Acknowledgment. The author acknowledges with gratitude the assistance given by Dr. J. D. Edwards of the Veteran's Administration Hospital, Houston, Tex., and the Perkin Elmer Corp. for preparing infrared spectrograms. The author wishes to thank the Research Corp. for the financial support without which this study would not have been possible.

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Some Reactions of 2,6-Dimethyl-4-pyrone

L. L. WOODS

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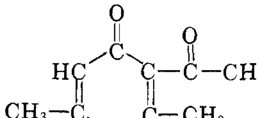
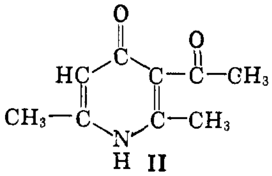
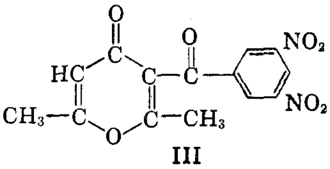


I



II



III

A continuing study of the fundamental chemistry of 4-pyrones has led to an examination of the reactivity of 2,6-dimethyl-4-pyrone, which offers the signal advantage of being easily prepared from dehydroacetic acid,[1] but is a pyrone of considerable stability with both of the reactive 2- and 6-positions filled.

Numerous experiments have been attempted to ascertain with what reagents the compound would react and the first of these was found to be mercuric chloride. Since the mercurated pyrone was found to retain its mercury very tenaciously other avenues of nuclear substitution were sought.

The hydroxylation method of Tickle[2] was reviewed with the idea that an improvement of the procedure might offer a means of procuring enough 2,6-dimethyl-3-hydroxy-4-pyrone to serve as source material for further experimentation. However, in the author's hands so little of the compound was obtained that the reactions reported could not be confirmed. Modification of this experiment produced a pyrone-peroxide whose structure has not, as yet, been established. However, the fact that the pyrone undergoes direct mercuration indicates the presence of at least a measure of aromatic character.

In attempts to uncover other aromatic substitutions, a considerable number of methods of acylation were attempted using fuming stannic chloride, polyphosphoric acid, boron trifluoride etherate, and hydroiodic acid as catalysts. All were failures. The Crafts reaction with acetic anhydride was found, however, to effect acetylation in low yield.

2,6-Dimethyl-3-acetyl-4-pyrone (I) has a melting point very near that of 2,6-dimethyl-4-pyrone and cannot be separated from it by solvents; only fractional vacuum sublimation gave reasonable results. The preparation of the lutidone (II) and its 2,4-dinitrophenylhydrazone confirms the structure of I.

Since the previously described experiments have shown that acylation can be accomplished on the pyrone, many methods were tried in an attempt to improve yields and produce a crude compound of relatively high purity. The use of fused zinc chloride as a catalyst at the elevated temperatures furnished by refluxing xylene as a solvent makes possible the easy accomplishment of both objectives as described in the preparation of 2,6-dimethyl-3-(3,5-dinitrobenzoyl)-4-pyrone (III).

EXPERIMENTAL[3]

Mercuration of 2,6-dimethyl-4-pyrone. A mixture of 6.2 g. of 2,6-dimethyl-4-pyrone, 27.1 g. of mercuric chloride and 50 ml. of absolute ethanol was heated under reflux until all the reactants had gone into solution. The mixture was thoroughly chilled and the precipitate was filtered off and air dried. Recrystallization of the crude substance twice from absolute ethanol produced pale yellow needles, m.p. 150–151°. Treatment of this substance with acids, bicarbonates or subliming it failed to remove the mercury.

Anal. Calcd.: for $C_7H_8HgCl_2O_2$: C, 21.25; H, 2.03; Cl, 17.91. Found: C, 20.58; H, 1.82; Cl, 18.22.

Since the analytical results do not agree with the calculated values for the above compound, another run was made and the product recrystallized four times from ethanol. The analysis was C, 20.59; H, 1.69; Cl, 18.15. Obviously, the material was a pure compound with such constancy of composition and no change of melting point, but not of postulated structure.

Peroxide of 2,6-Dimethyl-4-pyrone. To a mixture of 40 ml. of 50% hydrogen peroxide and 30 ml. of water containing ten drops of concentrated sulfuric acid was added 18.6 grams of 2,6-dimethyl-4-pyrone.

The mixture was allowed to stand at room temperature until all the pyrone had dissolved and then gently warmed to 30–40° for 0.5 hr. Storage of the sample in the refrigerator for 24 hr. produced 16.7 g. of white prisms. Five g. of the above sample was heated under reflux with benzene in an all-glass assembly fitted with a Dean-Stark water separator for 90 min. Upon cooling of the benzene solution about 3 g. of heavy spars of the pyrone-peroxide crystallized out, m.p. 95–96.5°, very slow heating.

The peroxide exhibits a peculiar color reaction with dilute solutions of ferric chloride in that a purple color develops after about 10 min., persists for nearly 2 hr. and then gradually fades. Solutions of potassium iodide were slightly discolored by the compound only upon long standing.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16. Found: C, 54.06; H, 5.45.

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(1) F. Feist, *Ann.*, **257**, 253 (1890).

(2) T. Tickle, *J. Chem. Soc.*, **81**, 1004 (1902).

(3) All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were determined on a Fisher-Johns melting point assembly.

The compound was not acidic. It reacted with benzoyl chloride in benzene after a reflux period of 2 hr. The product, upon analysis, did not have the proper composition for the mono- or dibenzoic ester of any hydroxy compound, alcoholic or phenolic. This test indicated the absence of hydroxyl radicals in the peroxide.

2,6-Dimethyl-3-acetyl-4-pyrone (I). Twelve and four-tenths g. of finely powdered 2,6-dimethyl-4-pyrone, 50 g. of powdered anhydrous aluminum chloride, and 100 ml. of carbon disulfide were quickly and thoroughly shaken in a 500 ml. flask to which was attached a reflux condenser fitted with a gas trap. To the above mixture 15 ml. of acetic anhydride was slowly dropped in. After all the anhydride had been added and the reaction had subsided somewhat the flask was shaken and gently heated for 30 min. The heat was then discontinued and the reaction was allowed to complete itself by standing overnight at room temperature. The carbon disulfide was then decanted from the greyish semisolid and discarded. The residue in the flask was treated with 100 g. of shaved ice followed by 20 ml. of concentrated hydrochloric acid.

The acetylated pyrone was obtained by extracting the resulting solution with benzene and evaporating the solvent. The yield was 3.4 g. The tan solid was recrystallized from boiling heptane and then sublimed to give a pale yellow powder, I, m.p. 125.5–127°.

A mixed melting point of I with an authentic sample of 2,6-dimethyl-4-pyrone was 50–55°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.04; H, 6.06. Found: C, 65.34; H, 6.34.

2,4-Dinitrophenylhydrazone of I. One g. each of I and 2,4-dinitrophenylhydrazine were refluxed together in 100 ml. of ethanol for 5 min., filtered into 100 ml. of water containing 20 drops of concentrated hydrochloric acid, and chilled overnight in the refrigerator. The precipitate was recrystallized from absolute ethanol giving 0.8 g. maroon-purple aggregates which sublimed above 180°, softened above 185°, and melted at 189–191°.

Anal. Calcd. for $C_{15}H_{14}N_4O_6$: N, 16.17. Found: N, 16.30.

2,6-Dimethyl-3-acetyl-4-lutidone (II). One g. of I and 20 ml. of ammonium hydroxide were heated in a pressure bottle at 75° for 1 hr. The solution was filtered, evaporated to dryness on a steam bath to a purple solid, and then sublimed to a pale yellow powder which melted at 226–228.5°, rapid heating.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.47. Found: C, 65.18; H, 7.04; N, 8.24 (Dumas).

2,4-Dinitrophenylhydrazone of II. The 2,4-dinitrophenylhydrazone was prepared by refluxing 1 g. each of II and 2,4-dinitrophenylhydrazine in 50 ml. of absolute ethanol for 5 min. The hydrazone was purified by recrystallizing it twice from absolute ethanol to give 0.3 g., m.p. 203°.

Anal. Calcd. for $C_{15}H_{15}N_5O_5$: N, 20.28. Found: N, 20.44.

2,6-Dimethyl-3-(3,5-dinitrobenzoyl)-4-pyrone [III]. A mixture of 12.4 g. of 2,6-dimethyl-4-pyrone, 21.2 g. of 3,5-dinitrobenzoic acid, 30 g. of fused zinc chloride, and 100 ml. of dry xylene was heated under gentle reflux for 48 hr. The mixture was cooled to −5°C., the xylene decanted, and the black residue vigorously shaken with 100 ml. of boiling water. Extraction with benzene of the residue and evaporation left solid black aggregates which weighed 29 g. The analytical sample, light tan needles, was obtained by recrystallization of 1.5 g. of the compound from 100 ml. of heptane. It melted at 113–114°.

Anal. Calcd. for $C_{14}H_{10}N_2O_7$: C, 52.83; H, 3.16; N, 8.80. Found: C, 52.49; H, 3.40; N, 8.54.

The infrared spectrum[4] of the compound, in chloroform solution, gave an absorption band at 1545 cm.$^{-1}$ for the benzenoid nitro groups. The pyrone structure[5,6] was indicated by a band at 1660 cm.$^{-1}$ An absorption peak at 1715 cm.$^{-1}$ indicated the nonpyrone carbonyl.

2,4-Dinitrophenylhydrazone of the lutidone from III. Two g. of III was dissolved in a small amount of ethanol and then an equal volume of concentrated ammonium hydroxide was added. The solution was allowed to stand overnight in a stoppered flask, following which the mixture was evaporated to dryness on a steam bath. One gram of the grey solid was placed in 100 ml. absolute ethanol along with 1 g. of 2,4-dinitrophenylhydrazine. The mixture was refluxed for 5 min., filtered, and then diluted with an equal volume of water. The orange solid was recrystallized from absolute ethanol, m.p. 199–200.5°.

Anal. Calcd. for $C_{20}H_{15}N_7O_9$: N, 19.71. Found: N, 19.50.

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(4) Infrared spectra were determined on a Perkin-Elmer Model 21 Infrared Spectrophotometer.

(5) L. L. Woods, *J. Am. Chem. Soc.*, **75**, 3608 (1953).

(6) L. L. Woods, *J. Am. Chem. Soc.*, **77**, 3161 (1955).

Reactions Between Chloro-*p*-benzoquinones and β-Naphthol

ABDEL-MEGUID OSMAN

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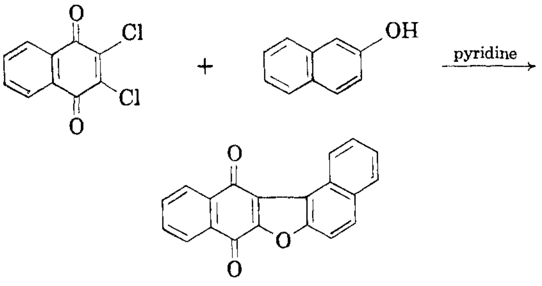
2,3-Dichloro-1,4-naphthoquinone condenses with β-naphthol in the presence of pyridine to give dinaphthylfuranoquinone (I).[1,2]



I

The condensation of chloro substituted *p*-benzoquinones with β-naphthol now has been investigated. Thus, when chloranil was allowed to react with β-naphthol in the presence of pyridine, two molecules of the naphthol condensed with one molecule of the quinone to yield a red crystalline substance believed, by analogy to be naphtho-[*1′,2′-4,5*]furo[*2,3-h*]benz[*c*]dibenzofuran 8,16-quinone (II). This compound was stable toward heat and oxygen and developed a blue color with concentrated sulfuric acid, a color which is characteristic of brazan- and furanquinones.[1,2] Zinc-dust and glacial acetic acid effected its reduction to the corresponding hydroquinone, the isolation of which

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(1) B. Eistert, *Ber.*, **80**, 52 (1927).

(2) Ng. Ph. Buu Hoï, *J. Chem. Soc.*, 489, 4699 (1952).