values of the energy of adhesion between additive and water and total energy of adhesion are 41 ergs/sq. cm. and 93 with *n*-heptane and 92 and 165 with *n*-heptanol, respectively.[6] The high dipole moment of the water does not give a very strong induced dipole in the hydrocarbon and thus there is probably no solubilized hydrocarbon molecules passing from the interior of the micelle into the palisade layer of the soap micelle. As this attraction increases through $-SH$, $-NH_2$, $-OH$ and $-COO^-$, this high dipole moment of the water results in more penetration of these molecules into the polar end of the palisade in about the above order.

Summary

The use of long chain alcohols, *n*-heptanol through *n*-dodecanol, as additives has been found to markedly increase the solubilization of *n*-heptane in potassium *n*-tetradecanoate solutions. Use of long-chain alcohols as additives have a much greater enhancement of solubilizing power than equivalent amounts of added soaps of the same chain length. When the polar group on the additive is changed, it is found that for equal chain lengths $-COO^- < -OH < -NH_2 < -SH$ in the enhancement of solubilization. This is explained by a greater penetration into the palisade layer of the soap micelle of these various polar compounds in the same order noted in the increase in solubilizing power. This is in agreement with the attraction of these polar groups for the water layer due to the high dipole moment of the latter.

ST. PAUL, MINN. RECEIVED OCTOBER 24, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Hydrogenolysis of Certain Substituted Aromatic Acids and Carbonyl Compounds by Lithium Aluminum Hydride

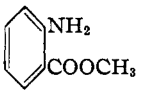
BY LLOYD H. CONOVER[1] AND D. S. TARBELL

The observation[2] that the 5-carbethoxy group, in certain 2-amino-5-carbethoxythiazole derivatives, is reduced to a methyl group by lithium aluminum hydride led us to study the behavior toward this reagent of some analogously substituted benzene derivatives. The results indicate that an aromatic acid, carbonyl compound or carbinol, which contains an amino group ortho or para to the oxygen function, undergoes hydrogenolysis to a methyl or methylene group, when it is treated with excess lithium aluminum hydride.[2a] Although this point is not established beyond doubt, the hydrogenolysis reaction appears to require the presence of a strongly electron-donating group in the ortho or para position. In support of this, it was found that *m*-aminobenzoic acid is reduced only to *m*-aminobenzyl alcohol, and ethyl benzoate to benzyl alcohol, under conditions which reduce *o*- or *p*-aminobenzoic acids to the corresponding toluidines. A possible explanation for the lack of reactivity of compounds containing active hydrogens lies in the immediate formation of an insoluble precipitate by reaction between the compound and lithium aluminum hydride. Such precipitation is marked both in the case of *m*- and *p*-aminobenzoic acid; thus here it does not seem to be the determining factor.

The hydroxyl group might be expected to promote the hydrogenolysis, just as the amino group does, but the hydroxy compounds examined—*p*-hydroxybenzoic acid, ethyl *p*-hydroxybenzoate, methyl salicylate and 2,4-dihydroxybenzaldehyde—showed no detectable amount of the expected cresol derivatives. Since mixing of the reactants in these cases resulted in virtual solidification of the reaction mixtures, the failure of these reactions may well be traceable to the precipitation phenomenon. This possibility is supported by the fact that the only methoxy compound studied, 4,4'-dimethoxybenzophenone, gave a considerable amount of 4,4'-dimethoxydiphenylmethane.

The 2-amino-5-carbethoxythiazoles were reduced to 2-amino-5-methyl compounds merely by standing in ether solution at room temperature with excess reducing agent.[2] The benzene derivatives did not give very good yields of hydrogenolysis products under these conditions; the yields were much greater, however, when the reduction was carried out in ether–dibutyl ether mixtures (sometimes containing benzene) at about 80° for several days. Temperatures above 100° were unsatisfactory, probably due to the instability of lithium aluminum hydride at these temperatures.[3]

The reduction apparently proceeds with the rapid formation of the benzyl alcohol, which undergoes hydrogenolysis to yield the oxygen-free compound. These relationships were demonstrated with methyl anthranilate I, which, treated with excess lithium aluminum hydride at 65° for



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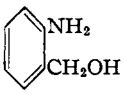

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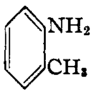

III

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[1] Abbott Laboratories Fellow, 1948–1950.

[2] Conover and Tarbell, THIS JOURNAL, **72**, in press (1950).

[2a] Witkop, *ibid.*, **72**, 614 (1950), has reported the hydrogenolysis of an *o*-aminoketone (spiro-(cyclopentane-1,2'-pseudoindoxyl)) by an excess of lithium aluminum hydride.

[3] Finholt, Bond and Schlesinger, *ibid.*, **69**, 1199 (1947).

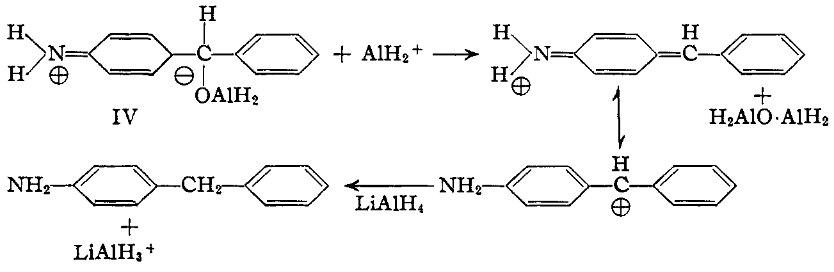
TABLE

Compound	Time and temperature	Equivalents excess $LiAlH_4$	Carbinol, %	Hydrogenolysis product, %	Isolation procedure
Anthranilic acid	22 hr. 25°	4	*o*-Aminobenzyl alcohol 83	*o*-Toluidine 3[a]	A-2
Methyl anthranilate	5 minutes 65°	4	*o*-Aminobenzyl alcohol 50	5[b]	B-2-a
Methyl anthranilate	15 hours 65°	4		39[b]	B-2-a
o-Aminobenzyl alcohol	6 days 90°	8		*o*-Toluidine 53[b]	B-2-a
p-Aminobenzoic acid	29 hours 65°	4		*p*-Toluidine 47[c]	A-1
p-Aminobenzophenone	1 hour 80°	5	*p*-Aminobenzhydrol 15[e]	*p*-Aminodiphenylmethane 57[d]	B-2-a
p-Aminobenzophenone	3 hours 80°	0.5	*p*-Aminobenzhydrol 97[e]	*p*-Aminodiphenylmethane 2	B-3-a
p,p'-Diaminobenzophenone	3 days 60°	7		*p,p'*-Diaminodiphenyl methane 32[f,g]	B-2-a
p-Dimethylaminobenzaldehyde	7 days 80°	3	[i]	N,N-Dimethyl-*p*-toluidine 78[h]	B-2-a
p,p'-Dimethoxybenzophenone	11 days 90°	Approx. 20		*p,p'*-Dimethoxydiphenylmethane 46[j]	B-1-a
m-Aminobenzoic acid	11 days 85° and lower	12	*m*-Aminobenzyl alcohol 72[k]		B-2-b

[a] Isolated as the trinitrobenzene derivative, m. p. 125–126°, and phenylthiourea derivative, m. p. 135–136°. [b] Isolated by distillation; identified as the trinitrobenzene and phenylthiourea derivative. [c] Isolated by distillation and identified as the phenylthiourea derivative, m. p. 140–140.5°. [d] Isolated crystalline, m. p. 34–35°, and as the phenylthiourea, m. p. 147–148°. [e] Isolated crystalline, m. p. 116–117°; characterized as the phenylthiourea derivative, m. p. 138–139°. *Anal.* Calcd. for $C_{20}H_{18}N_2OS$: C, 71.82; H, 5.42. Found: C, 71.65; H, 5.47. [f] On the basis of starting material consumed; 62% of the starting material was recovered. [g] Obtained crystalline, m. p. 92–93°; the m. p. is reported variously as 85 to 94°, and the corresponding benzhydrol melts at 98°. The identity of the compound was proved by reaction with benzaldehyde to form the bis-Schiff base, m. p. 125–126°, and by acetylation to the diacetyl derivative, m. p. 228–230°. Both derivatives agree with those reported for *p,p'*-diaminodiphenylmethane. [h] Identified as the TNB derivative, m. p. 123–124°, and the methiodide, 218–219°. [i] There were indications of higher-boiling material which may have been the carbinol. [j] Isolated crystalline and purified by chromatography on alumina; m. p. 52–53° (reported, 52°). [k] Obtained crystalline, m. p. 95–96°; (no *m*-toluidine, m. p. −31°, observed); m. p. of hydrochloride, 124–125°, both in agreement with the literature.

five minutes, yielded 50% of the carbinol II and 5% of the hydrogenolysis product III; when the reduction was allowed to go fifteen hours at 65°, however, using the same procedures, 39% of III was obtained and no II could be isolated. It was also shown that *o*-aminobenzyl alcohol was converted to *o*-toluidine in 53% yield after six days at 90°.

Trevoy and Brown[4] have presented evidence indicating that reduction by lithium aluminum hydride is a nucleophilic displacement by structures which furnish hydride ions. This process would readily lead to the formation of arylcarbinols from aromatic acids or carbonyl compounds. A high electron density at the substituted methylene group, as in IV, seems to favor the hydrogenolysis; this would be expected to retard nucleophilic displacement of the hydroxyl group by hydride ion, or source of hydride ion. Since the experiments on *p*-aminobenzophenone suggest a dependence of the rate of hydrogenolysis on the concentration of lithium aluminum hydride, the reaction probably does not proceed by a simple unimolecular ionization. A reasonable mechanism would involve attack on the oxygen of the carbinol derivative IV by a positive ion such as AlH_2^+ furnished by the reducing agent, followed by scission of the carbon–oxygen bond. This cleavage would be facilitated both by the amino substituent on the ring, and the attacking positive ion. The resonance stabilized carbonium ion formed by this process would rapidly pick up a hydride ion from the reducing agent.



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[4] Trevoy and Brown, THIS JOURNAL, 71, 1675 (1949); Eliel, *ibid.*, 71, 3970 (1949).

It might be expected that the electron-donating effect of the primary amino group would be greater than the tertiary amino group, because the former would be converted to a salt (–NH^-Li^+ or –$N^{--}2Li^+$), by the reagent; this effect is probably more than compensated for by the insolubility of the lithium salts in the reaction medium.

Experimental[5]

General Procedure.—The reactions were carried out in solvents dried over sodium; the lithium aluminum hydride was used in about 1.0 m. solution in diethyl ether, the concentration of which was determined by titration.[6]

For each mole of a compound being reduced the stoichiometric amount of lithium aluminum hydride was taken as that required for reaction with all the active hydrogens in the molecule, plus one equivalent more than that needed to reduce the oxygen function to a carbinol. (For example, one mole of *p*-aminobenzophenone required two equivalents (one-half mole) of lithium aluminum hydride for reaction with the amino hydrogens, one equivalent for reduction of the ketone to a carbinol, and an additional equivalent for hydrogenolysis to the diphenylmethane.)

The equivalents employed in excess of this amount are recorded in the table.

The solid products were purified by crystallization, occasionally with a preliminary extraction with ligroin to separate the product from gummy residues. The products were identified as suitable solid derivatives, which had the expected m. p.'s; in several cases, mixed m. p.'s were taken with known samples. Some of the details about identification of the products are omitted, as the compounds are well known.

Isolation Procedures (A).—To the reaction mixture was added sufficient water-saturated diethyl ether to decompose the excess lithium aluminum hydride and hydrolyze the addition complex. At least twenty-four hours were allowed for the hydrolysis to be completed. The inorganic precipitate was then filtered off, washed with ethanol and (1) discarded or (2) treated further to remove adsorbed organic material. The filtered solvent solution and ethanol washings were combined.

(B) To the reaction mixture was added (1) 10% sulfuric acid (200 cc.) or (2) 10% sodium hydroxide (200 cc.) or (3), saturated Rochelle salts (200 cc.) and 10 cc. of 5% sodium hydroxide. After hydrolysis the solvent layer was separated and the aqueous layer extracted with five 200-cc. portions of diethyl ether. The aqueous residue from the extractions was (a) discarded or (b) continuously extracted for twenty-four to forty-eight hours to obtain additional organic product.

The combined solutions from (A) or the combined extracts from (B) were dried over Drierite and the solvents removed, usually under reduced pressure.

Summary

Aromatic acids, esters, aldehydes and ketones, with an amino group ortho or para to the oxygen function, have been found to undergo hydrogenolysis by excess lithium aluminum hydride, with conversion of the oxygen function to a methyl, or methylene group, in the case of ketones. The reaction apparently goes through the intermediate formation of the benzyl alcohol, which has been shown to undergo hydrogenolysis to a methyl group. The mechanism of the reaction has been discussed.

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[5] Melting points are corrected; boiling points uncorrected.

[6] Krynitsky, Johnson and Carhart, *Anal. Chem.*, **20**, 311 (1948).

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, N. Y., AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILL.]

The Reaction of Cyclopentane with Mercury 6($^3P_1$) Atoms[1]

BY G. A. ALLEN,[2] D. L. KANTRO AND H. E. GUNNING

Investigation by Gunning and Steacie[3] of the reaction of cyclopropane with mercury 6($^3P_1$) atoms at 30.0° indicates that this reaction proceeds mainly through the initial formation of the trimethylene biradical by direct scission of a C–C bond. This differs markedly from the behavior of the paraffins,[4–8] which appear to react with mercury 6($^3P_1$) atoms at room temperature by the initial splitting of a C–H bond. Furthermore, cyclopropane contrasts strongly with the olefins[9–14] and diolefins,[11,15] whose reactions seem to proceed at the same temperature mainly by an excited molecule mechanism.

Accordingly, it was thought of interest to investigate the reaction of cyclopentane with mercury 6($^3P_1$) atoms in a static system at 30.0°, with a view to discovering whether its initial quenching process would resemble that of cyclopropane, the paraffins, or the olefins.

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[1] This work was supported in part by Contract N6-onr-241, Task I, with the Office of Naval Research, U. S. Navy, and in part by Contract AT(11-1)-43, with the U. S. Atomic Energy Commission. A portion of this paper was used as part of a dissertation submitted by G. A. A. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Rochester. Presented before the Division of Physical and Inorganic Chemistry at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

[2] Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

[3] H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **17**, 351 (1949).

[4] K. Morikawa, W. S. Benedict and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

[5] (a) E. W. R. Steacie and R. L. Cunningham, *ibid.*, **8**, 800 (1940); (b) B. de B. Darwent and E. W. R. Steacie, *ibid.*, **16**, 381 (1948); (c) E. W. R. Steacie and D. J. Dewar, *ibid.*, **8**, 571 (1940).

[6] B. de B. Darwent and E. W. R. Steacie, *ibid.*, **13**, 563 (1945).

[7] A. W. Hay and C. A. Winkler, *Can. J. Research*, **B21**, 149 (1943).

[8] B. de B. Darwent and C. A. Winkler, *J. Phys. Chem.*, **49**, 150 (1945).

[9] D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **9**, 829 (1941).

[10] D. J. LeRoy and E. W. R. Steacie, *ibid.*, **10**, 676 (1942).

[11] H. E. Gunning and E. W. R. Steacie, *ibid.*, **14**, 57 (1946).

[12] H. E. Gunning and E. W. R. Steacie, *ibid.*, **16**, 926 (1948).

[13] H. E. Gunning and E. W. R. Steacie, *ibid.*, **14**, 581 (1946).

[14] G. A. Allen and H. E. Gunning, *ibid.*, **16**, 1146 (1948).

[15] H. E. Gunning and E. W. R. Steacie, *ibid.*, **12**, 484 (1944).