The Identification of 2-Methyl-1,4-naphthoquinone

BY ARMANDO NOVELLI AND JOSE S. CONTICELLO

2,4-Dinitrophenylhydrazine was proposed by Novelli[1] as a very sensitive reagent for 2-methyl-1,4-naphthoquinone (menadione), and it has been used for quantitative determinations.[2]

The reaction involves some inconvenience in that the colored substance formed is insoluble in water, and must be extracted with amyl alcohol; furthermore, when the amount of menadione is very small, the yellow color of 2,4-dinitrophenylhydrazine interferes with the green color of the reaction product. In order to avoid these disadvantages, we have tried other arylhydrazines of which the *p*-carboxy- and *p*-sulfonphenylhydrazine were the most convenient. The first is used in 1% alcoholic solution, and the latter in cold, saturated aqueous solution.

The reaction is carried out as follows: to 0.1–1 ml. of the solution of menadione, add 1 ml. of either of the reagent solutions, heat at 70–80° for ten minutes, cool and add 1 ml. of 1% sodium hydroxide solution. The reddish-violet color which appears is stable and its intensity is strictly proportional to the concentration of quinone present. One γ can be detected in this way.

(1) Novelli, *Science*, **93**, 358 (1941).

(2) Vonesch, *An. Farm. y Bioquim.*, **12**, 10 (1941); Giral and Iglesias, *Ciencia*, **3**, 157 (1942); Menotti, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 418 (1942).

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p-Dimethylamino Derivatives of Nitrostyrene

BY DAVID E. WORRALL AND LEO COHEN

Since a nitrostyrene containing a basic substituent has not as yet been described, we have condensed dimethylaminobenzaldehyde with two nitroparaffins and examined the products. The presence of the substituted amino group increases the ease of the condensation, inhibits the tendency to polymerize so characteristic of nitrostyrene itself and to a marked extent deepens the color of the resulting unsaturated nitro compound. It also destroys the weak additive capacity of the conjugated unsaturated system for organic bases.

Experimental

1-Nitro-2-(*p*-dimethylaminophenyl)-ethene.—A mixture of 14.9 g. (0.1 mole) *p*-dimethylaminobenzaldehyde and 18.3 g. (0.03 mole) nitromethane was placed in a flask which was then heated on a water-bath until a dark green solution resulted. Then 0.43 g. of amylamine was added. On heating the mixture for one minute, the solution turned dark brown, solidifying within twenty minutes to a red crystalline mass. The mixture was filtered after standing overnight. The residue recrystallized from 2-nitropropane yielded 16 g. of sparkling, ruby red plates, m. p. 179–180.5°.

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.5; H, 6.3. Found: C, 62.2; H, 6.4.

It dissolved readily in hydrochloric acid, presumably through salt formation. The colorless solution became red on further dilution with water. Concentrating the acid solution produced colorless crystals which rapidly became discolored when attempts were made to isolate them. The original substance was only sparingly soluble in the common solvents but dissolved readily in the nitroparaffins on heating. Attempts to polymerize the substance by alkaline reagents or to add *p*-toluidine failed. A crystalline product was obtained by careful heating with an excess of phenylhydrazine. It was identified through analysis and a mixed melting point as the phenylhydrazone of dimethylaminobenzaldehyde.

1-Nitro-2-bromo-2-(*p*-dimethylaminophenyl)-ethene.—A mixture of 1.4 g. of the nitro compound and 1.2 g. of bromine in 10 cc. of chloroform was heated under a reflux condenser for thirty minutes followed by several hours exposure to sunlight. After concentration to a small volume at room temperature, the resulting light yellow needles were separated, washed with ether and immediately warmed on a water-bath for half an hour with alcoholic potassium acetate. The mixture was poured into a large volume of ice water. The product separated from alcohol as dark red platelets, m. p. 121°.

Anal. Calcd. for $C_{10}H_{11}BrN_2O_2$: Br, 29.5. Found: Br, 29.1.

2-Nitro-1-(*p*-dimethylaminophenyl)-1-propene.—A similar condensation of the aldehyde and nitroethane after several days produced a fair yield of red plate-like crystals, m. p. 118–120°.

Anal. Calcd. for $C_{11}H_{14}N_2O_2$: C, 64.1; H, 6.8. Found: C, 64.1; H, 6.8.

Attempts to condense nitropropane failed.

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Trimethyl Silane and Trimethyl Silicon Chloride

BY A. G. TAYLOR AND B. V. DE G. WALDEN

Mono- and dimethyl silicon chlorides have been described by Gilliam, Liebhafsky and Winslow[1] who drew attention to their b. p.'s in relation to tetramethyl silane and silicon tetrachloride. Referring to work in the same laboratory the b. p.'s are given by Rochow[2] as 66.0–67.0° at 766 mm. for the monomethyl and 69.0–70.2° at 744.5 mm. for the dimethyl derivative.

These authors used the reaction between silicon tetrachloride and magnesium methyl chloride to prepare mixtures of monomethyl silicon trichloride, dimethyl silicon dichloride and trimethyl silicon chloride, together with ether, from which by fractionation they isolated specimens corresponding in composition and vapor density fairly closely with monomethyl silicon trichloride and dimethyl silicon dichloride.

We have prepared trimethyl silicon chloride by direct chlorination of trimethyl silane which was made from silicochloroform. This method previously has been used by Kraus and Nelson[3] for the preparation of triethyl silane and triethyl silicon bromide.

(1) Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1941).

(2) Rochow, U. S. Patent 2,286,763 (1942).

(3) Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934).

Experimental

Silicochloroform.—This was prepared by the action of hydrogen chloride gas on ferrosilicon containing 95–97% silicon.[4,5] The volatile products were condensed by alcohol and solid carbon dioxide and a fraction (75%) boiling between 28 and 36° was refractionated and a fraction boiling close to 31.8° collected (44.6% of original condensate).

Anal. Silicon and chlorine were determined after reaction with water as silica and hydrogen chloride. Calcd.: Si, 20.72; Cl, 78.53. Found: Si, 20.2, 20.6, 20.6; Cl, 79.6, 78.7, 78.7.

Trimethyl Silane.—To 500 cc. of an ether solution containing 175 g. of methylmagnesium bromide was added slowly with strong cooling and stirring 60 g. of silicochloroform in 150 cc. of ether. The reflux condenser was cooled by circulating cold brine. After completion of the reaction, the reflux condenser was allowed to rise to room temperature and connection made to a cooled receiver through another condenser cooled by alcohol and solid carbon dioxide. Cooled dilute sulfuric acid was added slowly and trimethyl silane together with some ether distilled over. Concentrated sulfuric acid was added to the receiver and allowed to stand cold overnight. Trimethyl silane was then distilled off; b. p. uncor. 9 to 11°. A small amount of dissolved gas assumed to be methane was lost below 0°. The yield was poor. In each of several experiments 15 cc. of trimethyl silane was obtained from 40 cc. of silicochloroform.

Trimethyl Silicon Chloride.—Trimethyl silane was treated at −20° with chlorine and then allowed to stand at room temperature until most of the hydrogen chloride had escaped. A fraction boiling between 58 and 63° was collected and redistilled and collected between 57 and 59.4° at 747 mm. This represented 75% of the original total. There was a small residue, non-volatile at 100°, left from the first distillation.

Anal. Silicon content by adding concd. sulfuric acid, warming, then adding concd. nitric acid and finally weighing silica. Cl content by hydrolyzing and titration. Calcd.: Si, 25.85; Cl, 32.67. Found: Si, 25.4, 25.9, 25.8, 25.6; Cl, 32.1, 32.2, 33.0. Taking CH_3 by difference, the mean percentages correspond to $(CH_3)_{2.99}SiCl_{1.00}$.

Vapor Pressure of Trimethyl Silicon Chloride.—This was determined by the method of Smith and Menzies.[6] Temperatures were read on a thermometer corrected by reference to the b. p.'s of purified ether, carbon tetrachloride, and water. Interpolation by least squares gives

t, °C.	28.9	35.3	40.0	45.2	49.8	55.0	56.1
p, mm.	308	366	427	481	575	676	725

$\log_{10}p = 6.926 - 1344/T$. The b. p. at 760 mm. is calculated to be 59°; density, d^{25}_4, 0.846; freezing point, approx. −40°.

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(4) Buff and Wöhler, *Ann.*, **104**, 94 (1857).

(5) Booth and Stillwell, THIS JOURNAL, **56**, 1529 (1934). Other references are given in this paper.

(6) Smith and Menzies, *ibid.*, **32**, 897 (1910).

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The Viscosity of the Methyl Ester of Dilinoleic Acid

BY DAVID W. YOUNG AND RUTH E. BIERTUEMPFEL

The purpose of this note is to present viscosity measurements on a pure sample of methyl dilinoleate over a range of temperature from −40 to 212°F. (−40–100°C.).

Experimental Procedure

The ester used for this work had been purified by double distillation in a molecular still by Dr. John C. Cowan in the Northern Regional Research Laboratory. The ester had an index of refraction of n^{30}_D 1.4766. Recently the method used to formulate and purify the methyl dilinoleate from soybean oil has been reported.[1]

The kinematic viscosity method used in the study is intended for determining the viscosity of any product which is a true viscous liquid at the temperature of the test. The viscometers available were the Ubbelohde type with one capillary tube. Care was taken to calibrate each viscometer against standard oils of known viscosity as determined in the National Bureau of Standards. The viscosity method is given under American Society for Testing Materials, Designation D 445-42 T.

For the viscosity determination at −40° the procedure given by Baldeschwieler and Wilcox[2] was used.

Results

Experimental results are listed in Table I and Fig. 1. A straight line relationship exists when kinematic viscosity is plotted as a function of temperature on A. S. T. M. tentative viscosity-temperature chart (D 341-37 T). The temperature coördinate has been extended 10°, that is, to −40°, in order to present complete data.

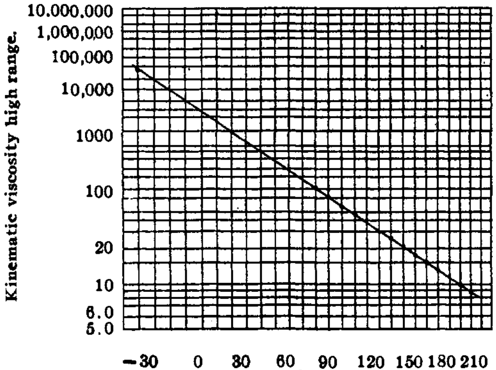

Fig. 1.

TABLE I

KINEMATIC VISCOSITY OF METHYL DILINOLEATE

Temp., °F.	Viscosity in centistokes
−40	42,464
80	102.5
90	78.3
100	60.0
110	48.0
140	25.4
150	21.1
160	17.8
170	15.2
180	13.1
200	10.0
210	8.70

It was held that these results would be of interest as the pure material is rather difficult to

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(1) Cowan and Wheeler, THIS JOURNAL, **66**, 84 (1944).

(2) Baldeschwieler and Wilcox, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 221 (1939).