varied from 19 to 23%. Biphenyldiphenylmethane, if present, could not be recovered in these experiments due perhaps to difficulty in crystallization.

In another series of experiments, the powdered, ether-free Grignard reagent was suspended in the solvent, the triphenylchloromethane dissolved in the same solvent was added, and the mixture shaken at room temperature for at least two days. Approximately three times the theoretical amount of the reagent was used as before, and the same color effect was observed. Five solvents were tried and the yields of tetraphenylmethane and biphenyldiphenylmethane, respectively, were as follows: in benzene (8 runs), 21 to 29%, 13 to 35%; in toluene, 25, 9%; in bromobenzene, 24, 9%; in ethylene dichloride, 20, 8%; in dioxane (3 runs), 17 to 22%, 33 to 49%.

In several of the benzene runs, the uncrystallizable residues were distilled in a molecular still[10] at a temperature below 200° and at a pressure of 0.001 mm., no evidence of decomposition being noted. In addition to tetraphenylmethane and biphenyldiphenylmethane, the following compounds were isolated from the distillates and identified by mixed melting points with authentic samples: triphenylmethane, 2 to 14% yield; dibiphenylphenylmethane, 2.5 to 3.5% yield; 4-phenyl-tetraphenylmethane, 0.5 to 0.8% yield; tribiphenylmethane and three unidentified compounds in traces.

Trisubstituted Tetraphenylmethanes.—In each case, an ether solution of phenylmagnesium bromide in excess was added at room temperature to a benzene solution of the appropriate triarylchloromethane. The reaction mixture was decomposed in the usual manner, the product steam distilled and the residue crystallized from benzene plus petroleum ether. Only one compound was isolated in each case.

Tetraphenylmethane	Yield, %	M. p., °C.	Crystalline form
4,4′,4″-tribromo[a]	43–45	234–235	Needles
4,4′,4″-trichloro[a]	38–49	207–207.5	Needles
4,4′,4″-trimethyl[b]	31–41	177–178	Needles

	Analyses, %					
	Calcd.			Found		
Formula	C	H	Halogen	C	H	Halogen
$C_{25}H_{17}Br_3$	53.87	3.08	43.05	53.97	3.04	42.73
$C_{25}H_{17}Cl_3$	70.84	4.04	25.12	70.40	4.11	25.16
$C_{28}H_{26}$	92.76	7.24		92.40	7.17	

[a] Insoluble in ether and cold benzene, somewhat soluble in carbon tetrachloride, and slightly soluble in hot acetic acid. [b] Soluble in benzene and in hot acetic acid.

Summary

The reaction between triphenylchloromethane and phenylmagnesium bromide has been discussed. With ether-free Grignard reagent, a yield of 25 to 30% of tetraphenylmethane is obtained.

The difference in the yields of tetraphenylmethane obtained under different conditions is explained on the basis of a shifting of the equilibrium between the benzenoid and the quinonoid modification of triphenylchloromethane.

ANN ARBOR, MICHIGAN RECEIVED FEBRUARY 7, 1936

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[10] Hickman and Sandford, *J. Phys. Chem.*, **34**, Fig. 6, 643 (1930).

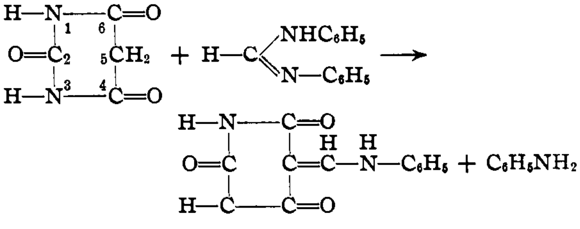
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MISSOURI]

Some Nitrogen Substituted Barbituric Acids and their Derivatives[1]

BY DOROTHY NIGHTINGALE AND CLAUDE H. ALEXANDER

In order to study some reactions of a series of aryl nitrogen substituted barbituric acids, it was necessary to prepare and identify a number of these acids not described in the literature. Whiteley[2] has prepared 1,3-diphenylbarbituric acid and 1,3-diphenyl-2-thiobarbituric acid. Macbeth, Nunan and Traill[3] have prepared 1-phenylbarbituric acid. For identification, the 5,5-bis-*p*-nitrobenzyl, 5-cinnamylidene and 5-anilinomethylene derivatives of these barbituric acids were prepared.

The reaction of barbituric acid and formamidines has been studied extensively in this Laboratory by Professor Sidney Calvert and his students, and was first described by W. N. Jones.[4] The 5-anilinomethylene barbituric acid is formed from barbituric acid and diphenylformamidine as follows



Experimental

The malonyl chloride procedure of Whiteley was used in preparing and purifying the nitrogen-

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[1] Abstract of a thesis submitted by Claude Hudson Alexander in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Whiteley, *J. Chem. Soc.*, **91**, 1330 (1907); *Proc. Chem. Soc.*, **25**, 121 (1909).

[3] Macbeth, Nunan and Traill, *ibid.*, **1248** (1926).

[4] Webster N. Jones, Thesis, University of Missouri, 1909.

substituted barbituric acids, using 0.2 molecular quantities of malonyl chloride and of substituted urea. The malonyl chloride was prepared by the directions of Staudinger and Bereza.[5] The yields averaged about 50%. It is not necessary that all of the urea be in solution when the malonyl chloride is added, but all reagents must be anhydrous and the solids finely pulverized, especially in the preparation of the malonyl chloride. The thioureas tend to yield tarry products from which it is often impossible to obtain crystals.

TABLE I

Barbituric acid derivative	Formula	M. p., °C.	% Nitrogen Calcd.	% Nitrogen Found
1-*p*-Tolyl	$C_{11}H_{10}N_2O_3$	244	12.84	12.87
1,3-Di-*p*-tolyl	$C_{18}H_{18}N_2O_3$	213	9.09	9.05
1,3-Di-*o*-tolyl	$C_{18}H_{18}N_2O_3$	171	9.09	8.96
1-*p*-Phenetyl	$C_{12}H_{12}N_2O_4$	211	11.29	11.23
1,3-Di-*p*-phenetyl	$C_{20}H_{20}N_2O_5$	167	7.61	7.50
1,3-Di-*o*-tolyl-2-thio	$C_{18}H_{18}N_2O_2S$	217	8.64	8.55

Aryl Nitrogen Barbituric Acids and *p*-Nitrobenzyl Bromide.—Lyons and Dox[6] have shown that *p*-nitrobenzyl bromide reacts with the alkyl barbituric acids having replaceable hydrogen and suggest it as a reagent for their identification. The following 5,5-bis-*p*-nitrobenzyl derivatives of the aryl nitrogen substituted barbituric acids were prepared and purified according to their directions, using 0.01 mole of acid and 0.02 mole of *p*-nitrobenzyl bromide. The melting points of most of these derivatives are too high for convenience.

TABLE II

Barbituric acid used	5,5-Bis-*p*-nitrobenzyl derivatives Formula	M. p.	% Nitrogen Calcd.	% Nitrogen Found
1-Phenyl	$C_{24}H_{18}N_4O_7$	>295	11.82	12.04
1,3-Diphenyl	$C_{30}H_{22}N_4O_7$	>300	10.16	10.01
1-*p*-Tolyl	$C_{25}H_{20}N_4O_7$	245	11.48	11.43
1,3-Di-*p*-tolyl	$C_{32}H_{26}N_4O_7$	>300	9.69	9.75
1,3-Di-*o*-tolyl	$C_{32}H_{26}N_4O_7$	>300	9.69	9.57
1-*p*-Phenetyl	$C_{26}H_{22}N_4O_8$	240	10.81	11.00

Aryl Nitrogen Barbituric Acids and Cinnamaldehyde.—Whiteley[2] describes a number of aldehyde derivatives of 1,3-diphenylbarbituric acid and 1,3-diphenyl-2-thiobarbituric acid. Cinnamaldehyde was used in this study, since its condensation products are only slightly soluble in hot alcohol and separate rapidly from solution after a few minutes of heating. The barbituric acid was dissolved in hot alcohol and a slight excess of cinnamaldehyde added. The bright yellow crystals (brick red in the case of 1,3-di-*o*-tolyl-2-thiobarbituric acid) of the 5-cinnamylidenebarbituric acid were separated from the hot solution by filtration and washed with hot alcohol. The yields are nearly quantitative and enough derivative for melting points can be obtained from 0.2 g. of acid. Unfortunately, most of these cinnamylidene derivatives begin definitely to decompose within about 5° of the temperatures of complete decomposition given in Table III, and the temperature seems to vary somewhat with the rate of heating.

TABLE III

Barbituric acid used	5-Cinnamylidene derivatives Formula	M. p.	% Nitrogen Calcd.	% Nitrogen Found
1-Phenyl	$C_{19}H_{14}N_2O_3$	271	8.81	8.84
1-*p*-Tolyl	$C_{20}H_{16}N_2O_3$	275	8.43	8.48
1,3-Di-*p*-tolyl	$C_{27}H_{22}N_2O_3$	260	6.64	6.72
1,3-Di-*o*-tolyl	$C_{27}H_{22}N_2O_3$	223	6.64	6.60
1-*p*-Phenetyl	$C_{21}H_{18}N_2O_4$	258	7.74	7.73
1,3-Di-*o*-tolyl-2-thio	$C_{27}H_{22}N_2O_2S$	248	6.39	6.44

Aryl Nitrogen Barbituric Acids and Diphenylformamidine.—In this study, only diphenylformamidine has been used, since it is so easily prepared and reacts rather more readily with the barbituric acids than do most of the substituted formamidines. It yields the 5-anilinomethylene derivatives. The compounds described in Table IV are prepared as follows: 0.01 mole of the barbituric acid is dissolved in hot alcohol, 0.01 mole of diphenylformamidine is added and the solution heated. In most cases, the pale yellow needles of the pure 5-anilinomethylene derivative separate rapidly from the hot solution. The crystals are collected on a filter and washed with hot alcohol. Yields are nearly quantitative and sufficient condensation product for melting points can be obtained from 0.2 g. of acid. The compounds melt with only slight decomposition.

TABLE IV

Barbituric acid used	5-Anilinomethylene derivative Formula	M. p., °C.	% Nitrogen Calcd.	% Nitrogen Found
1-Phenyl	$C_{17}H_{13}N_3O_3$	271	13.69	13.86
1,3-Diphenyl	$C_{23}H_{17}N_3O_3$	228	10.97	10.77
1-*p*-Tolyl	$C_{18}H_{15}N_3O_3$	290	13.09	13.06
1,3-Di-*p*-tolyl	$C_{25}H_{21}N_3O_3$	258	10.22	10.17
1,3-Di-*o*-tolyl	$C_{25}H_{21}N_3O_3$	198	10.22	10.14
1-*p*-Phenetyl	$C_{19}H_{17}N_3O_4$	248	11.97	11.95
1,3-Di-*p*-phenetyl	$C_{27}H_{25}N_3O_5$	207	8.91	8.86
1,3-Diphenyl-2-thio	$C_{23}H_{17}N_3O_2S$	>300	10.52	10.48
1,3-Di-*o*-tolyl-2-thio	$C_{25}H_{21}N_3O_2S$	237	9.83	9.79

Of these three classes of reagents, diphenylformamidine is the most satisfactory as an identifying

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(5) Staudinger and Bereza, *Ber.*, **41**, 4461 (1908).

(6) Lyons and Dox, THIS JOURNAL, **51**, 288 (1929).

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.

COLUMBIA, MISSOURI RECEIVED FEBRUARY 4, 1936

[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

$$\mathrm{2R{-}C{\equiv}C{-}MgBr + 2(C_2H_5)_2SO_4 \longrightarrow (R{-}C{\equiv}C)_2Mg + Mg(C_2H_5SO_4)_2 + 2C_2H_5Br}$$

$$\mathrm{(R{-}C{\equiv}C)_2Mg + 2(C_2H_5)_2SO_4 \longrightarrow 2R{-}C{\equiv}C{-}C_2H_5 + Mg(C_2H_5SO_4)_2}$$

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

$$\mathrm{R{-}C{\equiv}C{-}MgBr + (C_2H_5)_2SO_4 \longrightarrow R{-}C{\equiv}C{-}MgOSO_3C_2H_5 + C_2H_5Br}$$

$$\mathrm{R{-}C{\equiv}C{-}MgOSO_3C_2H_5 + (C_2H_5)_2SO_4 \longrightarrow R{-}C{\equiv}C{-}C_2H_5 + Mg(C_2H_5SO_4)_2}$$

Both sets of equations add to the following

$$\mathrm{R{-}C{\equiv}C{-}MgBr + 2(C_2H_5)_2SO_4 \longrightarrow R{-}C{\equiv}C{-}C_2H_5 + C_2H_5Br + Mg(C_2H_5SO_4)_2}$$

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).