reagent, since the resulting derivatives have definite melting points and are so readily obtained in pure form from small amounts of materials.

Summary

A number of new nitrogen substituted barbituric acids and some of their derivatives have been described.

Diphenylformamidine is suggested as an identifying reagent for nitrogen substituted barbituric acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation of Dialkylacetylenes from Acetylenic Grignard Reagents and Alkyl Sulfates[1]

BY S. DOLORETTA THORN, G. F. HENNION AND J. A. NIEUWLAND

Introduction

As a part of our study of the chemistry of the alkylacetylenes we have been interested for some time in methods of obtaining these conveniently and in pure condition. This paper reports a method for preparing the straight-chain dialkylacetylenes through the agency of the Grignard reagent.

The literature reveals that dialkylacetylenes have been prepared by alkylation of sodium acetylide, by various desaturation reactions and by molecular rearrangement of alkylacetylenes.[2,3] Grignard and Tcheoufaki reported[4] that acetylene monomagnesium bromide and dimagnesium bromide react with alkyl halides to form mono and dialkylacetylenes, respectively, in varying yield.

In our experience the monoalkylacetylene Grignard reagents are quite inert to the simple alkyl halides. In one instance amylacetylene magnesium bromide was refluxed with methyl iodide in dry ether for several weeks without observing alkylation of the Grignard reagent. Attempts to catalyze the reaction with various metals and (or) their salts[5] proved futile. Repetition of the experiment using a mole of methyl sulfate in place of methyl iodide resulted in a vigorous reaction. After treating the product in the usual way, amylacetylene was recovered unchanged. It was subsequently found that the use of two moles of alkyl sulfate per mole of acetylenic Grignard reagent effected smooth alkylation yielding the dialkylacetylene in satisfactory yield. This is in accord with the experience of Cope[6] and Suter and Gerhart[7] who investigated quantitatively the reaction of alkyl sulfates with other Grignard reagents.

By analogy with the work of these investigators, the equations for the main reactions involved are probably the following

$$2\mathrm{R{-}C{\equiv}C{-}MgBr} + 2(\mathrm{C_2H_5})_2\mathrm{SO_4} \longrightarrow (\mathrm{R{-}C{\equiv}C})_2\mathrm{Mg} + \mathrm{Mg(C_2H_5SO_4)_2} + 2\mathrm{C_2H_5Br}$$

$$(\mathrm{R{-}C{\equiv}C})_2\mathrm{Mg} + 2(\mathrm{C_2H_5})_2\mathrm{SO_4} \longrightarrow 2\mathrm{R{-}C{\equiv}C{-}C_2H_5} + \mathrm{Mg(C_2H_5SO_4)_2}$$

It is likely, however, that the following reactions also occur to some extent giving rise to the same products

$$\mathrm{R{-}C{\equiv}C{-}MgBr} + (\mathrm{C_2H_5})_2\mathrm{SO_4} \longrightarrow \mathrm{R{-}C{\equiv}C{-}MgOSO_3C_2H_5} + \mathrm{C_2H_5Br}$$

$$\mathrm{R{-}C{\equiv}C{-}MgOSO_3C_2H_5} + (\mathrm{C_2H_5})_2\mathrm{SO_4} \longrightarrow \mathrm{R{-}C{\equiv}C{-}C_2H_5} + \mathrm{Mg(C_2H_5SO_4)_2}$$

Both sets of equations add to the following

$$\mathrm{R{-}C{\equiv}C{-}MgBr} + 2(\mathrm{C_2H_5})_2\mathrm{SO_4} \longrightarrow \mathrm{R{-}C{\equiv}C{-}C_2H_5} + \mathrm{C_2H_5Br} + \mathrm{Mg(C_2H_5SO_4)_2}$$

Since the procedure used in the preparation of the dialkylacetylenes was uniform, only one typical procedure is described. The physical constants for these compounds are given in Table I. In this table R′ is the group originating in the alkyl sulfate.

Experimental

Reagents.—The alkylacetylenes used were prepared by the action of the appropriate alkyl halide on sodium acetylide in liquid ammonia. The ethyl bromide and alkyl sulfates were Eastman Kodak Company products.

Reaction of Ethyl Sulfate with Butylacetylene Magnesium Bromide.—To ethylmagnesium bromide (0.5 mole), prepared in the usual manner, 41 g. (0.5 mole) of *n*-butyl-

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[1] Tenth paper on the chemistry of the alkylacetylenes and their addition compounds; previous paper, THIS JOURNAL, **58**, 611 (1936).

[2] Béhal, *Ann. chim.*, [6] **15**, 408–432 (1888).

[3] Bourguel, *ibid.*, [10] **3**, 191–235 (1925).

[4] Tcheoufaki, *Contr. Inst. Chemi. Natl. Acad. Peiping*, **1**, 127–149 (1934).

[5] *Cf.* previous paper in this series.

[6] Cope, THIS JOURNAL, **56**, 1578 (1934).

[7] Suter and Gerhart, *ibid.*, **57**, 107 (1935).

TABLE I

PHYSICAL PROPERTIES OF R—C≡C—R′

Nature of R	Nature of R′	B. p., °C.	Mm.	d^{20}_4	$n^{20}D$	MR Calcd.	MR Found
CH_2=CH—	C_2H_5—	83	747	0.748	1.4523	27.44	28.84
C_4H_9—	CH_3—	110–111	747	.748	1.4230	32.53	32.72
C_4H_9—	C_2H_5—	129–130	747	.748	1.4261	37.15	37.62
C_5H_{11}—	C_2H_5—	153–155	745	.765	1.4299	41.77	41.80
C_6H_{13}—	CH_3—	155–156	747	.769	1.4331	41.77	41.85

acetylene diluted with its own volume of dry ether was added dropwise with constant stirring by means of a mercury-sealed motor-driven stirrer. The mixture was allowed to stand overnight and then refluxed with stirring for two and one-half hours. To this preparation was added slowly 170 g. (1.1 moles) of ethyl sulfate diluted with ether. The mixture was again refluxed with stirring for twelve hours. At the end of that time, some of the ether and ethyl bromide formed was removed by distillation through an efficient fractionating column. When the reaction mixture had become quite pasty it was treated with cold dilute hydrochloric acid sufficient to dissolve all solid. The organic layer was removed, washed with distilled water and then with 250 ml. of 20% sodium hydroxide and dried over calcium chloride to which a few pellets of potassium hydroxide had been added. Fractionation gave 38.4 g. (70% yield) of octine-3, b. p., 130–131 at 745 mm.

The product was frequently contaminated with sulfur dioxide which was easily removed, however, by washing with dilute alkali followed by drying and redistillation.

In the preparation of ethylvinylacetylene, the vinylacetylene was passed as a gas into the ethylmagnesium bromide contained in a three-necked flask fitted with a liquid ammonia condenser.[8] The vinylacetylene magnesium bromide was treated with ethyl sulfate and the product purified as described above.

Summary

A number of dialkylacetylenes have been prepared by alkylation of acetylenic Grignard reagents with alkyl sulfates.

[8] Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

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The Mechanism of Carbohydrate Oxidation. XIX. The Preparation of Disaccharide Antipodes

BY LEONARD C. KREIDER AND WM. LLOYD EVANS

Beginning with the classical work of Emil Fischer on the configuration of the sugars, chemists have been deeply interested in the synthesis of the optical antipodes of the carbohydrates, compounds in which the characteristic physical constants of each member of the pair are exactly like those of the other member, save only the constants relating to optical properties, in which case the numerical values are identical, but carry the opposite sign. Among the carbohydrates many examples of optical antipodes have been prepared in the monosaccharide series and in the simple glycosides of the monosaccharides. Optical antipodes among the disaccharides are theoretically possible, but a search of the literature failed to disclose any known examples. It occurred to the authors that if a molecule of the optically inactive keto-triose, dihydroxyacetone, could be joined in true biosidic linkage with a molecule of the *d*-form of an optically active monose a true optically active disaccharide would result. Then if dihydroxyacetone could be joined in the same manner to the *l*-form of the same optically active monose, a second optically active disaccharide would be formed which should be *the exact optical antipode of the first.*

Four recent events made the preparation of such disaccharide pairs possible: (1) the preparation of dihydroxyacetone mono-acetate;[1] (2) an improved method for the preparation of *d*-arabinose;[2] (3) an improved method for the preparation of *l*-xylose[3] which resulted from research on vitamin C and (4) evidence that dihydroxyacetone can be incorporated readily as a constituent of a disaccharide.[4]

The experimental part that follows describes

[1] H. O. L. Fischer, E. Baer and L. Feldmann, *Ber.*, **63**, 1732 (1930).

[2] R. C. Hockett and C. S. Hudson, THIS JOURNAL, **56**, 1632 (1934).

[3] L. Vargha, *Ber.*, **68**, 18 (1935); H. Appel, *J. Chem. Soc.*, 425 (1935).

[4] L. C. Kreider and W. L. Evans, THIS JOURNAL, **57**, 229 (1935).