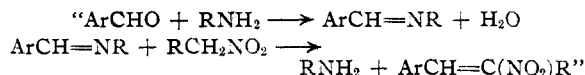


reaction had yielded a nitroölefin, since Hass and Riley¹ state: "Although inorganic bases cause aromatic aldehydes to react with paraffins, yielding nitro alcohols, these reagents in the presence of amines yield nitroölefins. This reaction may be formulated as follows



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, $\text{C}_6\text{H}_5\text{CH=N-N=CHC}_6\text{H}_5$, 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 $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2$: 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

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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*, **73**, 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, 1940.

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-2-oxide was selected as a more favorable case. 2,2-Dimethylnonan-3-one was prepared by 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 $\text{C}_{11}\text{H}_{20}\text{O}$: 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 $\text{C}_{13}\text{H}_{25}\text{ON}_3$: 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 $[\alpha]^{15}_D - 0.40$. The fact that this was obtained from pinacolyl alcohol of $[\alpha]^{15}_D + 7.8$, 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 $k = k_A + k_B$ where k_A and k_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).