$$C_{6}H_{5}NHN=CH \qquad HC=N$$

$$C_{6}H_{5}NHN=C \qquad H^{+} \qquad C_{6}H_{5}N=N-C$$

$$C_{6}H_{5}NHN=CH \qquad C_{6}H_{5}NHNH_{2}+C \qquad NC_{6}H_{5}$$

$$II \qquad V$$

$$HC=N \qquad HC=N \qquad HC=N$$

$$H_{2}N-C \qquad HC-N-C_{6}H_{5} \qquad HC-N-C_{6}H_{5}$$

$$II \qquad V \qquad HC-N-C_{6}H_{5}$$

of a transient red intermediate, a yellow compound $C_{15}H_{12}N_4$ (III) was obtained. III differs from II by the elements of phenylhydrazine. Two molar equivalents of hydrogen were consumed by III to produce aniline and an amine, $C_9H_9N_3$ (IV). Because of the resistance of the second phenylhydrazine group to reduction it is most probably involved in a ring and III is given the structure 1-phenyl-4-benzeneazopyrazole and IV the structure 1-phenyl-4-aminopyrazole. A possible mode of formation of III is shown where the cation (V), one of the resonance forms of this highly colored intermediate loses phenylhydrazine leading to III.

Experimental

Oxidation of p-Glucosazone.—140.5 mg. of p-glucosazone was dissolved in 30 ml. of warm dioxane and rapidly cooled to 25°; 5 ml. of 0.425 M sodium periodate (5.1 molar equivalents) and 15 ml. of water was added. Almost immediately separation of the orange needles of the 1,2-bis-phenylhydrazone of mesoxaldehyde (I) began; 10-ml. aliquots were withdrawn, an excess of potassium nitrate solution added, and the acid present titrated to the methyl red end-point. This sample was then used for a periodate determination by the method of Fleury⁴: at the end of 0.25, 1 and 20 hours, the consumption of 2.84, 3.00 and 4.43 molar equivalents of oxidant and production of 1.9, 2.0 and 1.3 molar equivalents of acid. It appears that by 20 hours slow oxidation of formic acid has begun.

A blank determination showed no periodate consumption by the 60% dioxane and a control oxidation with α -methylo-glucopyranoside gave the normal reaction, *i.e.*, the uptake of 2 molar equivalents of oxidant and production of 1 of acid; 12 hours were required for the completion of the reaction.

In a duplicate oxidation after 0.5 hour the orange needles of I were filtered and washed with water, m. p. 196-197°, yield 102 mg. (85%).

Anal. Calcd. for $C_{15}H_{14}ON_4$: C, 67.67; H, 5.26. Found: C, 67.78; H, 5.18.

In a third oxidation by steam distillation of the reaction mixture, 40 mg. of the formal-dimedon compound was obtained, m. p. 187-188°.

1,2,3-Tris-phenylhydrazone of Mesoxaldehyde (II).—One gram of I was heated with an equal weight of freshly distilled phenylhydrazine at 120° for 0.5 hour as directed by von Pechmann, et al., for the conversion of the 1,3-bis-phenylhydrazone of mesoxaldehyde to II. The yellow crystals appearing on cooling were collected with benzene and recrystallized from benzene and methanol, to yield 0.3 g. of bright yellow needles, m. p. 181-182°; von Pechmann, et al., reported a melting point of 166°.

Anal. Calcd. for $C_{21}H_{20}N_6$: C, 70.78; H, 5.62; N, 23.60. Found: C, 70.93; H, 5.69; N, 23.59.

To obtain an authentic sample of II by the identical method used by von Pechmann, the 1,3-bis-phenylhydra-

(4) Fleury and Lange, J. Pharm. et Chim., 17, 107 (1933).

zone of mesoxaldehyde was first prepared. Our preparation of the latter substance melted at 181-183° rather than the 175-176° reported but agreed with the other recorded physical properties; crystalline, habit, color, etc. of

Anal. Calcd. for C₁₈H₁₄ON₄: C, 67.67; H, 5.26. Found: C, 68.00; H, 5.22.

The 1,3-bis-phenylhydrazone of mesoxaldehyde was converted to II, m. p. 181-182°, which was identical to the sample prepared from I.

The possibility of the occurrence of structural and geometric isomers of the 1,3-bis-phenylhydrazone of mesoxalde-

hyde and of II under slightly different experimental conditions may account for these discrepancies in melting point.

1-Phenyl-4-benzeneazopyrazole (III).—0.5 g. of II was covered with 5 ml. of acetic acid. The yellow crystals immediately became a brilliant red. The mixture was heated to boiling and within a half minute after solution had taken place, the red color had faded to a yellow. Water was added to turbidity and on cooling 0.3 g. of the yellow plates of III were collected, m. p. 124-125°.

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.55; H, 4.84; N, 22.61; mol. wt., 248. Found: C, 72.58; H, 4.97; N, 22.62; mol. wt. (Rast in camphor), 246.

The same transformation was brought about by recrystallization of II from ethanolic hydrochloric acid $(0.5\ N)$. If the acid solution is kept at room temperature the brilliant red color remains for several hours before the change to yellow becomes complete. von Pechmann's obtained a substance by the action of acetic anhydride on II melting at 125° to which he assigned the structure "1-phenyl-3-benzolazomethyl-4-benzolazo-5-methylpyrazole" with the formulation $C_{25}H_{20}N_6$. The elemental analyses reported would not distinguish between this formulation and $C_{15}H_{12}N_4$. We have prepared the compound following von Pechmann's directions and it appears to be indistinguishable from III in melting point, behavior in a mixed chromatogram, and in absorption spectra. III in ethanol showed a broad maximum at $335\ m\mu$ with $\log\ \epsilon$ of $4\ 4$

1-Phenyl-4-aminopyrazole (IV).—5.3 g. of III in 200 ml. of methanol was hydrogenated at atmospheric pressure over 300 mg. of platinum oxide. By two hours the hydrogen uptake was 2.1 molar equivalents and the reaction complete. The colorless solution was evaporated to give a paste of aniline and the crystals of IV. After two recrystallizations from benzene-petroleum ether, 0.7 g. of the colorless plates of IV was obtained, m. p. 104-105°.

Anal. Calcd. for $C_9H_9N_3$: C, 67.92; H, 5.66. Found: C, 67.93; H, 5.60.

The hydrochloride of IV obtained from ethanol-water melted at $245-250^{\circ}$.

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Condensation of Nitroalkanes with Anils

By Charles D. Hurd and James S. Strong

It was thought that Schiff bases should condense with nitroparaffins, since they are "ammono-aldehydes." Accordingly, benzylidineaniline was treated with both nitromethane and nitroethane. Reaction occurred in accordance with the equation $C_6H_5CH=NC_6H_5+RCH_2NO_2 \longrightarrow C_6H_5CH-NHC_6H_5$

RCHNO₂

It would not have been without precedent if this

reaction had yielded a nitroölefin, since Hass and Riley¹ state: "Although inorganic bases cause aromatic aldehydes to react with paraffins, yielding nitro alcohols, these reagents in the presence of amines yield nitroölefins. This reaction may be formulated as follows

"ArCHO + RNH₂ \longrightarrow ArCH=NR + H₂O $\begin{array}{c} \text{"ArCH} \rightarrow \text{RCH}_2\text{NO}_2 \longrightarrow \\ \text{RNH}_2 + \text{ArCH} = \text{C(NO}_2)\text{R"} \end{array}$

That a nitro amine was formed, therefore, instead of a nitroölefin, is of some interest.

N-(2-Nitro-1-phenylethyl)-aniline, prepared in this way in 65% yield from nitromethane, is the same substance as that obtained by Worrall² by addition of aniline to ω -nitrostyrene.

Under comparable conditions (refluxing in alcohol) benzalazine, C₆H₅CH=N-N=CHC₆H₅, and nitromethane did not react. Also, no reaction was observed between benzylideneaniline and 2-nitropropane during fifteen hours of refluxing in ethyl alcohol. The starting materials were recovered.

Experimental

N-(2-Nitro-1-phenylethyl)-aniline.—A mixture of 80 g. of benzylideneaniline, 50 cc. of nitromethane and 160 cc. of ethyl alcohol was refluxed for ten hours, then cooled to 0°, and filtered. The 41 g. of solid product, plus 28 g. more obtained by concentration of the filtrate, was recrystallized from alcohol; yield, 58 g. The melting point was 86-87

N-(2-Nitro-1-phenylpropyl)-aniline.—A mixture of 10 g. of benzylideneaniline, 5 cc. of nitroethane and 20 cc. of ethyl alcohol was heated under reflux for ten hours; no crystallization occurred on cooling. Evaporation of the solvent left an oil most of which crystallized on standing for a few days. The yield of yellow solid, m. p. 85-88°, was 4.9 g.

Anal. Calcd. for C₁₅H₁₆N₂O₂: mol. wt., 256; N, 10.9. Found: mol. wt., 264; N (by Mr. Kryzwicki), 10.5

- (1) Hass and Riley, Chem. Rev., 32, 409 (1943).
- (2) Worrall, This Journal, 49, 1598 (1927).

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A Partial Asymmetric Synthesis by the Meerwein-Ponndorf Reduction

By Lloyd M. Jackman, John A. Mills and James S. Shannon

The recent publication by Doering and Young¹ of a preliminary communication describing two Meerwein-Ponndorf reductions which resulted in partial asymmetric syntheses prompts us to record the results which we have obtained in similar experiments. The investigation of the possibility of obtaining an asymmetric synthesis in this type of reduction was undertaken in order to substantiate the current theory of the reaction mechanism^{2,3,4} by extending the stereochemical

- (1) Doering and Young, THIS JOURNAL, 72, 630 (1949).
- (2) Woodward, Wendler and Brutschy, ibid., 67, 1425 (1945).
- (3) Jackman and Mills, Nature, 59, 789 (1949).
- (4) Dewar, "Electronic Theory of Organic Chemistry." p. 136, 1949.

evidence obtained from the reductions of substituted cyclic ketones with various aluminum alkoxides.5

The reductions of β -phenylethyl methyl ketone and t-butyl methyl ketone with (+)-aluminum butan-2-oxide at temperatures of 110 and 150°, respectively, yielded totally inactive carbinols. Subsequently the reduction of 2,2-dimethylnonan-3-one with (+)-aluminum 3,3-dimethyl but-2oxide was selected as a more favorable case. 2,2-Dimethylnonan-3-one was prepared Cason's method⁶ from di-n-hexylcadmium and trimethylacetyl chloride in 47% yield and was obtained as a colorless liquid, b. p. 70° (7 mm.) (Anal. Calcd. for $C_{11}H_{22}O$: C, 77.65; H, 12.9. Found: C, 77.3; H, 12.85) which yielded a semicarbazone as colorless plates, m. p. 138° from methanol (Anal. Calcd. for C₁₂H₂₅ON₃: C, 63.45; H, 11.0. Found: C, 63.5; H, 11.1). The reduction was carried out in the absence of a solvent and at a temperature of 200°. Equimolecular amounts of alkoxide and ketone were used and distillation was allowed to take place very slowly over a period of six hours in order to remove the pinacolone as formed. It was not possible to make the reduction take place under milder conditions. After decomposition with dilute sulfuric acid, the residue was worked up and fractionated to give a sample (6% yield) of crude alcohol which had $[\alpha]^{15.4}$ D - 0.40. The fact that this was obtained from pinacolyl alcohol of $[\alpha]^{15.3}$ p + 7.8, that is, from an alcohol of the opposite sign of rotation, was not unexpected in the light of the results of Levene and Marker.7 These results suggest that the configurations are the same for both alcohols.

Reductions of these types may be postulated as proceeding by two simultaneous reactions each involving one of the two possible configurations of the cyclic transition state. Thus the total reaction rate is given by $k=k_{\rm A}+k_{\rm B}$ where $k_{\rm A}$ and $k_{\rm B}$ are the constants for the two simultaneous reactions. It is feasible that the temperature coefficients for k_A and k_B may differ widely and in such a way that higher temperatures would favor racemization. In any case as an increase in temperature results in an increase in k and as complete asymmetric synthesis is not to be expected (i.e., $k \neq k_A$; $k_B \neq 0$), reactions carried out at higher temperatures for a given time would not be as favorable as reductions at lower temperatures. These factors would account for the failure to obtain asymmetric syntheses with (+)-aluminum but-2-oxide at 110-150° while Doering and Young working at 36° and using the same reducing agent achieved a 6% asymmetric reduction of the seemingly less favorable ketone, 6-methylheptan-2-one.

In view of Doering and Young's communica-

- (5) Jackman, Macbeth and Mills, J. Chem. Soc., 2643 (1949).
- (6) Cason, Chem. Revs., 40, 15-32 (1947).
- (7) Levene and Marker, J. Biol. Chem., 91, 761-772 (1931).