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

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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).