reaction had yielded a nitroölefin, since Hass and Riley[1] 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

$$\text{"ArCHO} + \text{RNH}_2 \longrightarrow \text{ArCH=NR} + \text{H}_2\text{O}$$
$$\text{ArCH=NR} + \text{RCH}_2\text{NO}_2 \longrightarrow \text{RNH}_2 + \text{ArCH=C(NO}_2\text{)R"}$$

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 Worrall[2] by addition of aniline to ω-nitrostyrene.

Under comparable conditions (refluxing in alcohol) benzalazine, $C_6H_5CH{=}N{-}N{=}CHC_6H_5$, 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 $C_{15}H_{16}N_2O_2$: 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).

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED MAY 31, 1950

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 Young[1] 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 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 method[6] 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 $C_{12}H_{25}ON_3$: 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 $[\alpha]^{15.4}\text{D} - 0.40$. The fact that this was obtained from pinacolyl alcohol of $[\alpha]^{15.3}\text{D} + 7.8$, 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-

---

[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.

[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).

tion no further experiments of this type will now be carried out by us. Kinetic experiments are now in progress and it is hoped to evaluate the rate constants k, k_A and k_B for several pairs of alkoxides and corresponding ketones.

JOHNSON CHEMICAL LABORATORIES
UNIVERSITY OF ADELAIDE
ADELAIDE, SOUTH AUSTRALIA RECEIVED APRIL 25, 1950

Analysis of Ore Residues for Ionium and Protactinium[1]

BY L. I. KATZIN, Q. VAN WINKLE AND J. SEDLET

With the availability of large amounts of pitchblende ore residues, due to the processing of uranium for atomic power developments, it has been possible to consider the recovery of long-lived members of the uranium and actinium radioactive decay series in appreciable amount. These materials are of use as radiation sources, and sources of other isotopes, in addition to their intrinsic interest. This report deals with analysis of some residue fractions which have not previously been considered as sources for protactinium (Pa^{231}) and ionium (Th^{230}), but which may prove to be convenient sources of these materials.

The isotope Pa^{231} occurs in nature approximately to the extent that radium (Ra^{226}) occurs, which is about 0.15 part per million in pitchblende ore containing about 60% by weight of U_3O_8. The sum total of this material which has been extracted and purified, according to literature reports, is probably not significantly more than 2 g., considerably less than the amount of radium recovered.

After initial manipulations, pitchblende ores are usually treated with sulfuric acid and sodium nitrate, giving an acidic solution of uranyl salts (and other salts) with an insoluble residue in which is found the radium. Some polonium, ionium and protactinium dissolve with the uranium. A fraction at least of the protactinium presumably remains with the insoluble gangue, from the fact that protactinium has been obtained from such material. Thus, von Grosse[2] and Graue and Käding[3,4] used the ultimate residues following removal of the radium as their sources of protactinium.

The acid solution of uranyl nitrate is treated with excess sodium carbonate to precipitate some of the non-uranium materials appearing in solution, the uranium remaining in solution as the carbonate complex. It is to be expected that the protactinium dissolved in the first step should precipitate with the other hydroxides and carbonates at this point. The behavior of ionium is less definite, since thorium forms a soluble carbonate complex under the proper conditions. It seems likely that there might be at least a partial precipitation at this point. The analytical data bear out this presumption.

The carbonate solution of uranium is then treated with NaOH to precipitate uranium, the uranium dissolved in acid and reprecipitated with ammonia. It is to be expected that any protactinium and ionium present in the carbonate solution would follow the uranium through these steps. The ammonium diuranate is next calcined to U_3O_8, the oxide dissolved in nitric acid, and the concentrated nitrate solution extracted with ether. The ether solution of uranyl nitrate is washed repeatedly with portions of water until no further UX_1 activity (Th^{234}) can be detected. After steps for recovery of additional uranium from the washes and original solution, the residual solutes are combined and saved, together with any insoluble residue from treatment of the oxide with nitric acid. It is to be expected that this residue, therefore, may be a rich source of ionium, if an appreciable portion survives the carbonate precipitation.

In the classical isolations of protactinium,[2,3,4,5] the starting material was the ultimate residue remaining after extraction of radium, following preliminary removal of uranium. These residues were obtained from the Joachimsthal mine in Czechoslovakia. From the fact that these were residues from extensive chemical treatments, it might be expected that the isolation of protactinium from them might be beset by difficulties in addition to those inherent in the chemical nature of the protactinium. Therefore it was considered highly worthwhile to investigate a less refractory source. The carbonate precipitates from the uranium process were a logical point of attack, since they represented the probable site of any protactinium that might have dissolved in the original acid treatment, while at the same time the material had already been in solution and should be amenable to redissolution with simple acid treatment. The ionium content of this fraction similarly would be more available than that in the original ore or the radium residues. Another possible source of ionium is the residue of the ether extraction procedure, as already stated.

The analyses of these fractions, to be reported in this paper, show that the carbonate fraction is indeed a relatively rich and readily worked source of both protactinium and ionium, and that the ether extraction residues contain ionium essentially free of protactinium or polonium. Their ionium content is something over 6 parts per million. The data further show that more than half of the protactinium and ionium may

---

[1] Work done in 1944 under auspices of the Manhattan Engineer District at the "Metallurgical Laboratory," University of Chicago, predecessor of the Argonne Laboratory.

[2] A. von Grosse, *Ber.*, **61B**, 233 (1928).

[3] G. Graue and H. Käding, *Naturwissenschaften*, **22**, 286 (1934).

[4] G. Graue and H. Käding, *Angew. Chem.*, **47**, 650 (1934).

[5] A. von Grosse and M. Agruss, THIS JOURNAL, **56**, 2200 (1934); *Ind. Eng. Chem.*, **27**, 422 (1935).