The Reduction of Aldehydes and Ketones with Nickel–Aluminum Alloy in Aqueous Alkaline Solution[1]

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The selective reduction of many aldehydes and ketones of the type, ArCOR (R = H, aryl, or alkyl group) to either ArCH(OH)R or $ArCH_2R$ may be accomplished in good yield by the use of Raney nickel alloy in aqueous alkali. This selectivity can be achieved by the proper choice of reaction temperature. Aliphatic aldehydes and ketones could be reduced only to the carbinol stage under the conditions used. Both alkali-soluble and alkali-insoluble compounds undergo reduction, the latter by the addition of ethanol to the aqueous solution.

The reduction of carbonyl compounds with Raney nickel alloy in aqueous alkali has been studied by Papa, *et al.*[2] In this paper they report that a carbonyl group attached directly to an aromatic ring is reduced to a methylene group in a manner analogous to the Clemmensen reduction. The reduction of a carbonyl group not conjugated with the benzene ring, however, proceeds only as far as the alcohol.

Evdokimoff[3] reported the reduction of α-isonitrosopropiophenone with Raney alloy in 5% aqueous sodium hydroxide to 1-phenyl-2-aminopropanol. In view of the results of Papa and coworkers this product would not be anticipated since the carbonyl group is adjacent to the ring and should therefore be completely reduced.

The most obvious difference in the experimental procedures of these investigators was the lower reaction temperature used by Evdokimoff. The purpose of our investigation was to determine if the extent of reduction of aldehydes and ketones could be controlled by adjustment of the reaction temperature. Accordingly, we have carried out a series of carbonyl reductions at 10–20° and at 80–90°, the latter temperature range corresponding to the conditions used by Papa. Our results suggest that at the lower temperature range, reduction does not proceed beyond the carbinol stage regardless of the position of the carbonyl group relative to the aromatic ring. At the higher temperatures our results support the data of Papa; Clemmensen-type reduction occurs only when the carbonyl group is attached directly to the aromatic nucleus. These results are summarized in Table I.

A comparison of Table I with the reductions of the carbonyl compounds reported by Papa[2] reveals that salicylaldehyde, *o*-benzoylbenzoic acid, veratraldehyde, vanillin, acetophenone, 1-phenyl-2-propanone, and *p*-dimethylaminobenzaldehyde can be selectively reduced to give as the chief product either the carbinol or the hydrocarbon. Vanillin, however, also undergoes displacement of the methoxyl group at the higher temperature, whereas at the lower temperature used in our experiments, no such cleavage was observed.

With alkali-soluble carbonyl compounds the reduction procedure is remarkably smooth. For compounds insoluble in the basic medium, the addition of 25 ml. of ethanol enabled the reduction to proceed satisfactorily in most instances. Several compounds could not be reduced in spite of the addition of alcohol to increase the solubility. Compounds which resisted reduction included propiophenone, 2-heptanone, and benzophenone. The fact that *p*-hydroxypropiophenone and *p*-hydroxybenzophenone have been reduced under similar conditions[2] suggests that difficulties in reduction may be due to insufficient solubility in the basic aqueous solution. The influence of added solvent merits additional study since the products obtained sometimes vary with the solvent.[2]

The reduction of 4-phenyl-3-buten-2-one was of interest because the carbonyl group, though not attached to the ring, was nevertheless conjugated with the ring. At both low and high temperatures the product obtained was 4-phenyl-2-butanone. These results are consistent with those obtained by others[4] in the reduction of α,β-unsaturated ketones.

The convenience and rapidity with which these reductions can be carried out is worthy of mention. The lower reaction temperature permitted a more rapid addition of the alloy; foaming with subsequent loss of hydrogen is also minimized. Moreover, no special equipment or apparatus is needed.

Experimental

General Reduction Procedure at 10–20°.—The nickel-aluminum alloy used contained 50% nickel and 50% aluminum and was obtained from the Raney Catalyst Co., Chattanooga, Tennessee.

A weight of alloy calculated to give enough hydrogen to reduce 1.5 to 2 times the amount of substrate was used. One-tenth mole of solid sodium hydroxide in excess of the amount needed to dissolve completely any acidic starting material and to react with the aluminum in the alloy was then dissolved in enough water to make the solution approximately 10% sodium hydroxide by weight.

The sodium hydroxide solution was placed in a three-necked flask equipped with a thermometer and mechanical

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[2] D. Papa, E. Schwenk, and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).

[3] V. Evdokimoff· *Gazz. Chim. Ital.*, **81**, 725 (1951).

[4] L. Covert, R. Connor, and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1658 (1932).

TABLE I

Carbonyl compound	Reduction product[a]	Temp., °C.	% Yield
Salicylaldehyde	Saligenin	10–20	77
Salicylaldehyde	*o*-Cresol	90	76
o-Benzoylbenzoic acid	3-Phenylphthalide	10–20	80
o-Benzoylbenzoic acid	α-Phenyl-*o*-toluic acid	90	80
Levulinic acid	γ-Hydroxyvaleric acid γ-Lactone	10–20	53[b]
Levulinic acid	γ-Hydroxyvaleric acid γ-Lactone	90	65[b]
Vanillin	Vanillyl alcohol	10–20	85[c]
Veratraldehyde	Veratryl alcohol	10–20	66
3-Methyl-2-butanone	3-Methyl-2-butanol	10–20	68
Enanthaldehyde	1-Heptanol	10–20	57
1-Phenyl-2-propanone	α-Methylphenethyl alcohol	80–90	74
m-Hydroxybenzaldehyde	*m*-Hydroxybenzyl alcohol	10–20	77
m-Hydroxybenzaldehyde	*m*-Cresol	80–90	76
2-Pentanone	2-Pentanol	80–90	54
α-Isonitrosopropiophenone	Norephedrine	10–20	57[d]
Acetophenone	α-Methylbenzyl alcohol	10–20	75
4-Phenyl-3-buten-2-one	4-Phenyl-2-butanone	10–20	78
4-Phenyl-3-buten-2-one	4-Phenyl-2-butanone	80–90	61
Cyclopentanone	Cyclopentanol	10–20	67
p-Dimethylaminobenzaldehyde	*p*-Dimethylaminobenzyl alcohol	10–20	70[e]
2-Acetonaphthone	2-Naphthylmethylcarbinol	15–25	87[f]

[a] Solid products were identified by a comparison of the melting point with those reported in the literature. Mixed melting points with authentic material were taken in most cases. Liquids were converted to solid derivatives whose melting points had previously been reported. [b] The low yield may be due to incomplete extraction of the very soluble lactone from the aqueous solution. [c] The yield reported is that of the crude product which melted at 105°. [d] The yield is based on reacted starting material. Some unreacted ketoxime was recovered by acidification of the basic solution after extraction of the norephedrine with ether. [e] The reaction time was two hours as opposed to one hour for most of the other reductions. A small amount of N,N-dimethyl-*p*-toluidine was also obtained and identified as the picrate. [f] A two-hour reaction time was used. One hundred milliliters of ethanol was used to increase the solubility of the ketone.

stirrer. The basic solution was then cooled to 10° by means of an ice bath and external cooling was continued during the addition of the carbonyl compound and the alloy. Ketones were added in one portion at the beginning of the reaction, while aldehydes were added simultaneously with the alloy in portions to minimize the change of the unreduced aldehyde to undergo a Cannizzaro reaction or aldol condensation in the presence of base. For insoluble substrates, 25 ml. of 95% ethanol was added to increase the solubility. The alloy was added, while stirring, at a rate which permitted the temperature to be maintained at 10–20°.[5] Stirring was continued for 30 min. after the addition of the alloy had been completed. In most experiments the total reaction time was about 1 hr. At this point the procedure varied depending upon the solubility of the product in the basic solution.

Base-soluble Compounds.—The mixture was filtered through a Büchner funnel and the catalyst was thoroughly washed with water. It was necessary to keep the catalyst moist at all times because of the pyrophoric nature of the dry catalyst. If the product was an acid or phenol, the filtrate was acidified by addition of the filtrate, with stirring, to a cooled solution of dilute hydrochloric acid. Schwenk and Papa[2] point out that this method of acidification is less likely to cause coprecipitation of aluminum salts. The reduction product was isolated by filtration or ether extraction and purified by recrystallization or distillation.

Base-insoluble Compounds.—The mixture was filtered through a Büchner funnel and the catalyst washed with water, followed by a sufficient quantity of ethanol to dissolve the product. Similar precautions were used to keep the catalyst moist. The product was then salted out, if necessary, extracted with ether, the extracts were dried over magnesium sulfate, and the ether removed by distillation. The residue was then further purified by recrystallization or distillation *in vacuo*.

Following are typical procedures for a base-soluble and a base-insoluble carbonyl compound.

Reduction of Salicylaldehyde.—A solution containing 23 g. (0.58 mole) of sodium hydroxide in 225 ml. of water was placed in a 500 ml. three-necked flask equipped with a thermometer and mechanical stirrer and cooled to 10° with an ice bath. While stirring, 12.2 g. (0.1 mole) of salicylaldehyde and 25 g. of Raney alloy were added alternately in portions at such a rate that the temperature was kept below 20°. The addition was complete after 30 min. after which time the greenish color of the solution soon disappeared and the evolution of hydrogen become more rapid. Stirring was continued for an additional 30 min.

The catalyst was separated by filtration through a Büchner funnel and washed well with water, care being taken not to let the catalyst become dry. The basic filtrate was acidified by pouring it into a cooled, stirred solution of dilute hydrochloric acid. The acid solution was extracted with ether; the ether extracts were combined and dried over magnesium sulfate. Removal of the ether by distillation left a solid residue which weighed 9.5 g. after drying and melted at 81–84°. A sample recrystallized from water melted at 86–87° (lit.,[6,7] m.p. 84 and 86°). The yield of *o*-hydroxybenzyl alcohol is 77%.

Reduction of Acetophenone.—To a solution of 20 g. (0.5 mole) of sodium hydroxide in 200 ml. of water cooled to 15° were added 25 ml. of 95% ethanol and 24 g. (0.2 mole) of acetophenone. The mixture was stirred during the addition of 20 g. of Raney alloy while the temperature was maintained between 15–20° with the aid of external cooling.

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(5) In the reduction of 2-acetonaphthone the temperature was allowed to reach 25° at which temperature the ketone was considerably more soluble.

(6) H. Adkins and H. Cramer, *J. Am. Chem. Soc.*, **52**, 4354 (1930).

(7) L. Covert, R. Connor, and H. Adkins, *ibid.*, **54**, 1651 (1932).

This addition required 30 min. An additional 30 min. was allowed for complete reduction. The nickel catalyst was removed by filtration through a Büchner funnel and washed thoroughly with ethanol. The aqueous ethanolic filtrate was saturated with sodium chloride and the oil which separated was extracted with ether. Distillation of the ether extract after drying it with magnesium sulfate yielded 18 g. (75%) of a colorless oil, b.p. 104–105° (17 mm.), $n^{21}\text{D}$ 1.5269. Reported[8] for methylphenylcarbinol: b.p. 93° (16 mm.), $n^{25}\text{D}$ 1.5251.

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[8] E. Eliel, *J. Am. Chem. Soc.*, **71**, 3971 (1949).

The Thermal Decarboxylation of β-Alkoxycrotonic Acids. A New Synthesis of Isopropenyl Ethers

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A number of alkyl isopropenyl ethers have been obtained in good yield and in high purity by thermal decarboxylation of the corresponding β-alkoxycrotonic acids. It appears that the reaction may be useful as a preparative route to compounds of the type $R_1COR_2{=}CHR_3$, $R_1CSR_2{=}CHR_3$, and $R_1CNR_2R_3{=}CHR_4$; possible limitations of the procedure are outlined. *p*-Methoxybenzyl isopropenyl ether was found to rearrange to 4-*p*-methoxyphenyl-2-butanone.

The literature contains a number of scattered observations that substituted β-alkoxyacrylic acids are readily decarboxylated. In 1896, Autenrieth reported that β-benzoxycrotonic acid upon melting decomposed to form carbon dioxide and benzyl isopropenyl ether; the corresponding thioether was obtained in the same way.[1] Phenyl isopropenyl ether was similarly obtained by Ruhemann and Wragg.[2] A different course appeared to be followed by β-methoxymethoxycrotonic acid, which upon being heated yielded $CH_3(CH_3OCH_2O)$-$C{=}CHCOOCH_2OCH_3$ rather than the acetal $CH_3(CH_3OCH_2O)C{=}CH_2$.[3]

Although the simple decarboxylation affords a potentially useful method of preparing substituted vinyl ethers, sulfides, and amines, it appears to have been neglected since the early work, perhaps because other methods are often applicable. The alternative procedures however involve a number of drawbacks. Reppe's method of adding alcohols to acetylenic linkages requires high pressures; dehydrohalogenation of saturated β-chloro ethers[4,5] requires the use of solid sodium hydroxide and high temperatures, as well as an organic reactant often not easily available; catalytic cleavage of acetals often leads to extensive side reactions[6] and a recent procedure[7] involving the use of vinylmercury compounds is useful principally for thioethers and aryl vinyl ethers.

The precursor acids for the decarboxylation reaction are readily prepared from β-keto esters, and in view of the current lively interest in the reactions of vinyl ethers,[8a–e] it appeared desirable to learn the scope and principal limitations of the reaction. To date, it has been found that the decarboxylation of β-alkoxycrotonic acids proceeds easily and in high yields to give the pure vinyl ethers for most of the simple alkoxy groups, but side reactions become important when electron donating groups render the ether linkage sensitive to even weak acids.

The general approach is as follows:

$$CH_3COCH_2COOC_2H_5 \xrightarrow{PCl_5} CH_3CCl{=}CHCOOH \xrightarrow{OR^-}$$
$$CH_3COR{=}CHCOOH \xrightarrow{180^\circ} CH_3COR{=}CH_2$$

There appear to be no limitations in the first step, though the yield varies widely. For instance, if the starting material is ethyl acetoacetate, about 30–40% β-chlorocrotonic acid is obtained (after hydrolysis of the acid chloride initially formed) whereas with ethyl benzoylacetate the yield is nearly quantitative. Isolation of the product is mildly complicated by the fact that both *cis* and *trans* isomers may result; however, they need not be separated since both lead to the same product in the following step.

Jones[9] has observed that nucleophilic displacement of vinylic halide is greatly facilitated by the presence of a β-carbonyl group. Likewise we found that β-alkoxy acids are readily produced when a solution or suspension of sodium β-chlorocrotonate in an alcohol containing an excess of alkoxide ion is refluxed. The yields were generally fair (50–75%); in a few experiments premature decarboxylation lowered the yield. Since the acid chlorides

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[1] W. Autenrieth, *Chem. Ber.*, **29**, 1639 (1896).

[2] S. Ruhemann and E. Wragg, *J. Chem. Soc.*, **79**, 1185 (1901).

[3] J. L. Simonsen and L. Storey, *ibid.*, **95**, 2106 (1909).

[4] For some examples, see V. L. Tweedie and B. G. Barron, *J. Org. Chem.*, **25**, 2023 (1960).

[5] C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1910 (1938).

[6] W. J. DeJarlais, J. L. O'Donnell, and H. M. Teeter, *J. Am. Oil Chemists' Soc.*, **38**, no. 5, 241 (1961).

[7] D. J. Foster and E. Tobler, *J. Am. Chem. Soc.*, **83**, 851 (1961).

[8] (a) K. C. Brannock, *J. Org. Chem.*, **25**, 258 (1960); (b) H. Schechter and H. L. Cates, Jr., *ibid.*, **26**, 51 (1961); (c) C. D. Hurd and R. D. Kimbrough, Jr., *J. Am. Chem. Soc.*, **82**, 1373 (1960); (d) Z. A. Krasnaya and V. F. Kucherov, *J. Gen. Chem. USSR*, **30**, 3875 (1960); (e) M. Farina, M. Peraldo, and G. Bressan, *Chim. Ind.* (Milan), **42**, 967 (1960).

[9] D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 467 (1960).