Notes

Condensation of Acetylene with Aldehydes

HARRY A. STANSBURY, JR., AND WILLIAM R. PROOPS

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The condensation of acetylene with aldehydes to form secondary acetylenic alcohols has been studied extensively. The most widely used method is the reaction of sodium acetylide with the aldehyde in liquid ammonia.[1,2]

A more convenient and simpler method involves the reaction of acetylene with the aldehyde in a suspension of potassium hydroxide in nonhydroxylic ethers, such as acetals and ethylene glycol dialkyl ethers[3,4] The formation of a loose complex between potassium hydroxide and the ethereal oxygens has been suggested as the reason that the aldehyde did not form exclusively self-condensation products, as might be expected. However, the yields were good (60–71%) only when aldehydes more resistant to alkali, such as isobutyraldehyde and 2-ethylhexanal, were employed.[4] The surprisingly beneficial effect of small amounts of aliphatic alcohols on the reaction under five to ten atmospheres of acetylene pressure has been reported. Using 85% potassium hydroxide suspended in ethyl ether as the medium for the condensation of acetaldehyde with acetylene under a pressure of ten atmospheres at 0°, the addition of about 1% ethanol to the reaction mixture increased the yield of 3-butyn-2-ol from 20% to 43%.[5] In a subsequent article, these workers reported that even under twenty atmospheres of acetylene pressure, the yield of 3-butyn-2-ol was only about 40%.[6] The hazards of handling acetylene under pressure have long been recognized. We have now found that even higher yields of 3-butyn-2-ol may be obtained by operation at atmospheric pressure in the presence of potassium hydroxide suspensions in certain solvents. Very mobile and stable suspensions were prepared by grinding the potassium hydroxide at 0–10° in a cooled Waring Blendor. This procedure is more rapid and convenient than cooling the molten base from 150° while stirring in the solvent, as described by Bergmann *et al.*[4] Under optimum conditions using 85% potassium hydroxide (reagent grade) suspended in 1,2-dimethoxyethane, we were able to obtain 3-butyn-2-ol in 51% yield based on acetaldehyde. With 91.5% potassium hydroxide (technical grade) in 1,2-dimethoxyethane-dioxane mixture, the yield was 61%. Dimethylformamide and *N*-methylpyrollidone were each ineffective as solvents for this reaction.

This procedure was used to condense other aldehydes with acetylene. Other aldehydes employed and the yields of acetylenic carbinols were as follows: propionaldehyde (81%), butyraldehyde (82%), isobutyraldehyde (87%), 3-cyclohexenecarboxaldehyde (92%), 3,4-dihydro-2,5-dimethyl-2-formyl-2*H*-pyran (56%), 2-methylbicyclo[2.2.1]-5-hepten-2-carboxaldehyde (53%), 2-ethyl-2-hexenal (37%) and crotonaldehyde (22%). The following unsaturated aldehydes were condensed with acetylene under these conditions but no acetylenic alcohol could be isolated from the polymeric product: methacrolein, phenylacetaldehyde, cinnamaldehyde, and 2,4-hexadienal.

EXPERIMENTAL

A mixture of equal weights of potassium hydroxide and 1,2-dimethoxyethane was ground in a Waring Blendor at −5° for 0.5 hr. The resulting suspensions were transferred to a creased reaction flask and diluted with solvent to obtain a mixture containing 6.67 moles of potassium hydroxide and 1600 g. of 1,2-dimethoxyethane. After 11 g. of ethanol was added, the rapidly stirred suspension was saturated with acetylene at −10 to 0°. Then 3.33 moles of the aldehyde (containing 11 g. of ethanol) was added dropwise over a period of 2 hr. followed by an 0.5 hr. soaking period at −10 to 0°. A slight excess of acetylene was fed all during the reaction period. Ice water (894 g.) was added rapidly and the resulting aqueous layer was extracted with ethyl ether. The oil layer and extracts were combined, neutralized with carbon dioxide, filtered and fractionated to obtain the acetylenic alcohol.

UNION CARBIDE CHEMICALS CO.
RESEARCH DEPARTMENT
SOUTH CHARLESTON W. VA.

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[1] K. N. Campbell, B. K. Campbell, and L. T. Eby, *J. Am. Chem. Soc.*, **60**, 2882–4 (1938).

[2] E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 733–5 (1942).

[3] P. Seguin, *Bull. Soc. Chim.*, **12**, 948–9 (1945).

[4] E. D. Bergmann, M. Sulzbacher, and D. F. Herman, *J. Appl. Chem.*, **3**, 39–42 (1953).

[5] I. N. Nazarov, I. L. Kotlyarevsky, and V. F. Ryabchenko, *J. Gen. Chem. U.S.S.R.*, **23**, 2011 (1953).

[6] I. N. Nazarov, I. L. Kotlyarevsky, and V. F. Ryabchenko, *Bull. Acad. Sci. U.S.S.R., Div. Chem Sci.*, 980 (1956).

A Convenient General Method for the Preparation of Aldehydes. II

ANTHONY SISTI, JULIA BURGMASTER, AND MURRAY FUDIM

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In a previous publication[1] a new and general synthesis for the preparation of aldehydes was

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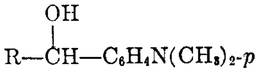
[1] M. Stiles and A. Sisti, *J. Org. Chem.*, **25**, 1691 (1960).

TABLE I

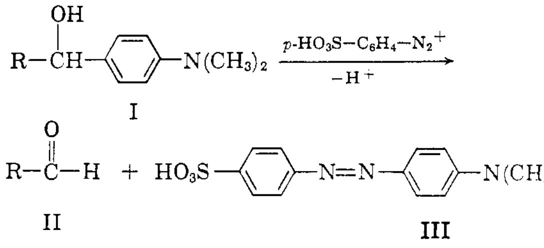
p-DIMETHYLAMINOPHENYLCARBINOLS (I)



$$R-\overset{\displaystyle OH}{\overset{|}{C}}H-C_6H_4N(CH_3)_2\text{-}p$$

R	Yield, %	M.P.	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
4-Methoxyphenyl	60	78–79	74.70	7.39	5.44	74.62	7.25	5.38
2-Methylphenyl	71	85–86	79.66	7.88	5.80	79.60	7.78	5.75
4-Methylphenyl	78	84–85	79.66	7.88	5.80	79.55	7.93	5.70
1,1-Diphenylvinyl	75	85–86	83.39	7.21	4.39	83.25	7.15	4.28
4-Pentenyl	74	34–35	76.71	9.58	6.39	76.61	9.75	6.25
n-Pentyl	71	36–37	76.02	10.40	6.33	76.15	10.60	6.20

reported. The method involved the reaction of *p*-dimethylaminophenylcarbinols with diazotized sulfanilic acid (Equation 1). The extension of this



(1)

procedure to the preparation of eleven additional aldehydes from the aromatic, aliphatic, and unsaturated aliphatic series is presented here.

This note offers further evidence that the technique has proved to be convenient for the preparation of moderate quantities of aldehydes (0.2–0.4 mole) in good yield and high purity. In addition, it substantiates the proposal[1] that the scheme is a general one, working equally well for the preparation of aliphatic, aromatic, and unsaturated aldehydes, and is relatively unaffected by steric or electrical effects in the aldehyde group.

Table I lists the aminocarbinols (I) prepared from the corresponding Grignard reagent and *p*-dimethylaminobenzaldehyde. For maximum yields of aldehydes it has been found that the aminocarbinols should be isolated and reasonably purified prior to being subjected to the cleavage reaction (Equation 1).

In Table II are listed additional examples of aldehydes prepared by the cleavage of aminocarbinols (I) by diazotized sulfanilic acid.

Presently under investigation are the extension of the method for the preparation of other representative aldehydes and the application of the method to the synthesis of a variety of ketones.

TABLE II

ALDEHYDES PREPARED BY EQUATION 1

	Yield, %	B.P./Mm., Found (Reported)	2,4-DNP,[a] M.P., Found (Reported)
4-Bromobenzaldehyde	68	M.p. 56–57 (56–57)[b]	257–258 (260–261)[c]
4-Chlorobenzaldehyde	65	63/65/2 (214–215/760)[d]	268–269 (270–271)[e]
4-Methoxybenzaldehyde	75	89–90/1.5 (245–248/760)[f]	253–254 (249–250)[g]
2-Methylbenzaldehyde	71	78–79/6 (94/10)[h]	190–193 (193–194)[i]
4-Methylbenzaldehyde	76	130–132/80 (203–205/760)[j]	233–234 (231–233)[k]
β-Phenylcinnamaldehyde	78	M.p. 46–47 (44)[l]	202–203 (196)[m]
5-Hexenal	70	118–120 (118–118.5)[n]	93–94 (93–94)[n]
Hexanal	60	128–129/750 (126–128/747)[o]	104–105 (104–105)[p]
Pentanal[q]	68	102–103/760 (102.5–103/760)[r]	98–99 (98)[p]
Octanal[q]	60	61.5–62.5/11 (65/11)[h]	104–105 (106)[p]
Heptanal[q]	75	150–151/750 (155/760)[s]	99–100 (106)[p]

[a] 2,4-Dinitrophenylhydrazone. [b] M. Koton, E. Moskvina, and F. Forinskii, *Zhur. Obshchei. Khim.*, **21**, 1843 (1951). [c] H. Snyder and G. Handrick, *J. Am. Chem. Soc.*, **66**, 1860 (1944). [d] L. Kahovec and K. Kohlrausch, *Z. Physik. Chem.*, **38**, 139 (1937). [e] J. Blanksma and M. Wackers, *Rec. trav. chim.*, **55**, 658 (1936). [f] E. Niedzielski and F. Nord, *J. Am. Chem. Soc.*, **63**, 1462 (1941). [g] A. Ainley and R. Robinson, *J. Chem. Soc.*, 369 (1937). [h] H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925). [i] F. King and H. Openshaw, *J. Chem. Soc.*, 353 (1936). [j] G. Coleman and D. Craig, *Org. Syntheses*, Coll. Vol. III, 583 (1955). [k] H. Strain, *J. Am. Chem. Soc.*, **57**, 760 (1935). [l] E. Kohler and R. Larsen, *J. Am. Chem. Soc.*, **57**, 1448 (1935). [m] H. Lorenz and R. Wizenger, *Helv. Chim. Acta*, **28**, 600 (1945). [n] M. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953). [o] G. B. Bachman, *J. Am. Chem. Soc.*, **55**, 4279 (1953) [p] C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2957 (1930). [q] The amino alcohol precursor of this aldehyde, prepared in the same manner as those in Table I, was used without purification. The yield may be taken as minimal. [r] P. Bruylants and L. Ernould, *Bull. sci. acad. roy. Belg.*, **17**, 1174 (1931) [s] M. L. Sherrill, *J. Am. Chem. Soc.*, **52**, 1991 (1930).

EXPERIMENTAL

p-Dimethylaminophenylcarbinols (I). The new aminocarbinols listed in Table I were prepared from the appropriate alkyl- or arylmagnesium bromide and *p*-dimethylaminobenzaldehyde as previously described.[1] The halides (except 1,1-diphenylvinyl bromide and 1-bromo-4-pentene) and the aldehyde were commercial products. The aminocarbinols were crystallized from benzene–petroleum ether (b.p. 30–60°) (except in the cases of 1-(4-dimethylaminophenyl)-1-pentanol, -1-hexanol, -1-heptanol, -1-octanol, and -5-hexene-1-ol, which were all crystallized from petroleum ether alone.

4-Dimethylamino-4'-bromobenzhydrol, m.p. 104–105° (reported[2] m.p. 107°), and 4-dimethylamino-4'-chlorobenzhydrol, m.p. 105° (reported[2] m.p. 103–104°), were prepared as previously described.[2] 1,1-Diphenylvinyl bromide, m.p. 49–50° (reported[3] m.p. 46–47°), and 1-bromo-4-pentene, b.p. 128–129° (reported[4] b.p. 128°), were prepared as previously described.[4]

Preparation of the aldehydes. The experimental procedure for the preparation of the aldehydes has been already described.[1]

Department of Chemistry
Adelphi College
Garden City, N.Y.

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(2) M. A. Mikailescu and P. Caragea, *Bull. sect. sci. acad. roumaine*, **12**, 7 (1929).

(3) G. Wittig, R. Kethur, A. Klein, and R. Wietbroch, *Ber.*, **69B**, 2084 (1936).

(4) C. L. Wilson, *J. Chem. Soc.*, **50** (1945).

Syntheses of Benzophenone and Benzaldehyde Methyl Ethyl and Dimethyl Acetals by an Electrolytic Method

B. Wladislaw and A. M. J. Ayres

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The electrolyses of di- and triphenylacetic acids in methanol failed to undergo the normal Kolbe reaction. Instead of the dimers, the respective methyl ethers were obtained. Working with diphenylacetic acid in methanol-pyridine V. d. Hoek and Nauta[1] obtained diphenylmethyl methyl ether in 35% yield.

Linstead, Shephard, and Weedon,[2] by electrolysis of triphenylacetic acid in methanol alone, obtained triphenylmethyl methyl ether in 60% yield. More recently, Finkelstein and Petersen[3] have obtained an improved yield (80%) of diphenylmethyl methyl ether using triethylamine instead of sodium methoxide.

No description of the electrolysis of α-alkoxy acids in methanol could be found in the literature. The study of the electrolyses of this class of compounds was initiated in order to find out whether it would lead to the acetals. Therefore some α-alkoxyphenyl- and -diphenylacetic acids have been investigated.

The electrolysis of α-methoxyphenylacetic acid in absolute methanol afforded in 61.6% yield of benzaldehyde dimethyl acetal. When α-methoxydiphenylacetic acid was electrolyzed, in a similar way, benzophenone dimethyl acetal was obtained in 74% yield.

It seemed that the anodic methoxylation could be also a possible route to the mixed acetals, which have been described very rarely in the literature. In fact, when α-ethoxyphenylacetic acid was electrolyzed in absolute methanol, benzaldehyde methyl ethyl acetal was obtained in 71.4% yield. The electrolysis of α-ethoxydiphenylacetic acid afforded benzophenone methyl ethyl acetal in 74% yield.

Work is under way to find out to what extent this method might be applied to the syntheses of aliphatic aldehyde and ketone acetals and of the thio analogs.

EXPERIMENTAL

All melting and boiling points are uncorrected.

Preparation of the alkoxy acids and their intermediates. α-Methoxyphenylacetic acid (m.p. 67–70°) was prepared by reaction of mandelic acid with dimethyl sulfate, using the procedure described by Reeve and Christoffel.[4]

Methyl α-methoxydiphenylacetate (b.p. 166–167/1 mm.) was prepared by reaction of benzilic acid with phosphorus pentabromide, followed by addition of absolute methanol, using the procedure described by Klinger and Nickell.[5]

α-Methoxydiphenylacetic acid (m.p. 107–110°) was prepared by stirring of the corresponding ester with excess aqueous potassium hydroxide solution (40%) for 25 hr. The melting points of 111–112°[6] and 107°[7] have been reported for this acid.

α-Ethoxyphenylacetic acid (b.p. 172°/17 mm.) was prepared by reaction of benzilic acid with ethyl iodide and silver oxide, following the indication of Mackenzie.[8]

Ethyl α-bromodiphenylacetate was prepared by treatment of ethyl benzilate with phosphorus tribromide and bromine, using the method described by Carothers.[9]

Ethyl α-ethoxydiphenylacetate. The crude ethyl α-bromodiphenylacetate (34 g.) was stirred with absolute ethanol (218 ml.) for 3 hr. The distillation of the residue afforded a liquid (27.6 g., 91% yield), b.p. 150°/ 1 mm.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.0; H, 7.0. Found: C, 76.2; H, 6.9.

α-Ethoxydiphenylacetic acid. Ethyl α-ethoxydiphenylacetate (9 g.) was heated under reflux for 5 hr. with potassium hydroxide (7.6 g.) in absolute ethanol (72 ml.). The solution, worked up in the usual way, gave α-ethoxydiphenylacetic acid (7.7 g., 95% yield), m.p. 113–116° (from carbon disulfide–light petroleum). A m.p. of 113–114° has been reported for this acid.[10]

Electrolyses procedure. The electrolysis cell consisted of a cylindrical glass vessel contining two parallel platinum plate electrodes, placed 1–2 mm. apart. They measured 3.5 × 2.5 cm. In each case absolute methanol was used, to which sufficient sodium had previously been added to neutralize about 3% of the acid. While the cell was cooled in an ice bath, a current of 1.2 amp. was passed until the electrolyte became slightly alkaline. This process usually required about twice as long as expected considering the current and the amount of acid employed.

Electrolysis of α-methoxyphenylacetic acid. The solution of α-methoxyphenylacetic acid (8.1 g.) in methanol (180 ml.), was electrolyzed. The solvent was evaporated under re-

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(1) A. J. v. d. Hoek and W. T. Nauta, *Rec. trav. chim.*, **61**, 845 (1942).

(2) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3624 (1952).

(3) M. Finkelstein and R. C. Petersen, *J. Org. Chem.*, **25**, 136 (1960).

(4) W. Reeve and J. Christoffel, *J. Am. Chem. Soc.*, **72**, 1482 (1950).

(5) H. Klinger and G. Nickell, *Ann.*, **390**, 365 (1912); H. Klinger, *Ann.*, **390**, 371 (1912).

(6) H. Staudinger and St. Bereza, *Ann.*, **380**, 271 (1911).

(7) K. Ziegler and F. Thielmann, *Ber.*, **56**, 1741 (1923).

(8) A. Mackenzie, *J. Chem. Soc.*, 753 (1899).

(9) W. H. Carothers, *J. Am. Chem. Soc.*, **48**, 3195 (1926).

(10) H. Klinger, *Ann.*, **390**, 371 (1912).