TABLE I

PROPERTIES OF VARIOUS PRODUCTS PREPARED FROM TRIOSES WITH 2,4-DINITROPHENYLHYDRAZINE

Method Temperature	HCl 5°	HCl 20°	HCl 35°	H_2SO_4 5°	H_2SO_4 20°	H_2SO_4 35°
PPt. color						
Gly[a]	Yellow	Yellow-orange	Orange	Orange	Orange	Orange
DHA[b]	Orange	Orange	[e]	[e]	Orange	[e]
Pyr[c]	Orange	[e]	[e]	[e]	Orange	[e]
Solubility in hot (1:1) 50% C_2H_5OH/C_2H_5OAc						
Gly	Complete	*ca.* 50%	*ca.* 50%	Trace	Trace	Trace
DHA	Trace	Trace			Trace	
Pyr	Trace				Trace	
M.p. material recrystallized by above						
Gly	166	166	164	—	—	—
DHA	—	—			—	
Pyr	—				—	
M.p. residue from solubility tests						
Gly	—	284[d]	289	298	298	298
DHA	253[d]	280[d]			284[d]	
Pyr	299				289[d]	

[a] Gly, glyceraldehyde. [b] DHA, dihydroxyacetone. [c] Pyr, pyruvaldehyde. [d] Recrystallized from dioxane to melt at 298°. [e] Not performed.

by Brady[8] in which 2,4-dinitrophenylhydrazine was dissolved in a small amount of concentrated sulfuric acid and the solution diluted with ethanol. This solution was added to an alcoholic solution of the triose. Each procedure was run at 5°, 20°, and 35°. The solutions were held at the required temperature for 2 hr. before mixing, and then allowed to react for 12 hr. Only the first crops of precipitate were retained.

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(8) O. L. Brady, *J. Chem. Soc.*, 1931, 756.

The Identification of $C_{12}H_8N_4O$, an Oxidation Product from α-Pyridil Monohydrazone[1]

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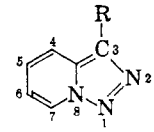
Treatment of α-pyridil (I) with tosyl hydrazide and the resulting derivative with aqueous alkali gives a product, $C_{12}H_8N_4O$, incorrectly identified as "azipyridil" (II).[2] Chemical and physical evidence require the formulation to be that of 1-α-picolinoylpyridotriazole (III, R = α−C_5H_4NCO).

$(\alpha\text{-}C_5H_4NCO)_2$ (I)

$\alpha\text{-}C_5H_4NC{=}N_2$
$\alpha\text{-}C_5H_4NC{=}O$ (II)



III

In acid solution pyridotriazole (III. R = H) and, at higher temperatures, 1-phenylpyridotriazole (III. R = C_6H_5) react with carboxylic acids to form esters of corresponding α-pyridylcarbinols.[3] In its resistance to attack by carboxylic acids, III (R = α-C_5H_4NCO) further demonstrates lack of triazole ring reactivity towards acids when electron withdrawing groups are at the 1-position. In boiling aniline, III (R = α − C_5H_4NCO) undergoes degradation of the triazole ring and the product,[2] di(α-pyridyl) acetanilide, suggests an intermediate formation of II. Transformation of III (R = α − C_5H_4NCO) into II apparently occurs more readily in the presence of iodine or bromine, each of which gives rise to the formation of α,α-dihaloketones as nitrogen is liberated.[2]

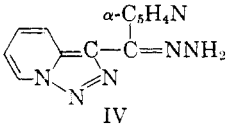
Hydrazine hydrate combines with III (R = α − C_5H_4NCO) to bring about the formation of the corresponding hydrazone (IV) and, if air is present, its oxidation product 1,1′-bipyridotriazole(V).[4]

(1) Partial support of this work under a National Institutes of Health Grant No. CY-2895 is gratefully acknowledged.

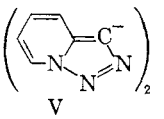
(2) B. Eistert and W. Schade, *Chem. Ber.*, 91, 1411 (1958).

(3) J. H. Boyer and L. T. Wolford, *J. Am. Chem. Soc.*, 80, 2741 (1958).

(4) J. H. Boyer, R. Borgers and L. T. Wolford, Jr., *J. Am. Chem. Soc.*, 79, 678 (1957).



IV



V

Infrared absorption data for III have been obtained from potassium bromide discs and from chloroform solution. Lack of absorption from 3.5 to 6.0 mμ clearly indicates the absence of an aliphatic diazo group in both the solid state and in solution at ordinary temperature.

EXPERIMENTAL[5]

1-α-Picolinoylpyridotriazole (III, R = C_5H_4NCO). According to the directions of Eistert and Schade[2] for the preparation of azipyridil, 1-α-picolinoylpyridotriazole (III. R = C_5H_4NCO), m.p. 151° was obtained in 66% yield.

Infrared absorption for 1-α-picolinoylpyridotriazole from (a) a potassium bromide disc (cm.$^{-1}$, % transmission): 3086, 18.5; 3040, 18.0; 1658, 7.1; 1634, 12.5; 1587, 28.6; 1572, 28.0; 1511, 7.4; 1479, 30.0; 1427, 15.2; 1416, 10.6; 1355, 29.9; 1328, 33.9; 1309, 42.2; 1271, 26.2; 1245, 27.1; 1225, 10.3; 1159, 21.7; 1151, 27.4; 1110, 39.1; 1091, 17.5; 1052, 34.9; 1010, 41.5; 993, 27.0; 940, 7.9; 890, 23.4; 812, 41.6; 768, 4.5; 752, 20.0; 742, 17.2; 723, 43.7; 703, 26.0; 673, 16.1; 648, 46.6; and (b) a chloroform solution (cm.$^{-1}$, absorptivity): 3425, 0.03; 2967, 0.15; 2445, 0.03; 1653, 0.82; 1634, 0.70; 1585, 0.34; 1572, 0.26; 1499, 0.33; 1471, 0.11; 1412, 0.40; 1359, 0.19; 1325, 0.21; 1274, 0.28; 1145, 0.36; 1107, 0.17; 1091, 0.42; 1045, 0.05; 1008, 0.31; 995, 0.36; 964, 0.06; 939, 0.70; 886, 0.50.

1-α-picolinoylpyridotriazole 3,5-dinitrobenzoate. A solution of 2.25 g. (0.01 mol.) of 1-α-picolinoylpyridotriazole and 2.12 g. (0.01 mol.) of 3,5-dinitrobenzoic acid in 75 ml. of *o*-xylene was heated at 110° for 2 hr. Upon cooling the crude salt, *1-α-picolinoylpyridotriazole 3,5-dinitrobenzoate,* m.p. 154–159° (dec.) separated in 75% yield. It recrystallized from ethyl acetate–ethanol as pale yellow needles, m.p. 158–159 (dec.).

Anal. Calcd. for $C_{19}H_{12}N_6O_7$: C, 52.30; H, 2.77; N, 19.28; O, 25.66. Found: C, 52.40; H, 2.69; N, 18.98; O, 25.68.

After treating 1.0 g. (0.002 mol.) of this salt with 10 ml. of 10% sodium hydroxide with stirring for 10 min., a solid was removed by filtration. Upon acidifying the filtrate, 0.4 g. (90%) of 3,5-dinitrobenzoic acid, m.p. and mixture m.p. 204–205°, was obtained. The solid phase from the alkaline reaction mixture was identified as 1-α-picolinoylpyridotriazole, melting point and mixture melting point 151°, 0.5 g. (90%).

Attempts to alkylate 3,5-dinitrobenzoic acid with 1-α-picolinoylpyridotriazole in tetralin at 160° led to an unidentified oil.

1,1′-Bipyridotriazole. A solution of 1.0 g. (0.005 mol.) of 1-α-picolinoylpyridotriazole and 0.16 g. (0.05 mol.) of hydrazine (as 95% aqueous hydrazine) in 30 ml. of *n*-butyl alcohol was refluxed for 2 hr. Colorless needles, 0.2 g. (17% of *1,1′-bipyridotriazole,* m.p. 245° (dec.), separated upon cooling, and after recrystallization from ethanol melted at 254–255° (dec.).

Anal. Calcd. for $C_{12}H_8N_6$: C, 61.02; H, 3.41; N, 35.55. Found: C, 61.09; H, 3.34; N, 35.60.

A mixture melting point determination with a sample prepared from a dihydrazone of α-pyridil and silver oxide[4] showed no depression. The previously reported[4] m.p. 272–274° (dec.) is in error.

Upon concentration of the solvent a second product separated from the reaction mixture in *n*-butyl alcohol as pale yellow needles, 0.6 g. (51%), m.p. 172–176°. Recrystallization from ethanol gave the *hydrazone of 1-α-picolinoylpyridotriazole,* m.p. 174–175°.

Anal. Calcd. for $C_{12}H_{10}N_6$: C, 60.49; H, 4.19; N, 35.28. Found: C, 60.53; H, 4.08; N, 35.64.

When the reaction between 1-α-picolinoylpyridotriazole and hydrazine was carried out under nitrogen, the hydrazone derivative was obtained in 90% yield with no trace of 1,1′-bipyridotriazole.

Acknowledgment. We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory for infrared absorption data.

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(5) Semimicro elemental analyses by Alfred Bernhardt, Mülheim (Ruhr) Germany. Melting points are uncorrected.

The Electrochemical Reduction of Michler's Ketone[1]

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In connection with another project, it became necessary to reduce Michler's ketone to the corresponding pinacol (*p,p*-dimethylaminodiphenylcarbinol) and to rearrange this material to the pinacolone. After rather unsuccessful attempts to prepare the pinacol by other means it was decided to reduce Michler's ketone electrochemically. The ensuing experiments resulted in some interesting results of theoretical and practical significance for electrochemical preparations and are reported herewith.

The reduction of ketones at a variety of cathodes to form pinacols has been widely used.[2a-4] Escherlich and Moest[5] found that Michler's ketone yields the pinacol with a copper electrode while both pinacol and hydrol are formed in almost equal amounts at a nickel cathode. The chief advantage of any given electrode under the usual conditions of uncontrolled cathode potentials is to limit the cathodic potential to the hydrogen overvoltage of the metal. It was therefore deemed simplest to use the method of Allen and Corwin[6] where the reduction is conducted at a controlled potential mercury cathode.

From polarographic results,[7] it is known that in acid solutions of *p*H 1.3 benzophenone is reduced

(1) Contribution No. 109 from the Research Council of Alberta.

(2) (a) K. Elbs and K. Brand, *Z. Electrochem.,* **8,** 783 (1902). (b) J. Tafel, *Z. Electrochem.,* **17,** 972 (1911).

(3) S. Swann, Jr., N. J. Leonard, and F. C. Howard, *Trans. Electrochem. Soc.,* **67,** 6 pp. preprint (1936).

(4) N. J. Leonard, S. Swann, Jr., and C. Fuller, *J. Am. Chem. Soc.,* **75,** 5127 (1953).

(5) F. Escherlich and M. Moest, *Z. Electrochem.,* **8,** 849 (1902).

(6) M. J. Allen and A. H. Corwin, *J. Am. Chem. Soc.,* **72,** 114 (1950).

(7) R. Pasternak, *Helv. Chim. Acta,* **31,** 753 (1948).