142° (18 mm.).[5] The phenolic ketone (84 g.) obtained from several runs was methylated by refluxing for four hours with dimethyl sulfate (44 g.) and 10% sodium hydroxide solution (280 ml.). After processing and fractionation there was obtained 62 g. (70%) of the desired product which boiled at 150–152° (9 mm.).

Anal. Calcd. for $C_{11}H_{13}O_2Cl$: C, 62.16; H, 6.16. Found: C, 62.05; H, 6.26.

The 2,4-dinitrophenylhydrazone melted at 148–149°.

Anal. Calcd. for $C_{17}H_{17}O_5N_4Cl$: C, 51.98; H, 4.36. Found: C, 52.01; H, 4.63.

2-Methoxy-5-bromoisobutyrophenone (II).—Aluminum chloride (60 g.) was dissolved in nitrobenzene (250 ml.) and cooled to −4°. Isobutyryl chloride (48 g.) was added rapidly; then *p*-bromoanisole (84 g.) was dropped in during two hours keeping the temperature at 0°. The mixture was allowed to stir for four hours while the temperature was gradually raised to 15°. Processing produced 74 g. (64%) of the ketone which boiled at 158–163° (10 mm.).

Anal. Calcd. for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.10. Found: C, 50.93; H, 5.31.

The 2,4-dinitrophenylhydrazone melted at 154–155°.

Anal. Calcd. for $C_{17}H_{17}O_5N_4Br$: C, 46.70; H, 3.92. Found: C, 46.39; H, 4.21.

When aluminum chloride (100 g.) was added to a mixture of *p*-bromoanisole (106 g.) and isobutyryl chloride (62 g.) in carbon disulfide (1200 ml.) at 5° and the mixture allowed to stand at room temperature for two days, there was obtained after processing 48 g. (35%) of demethylated ketone, b. p. 144–155° (12 mm.). This material was dissolved in sodium hydroxide solution and methylated as for the previous ketone to give II, 44 g. (85%).

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(5) von Auwers, Baum and Lorenz, ref. 4, report the boiling point as 130° at 20 mm.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

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The Action of 2,4-Dinitrophenylhydrazine on 6-Halogeno-Δ^4-cholestenones

BY D. H. R. BARTON[1] AND E. MILLER

Recently it was reported[2,3] that the action of 2,4-dinitrophenylhydrazine on the 6α- and 6β-chloro- and bromo-Δ^4-cholesten-3-ones in cold methanolic solution afforded an orange compound to which the molecular formula $C_{33}H_{48}N_4O_5$ was assigned. Further examination of this substance has shown that it contains no hydroxyl group (failure to acetylate; no band in infrared), but does contain a C═N grouping and a N–H grouping (infrared maxima at 6.16 and 3.03 μ, respectively, in chloroform solution) and a methoxyl group (Zeisel determination). Having regard to these facts and to the data previously recorded[2,3] we should like to propose the formula 6(α?)-methoxy-Δ^4-cholesten-3-one 2,4-dinitrophenylhydrazone for the orange compound and revise its molecular formula to $C_{34}H_{50}N_4O_5$.

It seems to us that the formulation of this substance is explained somewhat better by the suggestions of Mattox and Kendall[4,5] with regard to the mechanism of the 2,4-dinitrophenylhydrazine reaction with halogeno ketones, at least in ethanol solution, rather than by the alternative proposals of Djerassi,[6] which may apply only for reactions carried out in acetic acid.

Our previous observation[2] that the orange compound was obtained using ethanol and dioxane as solvents must be ascribed to the conditions of working up the reaction product. In each case the orange compound was filtered, washed with the same solvent as had been used for its preparation, and dried. The dry solid was dissolved in a small volume of chloroform and precipitated with methanol. This procedure was repeated once or twice more. The compound thus obtained was dried, dissolved in benzene and chromatographed. It was finally recrystallized very slowly from chloroform–methanol. Presumably etherification or trans-etherification occurred during one of the stages of this involved procedure.[7]

Experimental

For the orange compound prepared as described previously[2]: *Anal.* Calcd. for $C_{34}H_{50}N_4O_5$: C, 68.64; H, 8.48; N, 9.42; Cl, 0.00; OMe, 5.22. Found: C, 68.3^2; H, 8.3^2; N, 9.9^2; Cl, 0.0^2; OMe, 5.10, 5.17.

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(1) Harvard University Visiting Lecturer, 1949–1950.

(2) Barton and Miller, THIS JOURNAL, **72**, 370 (1950).

(3) Barton and Miller, *ibid.*, **72**, 1066 (1950).

(4) Mattox and Kendall, *ibid.*, **72**, 2290 (1950).

(5) We are indebted to Dr. Mattox for kindly sending us a copy of this paper prior to its publication.

(6) Djerassi, THIS JOURNAL, **71**, 1003 (1949).

(7) It is noteworthy that the absorption maximum in the u. v. of the 6-methoxy dinitrophenylhydrazone is somewhat displaced with respect to that for Δ^4-cholestenone dinitrophenylhydrazone.

IMPERIAL COLLEGE,
LONDON, S. W. 7, ENGLAND
HARVARD UNIVERSITY,
CAMBRIDGE 38, MASSACHUSETTS

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The Mannich Reaction with *o*-Phenylphenol

BY J. H. BURCKHALTER[1]

During the preparation of various Mannich phenols for antimalarial study,[2] three substances were isolated as their hydrochlorides from the reaction between equivalent amounts of 2-phenylphenol, paraformaldehyde and diethylamine. Two of these products are the isomeric α-diethylamino-6-phenylcresols (I and II); the third, α^2,α^4-bis-(diethylamino)-6-phenyl-2,4-xylenol (III), is the exclusive product when an excess of paraformaldehyde and diethylamine is used.[2]

One of the isomeric bases responds to Millon's test for an unsubstituted position ortho to a phenolic hydroxyl group and is therefore assigned the structure II. The other isomer is insoluble in dilute sodium hydroxide and should therefore have the structure I.[2,3] The structure of I was

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(1) Department of Pharmaceutical Chemistry, University of Kansas School of Pharmacy, Lawrence, Kansas.

(2) Burckhalter, Tendick, Jones, Holcomb and Rawlins, THIS JOURNAL, **68**, 1894 (1946).

(3) Decombé, *Compt. rend.*, **196**, 866 (1933).