400 cm^{-1} (–NH); mass spectrum *m/e* (rel intensity) 195 (M^+ − 18, 7.7), 194 (10), 180 (14), 179 (14), 178 (14), 165 (16), 107 (95), 106 (100), 105 (50), 104 (60), 90 (20), 79 (90), 77 (98). A mixture melting point with *threo*-2-amino-1,2-diphenylethanol, prepared by the method of Japp and Moir,[22a] was undepressed.

***cis*-*N*-(2-Benzamidoethenyl)benzamide.**—Excess benzoyl chloride was slowly added to imidazole (300 mg, 40 mmol) dissolved in 10% aqueous sodium hydroxide (10 ml). The precipitate was filtered, washed with water, and recrystallized from aqueous ethanol, affording 270 mg (35%) of *cis*-*N*-(2-benzamidoethenyl)benzamide: mp 204–206° (lit.[29] mp 205–206°); ir (Nujol) 3300, 3220 cm^{-1} (NH); mass spectrum *m/e* (rel intensity) 266 (M^+, 26.5), 145 (M^+ − 121, 5.9), 121 (7.0), 105 (C_6H_5CO, 100), 77 (C_6H_5, 47); nmr (DMSO-d_6) δ 6.4 (m, cis HC═CH, 2 H), 7.6 (m, C_{arom} H, 6 H), 7.9 (m, C_{arom} H, 4 H), 10.1 (d, J = 8 Hz, NH, 2 H).

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.30; H, 5.26. Found: C, 72.40; H, 5.31.

***trans*-*N*-(2-Benzamidoethenyl)benzamide.**—The cis isomer (100 mg, 4 mmol) was heated under nitrogen at 210° for 10 min. Recrystallization from 95% ethanol gave 50 mg (50%) of the trans isomer: mp 289–290° (lit.[30] mp 280–290°); ir (Nujol) 3310 cm^{-1} (NH); mass spectrum *m/e* (rel intensity) 266 (M^+, 28), 145 (M^+ −121, 6), 121 (8.5), 105 (C_6H_5CO, 100), 77 (C_6H_5, 50); nmr (DMSO-d_6) δ 7.3 (m, trans HC═CH, 2 H), 7.6 (m, C_{arom} H, 6 H), 8.0 (m, C_{arom} H, 4 H), 10.2 (d, J = 8 Hz, NH, 2 H).

Reaction of *p*-Tolualdehyde with Lithium Nitride.—*p*-Tolualdehyde (7.74 g, 64.5 mmol) in CCl_4 (20 ml) was added over 30 min to a refluxing stirred suspension of Li_3N (1.0 g, 28 mmol) in CCl_4 (80 ml) under nitrogen. After 10 hr, additional CCl_4 (100 ml) was added. The solution was cooled to 0° and the precipitate was filtered, washed with cold acetone, and extracted with a 20% sodium hydroxide solution. After filtration, the filtrate was acidified, affording 1.47 g of *p*-toluic acid, mp 175–179°, which was identical with an authentic sample. The base-insoluble residue was recrystallized from phenyl ether, giving 952 mg of pure *cis*-*N*-(2-*p*-toluamido-1,2-di-*p*-tolylethenyl)-*p*-toluamide (**7b**): mp 304–305°; ir (Nujol) 3210 (NH), 1640 cm^{-1} (C═O); mass spectrum *m/e* (rel intensity) 474 (M^+, 4) 472 (3), 353 (47), 339 (8), 238 (5), 119 (100), 91 (70); nmr (DMSO-d_6) δ 2.23 (s, C_{arom} CH_3, 6 H), 6.85–7.45 (m, C_{arom} H, 12 H), 7.68–7.95 (broad d, C_{arom} H, 4 H), 9.78 (s, NH, 2 H).

Anal. Calcd for $C_{32}H_{30}N_2O_2$: C, 81.00; H, 6.38; N, 5.96. Found: C, 81.15; H, 6.18; N, 5.63.

Column chromatography of the combined concentrated filtrates (5.2 g) on silica gel G (3 ft × 1 in.) eluting with cyclohexane–benzene–ethanol (65:25:10) and collecting 10-ml aliquots gave the following: fractions 11–13, *p*-xylyl *p*-toluate, 4.23 g, bp 234–240° (33 mm) [lit.[31] bp 213–217° (15 mm)], nmr (CCl_4) δ 2.30 (s, C_{arom} CH_3, 3 H), 2.33 (s, C_{arom} CH_3, 3 H), 5.19 (s, –CH_2–, 2 H), 7.1 (m, C_{arom} H, 6 H), 7.87 (d, J_{AB} = 8 Hz, 2 H); fraction 14, *p*-tolualdehyde, 109 mg, DNP mp 238–240° (lit.[32] mp 238–240°), and 2,4,5-tris-*p*-tolylimidazole, recrystallized from ethanol–water, 262 mg, mp 232–233° (lit.[33] mp 232–233°), nmr ($CDCl_3$) δ 2.38 (broad s, C_{arom} CH_3, 9 H), 7–8 (m, C_{arom} H, 12 H); fraction 15–22, *p*-methylbenzyl alcohol, 820 mg, mp 58° (lit.[34] mp 60°), ir (neat) 3320 (OH), 1035 cm^{-1}, nmr ($CDCl_3$) δ 1.87 (s, OH, 1 H, lost with added D_2O), 2.32 (s, C_{arom} CH_3, 3 H), 4.60 (s, –CH_2–, 2 H), 7.18 (s, C_{arom} H, 4 H); fraction 23–40, *N*-*p*-xylyl-*p*-toluamide, 337 mg, mp 164–166°, ir (Nujol) 3300 (NH), 1640 cm^{-1} (C═O), nmr (DMSO-d_6), δ 2.29 and 2.37

---

[23] A. Schonberg, *Chem. Ber.*, **54**, 242 (1921).

[24] Benzoic acid anhydride containing sodium benzoate was successfully used (84%) in this conversion, while acetic anhydride or propionic anhydride failed, and only unreacted **7a** was recovered.

[25] This solid is probably an intermediate, since further oxidation resulted in the same product distribution.

[26] A. W. Titherley, *J. Chem. Soc.*, **85**, 1673 (1904).

[27] The crude threo isomer was contaminated with traces of the erythro isomer[28] and the resultant mixture of diastereomers could be crystallized only with difficulty. The facts show that only minor amounts of erythro isomer were produced.

[28] *erythro*-2-Amino-1,2-diphenylethanol (mp 161–162°) was prepared by comparison purposes by the method of R. Lukes, J. Kovar, and K. Blaka [*Collect. Czech. Chem. Commun.*, **25**, 2179 (1960)].

[29] A. Windaus and F. Knopp, *Chem. Ber.*, **38**, 1169 (1905).

[30] P. Ruggli, R. Ratti, and E. Henzi, *Helv. Chim. Acta*, **12**, 332 (1929).

[31] L. Mascarelli and G. Russi, *Gazz. Chim. Ital.*, **42**, 92 (1912).

[32] J. Borstein, S. F. Bedell, P. E. Drummond, and C. L. Kosloski, *J. Amer. Chem. Soc.*, **78**, 86 (1956).

[33] Al. Spasov, St. Robev, and D. Popov, *God. Sofii. Univ., Fiz.-Mat. Fak. Kniga 2-Khim.*, **49**, 119 (1956); *Chem. Abstr.*, **51**, 12075*g* (1957).

[34] A. Schaap, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **84**, 1200 (1965).

(s, $C_{arom}CH_3$, 3 H), 4.46 (d, J = 6 Hz, $-CH_2-$, 2 H), 7.0 (d, J = 8 Hz, $C_{arom}H$, 2 H), 7.16 (s, $C_{arom}H$, 4 H), 8.1 (d, J = 8 Hz, $C_{arom}H$, 2 H), 8.82 (m, NH, 1 H).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.29; H, 7.16. Found: C, 80.35; H, 7.07.

Hydrolysis of *cis*-*N*-(2-*p*-Toluamido-1,2-di-*p*-tolylethenyl)toluamide.—Amide **7b** (54 mg, 1.1 mmol) was hydrolyzed, in an identical manner with amide **7a**, affording *p*-toluic acid, mp 177–180°, and 24 mg (91%) of 2,4,5-tris-*p*-tolyloxazole, which was recrystallized from absolute ethanol, mp 143–145° (lit.[24] mp 145°).

Pyrolysis of *cis*-*N*-(2-*p*-Toluamido-1,2-di-*p*-tolylethenyl)toluamide.—Amide **7a** (200 mg, 0.43 mmol) was pyrolyzed, in an identical manner with amide **7a**, affording a distillate (*p*-tolunitrile, *p*-toluic acid, and *p*-toluic acid anhydride) and a residue, which was recrystallized from ethanol giving 130 mg (90%) of 2,4,5-tris-*p*-tolylimidazole, mp 232–233°. Each compound was substantiated by spectral comparisons with authentic samples.

Registry No.—**7a,** 33511-25-0; **7b,** 33511-26-1; **9a,** 33511-27-2; lithium nitride, 26134-62-3; benzaldehyde, 100-52-7; *threo*-2-amino-1,2-diphenylethanol, 13286-63-0; *cis*-*N*-(2-benzamidoethenyl)benzamide, 33511-28-3; *trans*-*N*-(2-benzamidoethenyl)benzamide, 33511-29-4; *p*-tolualdehyde, 104-87-0; *p*-xylyl *p*-toluate, 21086-87-3; 2,4,5-*tris*-*p*-tolylimidazole, 33515-43-4; *p*-methylbenzyl alcohol, 589-18-4; *N*-*p*-xylyl-*p*-toluamide, 33515-44-5.

The Preparation and Oxidation of α-Hydroxyaldehydes[1]

P. BLUMBERGS* AND M. P. LAMONTAGNE

Ash Stevens Inc., Detroit, Michigan 48202

J. I. STEVENS

Chemical Process Laboratory, Edgewood Arsenal, Maryland 21010

Received May 17, 1971

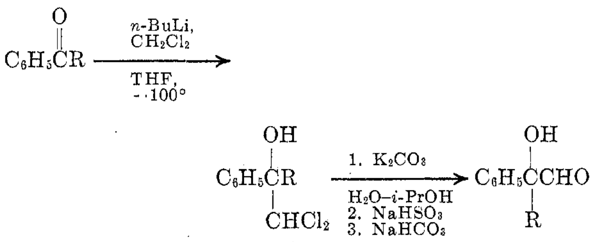
A series of α-hydroxyaldehydes have been prepared in 33–62% yield *via* the hydrolysis of the corresponding dichloromethylcarbinols. The latter compounds were conveniently prepared by the addition of dichloromethyllithium to the appropriate ketone at −100° in tetrahydrofuran. The glycolic aldehydes were oxidized to the corresponding glycolic acids by cold, neutral potassium permanganate in yields of 40–55%. Hydrolysis of trichloromethylcarbinols, obtained by the addition of trichloromethyllithium and the appropriate ketone, resulted in the elimination of chloroform to regenerate the parent ketone.

The syntheses of α-hydroxyaldehydes have been severely limited in the past. Freon[2] has added Grignard reagents to the oximes of difficultly accessible α-keto aldehydes to yield α-hydroxyaldoximes which could then be hydrolyzed by acid to the corresponding α-hydroxyaldehyde in low yields. Also, the hydrolysis of α-haloaldehydes[3,4] affords α-hydroxyaldehydes in low yields.

The purpose of this work, in part, was to investigate the synthesis of α-hydroxyaldehydes by the reaction of dichloromethyllithium with an alkyl aryl ketone followed by hydrolysis of the resulting dichloromethylcarbinols. Avy[5] reported the synthesis of dimethyldichloromethylcarbinol, but no aldehyde was isolated upon hydrolysis of this compound with calcium carbonate. Avy noted that hydrolysis of diethyldichloromethylcarbinol with boiling aqueous calcium carbonate did afford diethyl glycolic aldehyde, isolated as the semicarbazide derivative.

In our work, we found that dichloromethyllithium adds readily to alkyl aryl ketones at −100° in tetrahydrofuran to yield the corresponding dichloromethylcarbinols in yields of 75–85% (eq 1).[6] One example of this reaction was reported in 1964 by Kobrich and coworkers[6b] who treated benzophenone with the same reagent to obtain the corresponding dichloromethylcarbinol.

Hydrolysis of the dichloromethylcarbinols with potassium carbonate in aqueous isopropyl alcohol afforded a mixture of products which was shown by ir spectroscopy to contain the desired glycolic aldehyde. Distillation of the mixture resulted in extensive decomposition. However, the desired aldehydes could be isolated as the bisulfite adducts from which the free aldehydes could be readily regenerated.[7] The overall equations are shown in eq 1.



$$C_6H_5\overset{O}{\overset{\|}{C}}R \xrightarrow[\text{THF, }-100°]{n\text{-BuLi, }CH_2Cl_2} C_6H_5\overset{OH}{\underset{CHCl_2}{C}}R \xrightarrow[\text{H}_2\text{O}-i\text{-PrOH; 2. NaHSO}_3\text{; 3. NaHCO}_3]{\text{1. K}_2\text{CO}_3} C_6H_5\overset{OH}{\underset{R}{C}}CHO \qquad (1)$$

1, R = $CH(CH_2)_3$
2, R = $CH(CH_2)_2$
3, R = $CH(CH_2)_4$
4, R = $CH(CH_3)_2$
5, R = $CH(CH_2)_3$
6, R = $CH(CH_2)_2$
7, R = $CH(CH_2)_4$
8, R = $CH(CH_3)_2$

Investigation of the hydrolysis of compound 2 led also to the isolation of a solid α-hydroxyaldehyde dimer. The structure was assigned on the basis of ir and nmr spectral data and an acceptable elemental analysis. Treatment of the dimer with 4% meth-

---

[1] (a) This work was conducted at Ash Stevens Inc. under Edgewood Arsenal Contract No. DAAA15-67-C-0519. (b) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[2] P. Freon, *Ann. Chim.* (*Paris*), **11**, 480 (1939).

[3] A. Kirrmann and J. Druesne, *C. R. Acad. Sci.*, **259**, 3285 (1964).

[4] A. Kirrmann, P. Chancel, M. Vignalou, and P. Federling, *Bull. Soc. Chim. Fr.*, 707 (1950).

[5] M. A. Avy, *ibid.*, **49**, 12 (1931).

[6] Recent literature has described the preparation of α-chloroalkyllithium compounds by the reaction of polyhalomethanes with *n*-butyllithium in tetrahydrofuran or tetrahydrofuran–ether mixtures at −100°. These salts were reported to be stable indefinitely at −100° but decomposed spontaneously above −65°. Tetrahydrofuran was observed to have a great stabilizing influence on α-chloroalkyllithium structures. (a) D. Hoeg, D. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1965); (b) G. Kobrich, K. Flory, and W. Drischel, *Angew. Chem.*, **76**, 536 (1964); (c) G. Kobrich, H. R. Merkle, and H. Trapp, *Tetrahedron Lett.*, 969 (1965).

[7] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1962, p 149.