[CONTRIBUTION FROM THE INDUSTRIAL HYGIENE RESEARCH LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

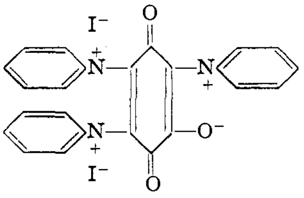
The Oxidation of Hydroquinone by Iodine in the Presence of Pyridine

BY HARRY D. BAERNSTEIN

The experiments of Ortoleva and Di Stefano[1] on the reaction of hydroquinone and iodine in the presence of pyridine received a correct interpretation by Barnett, Cook and Driscoll[2] who showed that the product of the reaction was a dihydroxyphenylpyridinium salt. The latter workers extended the reaction in several directions and showed that the products in certain cases could be converted to phenobetaines. They prepared several monopyridinium salts but failed to isolate their dipyridinium compound.

Schönberg and Ismail[3] described a mono and a dipyridinium betaine prepared from chloranil or bromanil with pyridine.

The present work describes a new method of obtaining the dipyridinium betaine and, in addition, describes a tripyridinium betaine of the probable structure:



1,1',1''-(2,5-Dihydro-3-hydroxy-2,5-dioxo-*p*-phenylene)-tripyridinium-betaine-diiodide

The iodine consumption values are strictly proportional to the quantity of hydroquinone present and thus serve as the basis for a new analytical determination of hydroquinone.

Experimental

Preparation of Dibetaine.—Hydroquinone, 4.4 g., and sodium bicarbonate, 40 g., were dissolved in 200 ml. of water. The mixture was stirred mechanically while a solution of 55 g. of iodine in 50 ml. of pyridine was dropped in slowly. A tar separated which was removed and washed and dissolved in sodium bisulfite solution. A yellow crystalline substance and a dark red solution resulted. The yellow crystals were separated and recrystallized from boiling water and, after drying *in vacuo* over sulfuric acid, weighed 4 g., 32%.

Anal. Calcd. for $C_{16}H_{10}N_2O_4 \cdot H_2O$: C, 61.50; H, 3.84; N, 8.98. Found: C, 61.20; H, 3.87; N, 9.01. The product did not melt below 310° nor did it lose moisture.

The analysis and properties of this substance are in satisfactory agreement with those of the "orange betaine" of Schönberg and Ismail. A sample prepared from chloranil according to their directions gave the same X-ray diffraction pattern as that prepared from hydroquinone. Furthermore, the same substance was obtained from bromanil, iodanil, dichlorohydroquinone, and quinone. It was also prepared from hydroquinone by oxidation with potassium ferricyanide.

The Reinecke Salt of Dibetaine.—Dibetaine, 1.0 g., was dissolved in dilute hydrochloric acid with heat and an excess of Reinecke salt added. The red crystalline compound which separated was filtered and washed with water and dried *in vacuo* over sulfuric acid.

Anal. Calcd. for $C_{20}H_{17}N_8S_4O_4Cr \cdot 3H_2O$: C, 36.00; H, 3.45; N, 16.80. Found: C, 36.35; H, 3.21; N, 16.77; melting point above 310°; moisture not determined.

Other derivatives prepared but not analyzed include picrate, phosphotungstate, and chloroplatinate. Crystalline derivatives have also been prepared with the nitrates of mercury, lead and silver, and the iodides of potassium and cadmium.

Preparation of Tripyridinium Betaine: (a) Isolation as Cadmium Salt.—The red mother liquor from the dibetaine was treated with an excess of cadmium sulfate solution and a red precipitate was obtained. Recrystallization from hot water gave a red crystalline substance which was dried *in vacuo* over sulfuric acid.

Anal. Calcd. for $C_{21}H_{15}N_3I_4CdO_3 \cdot 3H_2O$: C, 24.40; H, 2.04; N, 4.07; I, 49.20; Cd, 10.88; H_2O, 5.24. Found: C, 24.84; H, 2.09; N, 3.98; I, 49.62; Cd, 11.92; H_2O, 5.18; melting point above 310°; yield 65%.

(b) **Isolation as Picrate.**—The tar prepared as described above was dissolved in acetone and mixed with a saturated alcoholic solution of picric acid. Water was added and the mixture was warmed. A yellow precipitate formed which was recrystallized from boiling dilute alcohol and dried *in vacuo* over sulfuric acid; melting point was 301°.

Anal. Calcd. for $C_{33}H_{19}N_9O_{17} \cdot 2H_2O$: C, 46.70; H, 2.71; N, 14.85. Found: C, 46.27; H, 2.75; N, 14.99. Moisture determination was unsatisfactory. Only 1.98% weight loss was obtained and the compound decomposed.

The picrate can also be obtained by precipitation from a solution of the tar in aqueous sodium bisulfite.

If the oxidation of hydroquinone is conducted in 500 ml. of water and only 3 equivalents of pyridine are used and the iodine dissolved in potassium iodide solution, no dibetaine can be isolated. The tripyridinium compound can, however, be isolated in 65% yield as the cadmium iodide salt.

It has not been possible to isolate the red substance in a free condition.

Unlike the monopyridinium quinones described by Barnett, *et al.*, neither the dipyridinium nor the tripyridinium compounds can be reduced by sulfur dioxide.

This reaction can be utilized analytically for hydroquinone and has some advantages over the usual reaction which consumes only 2 atoms of iodine.

Iodine Uptake of Hydroquinone in the Presence of Acetate and of Pyridine.—A series of mixtures was prepared containing various amounts of 0.1 *M* hydroquinone, 50 ml. of water, 3.0 ml. of *M* acetate or *M* pyridine, an excess of 0.1 *N* iodine solution, and an excess of sodium bicarbonate. They were allowed to stand for one hour

TABLE I

IODINE CONSUMPTION BY HYDROQUINONE IN THE PRESENCE OF ACETATE AND OF PYRIDINE

	Acetate		Pyridine	
Hydroquinone, mg.	0.1 *N* iodine, ml.	M. equiv. iodine / Mmol. hydroquinone	0.1 *N* iodine, ml.	M. equiv. iodine / Mmol. hydroquinone
2.2	0.40	2.00	2.08	10.40
4.4	0.76	1.90	3.88	9.70
6.6	1.17	1.95	5.97	9.95
8.8	1.55	1.94	7.88	9.85
	Av.	1.95		9.97

---

(1) Ortoleva and Di Stefano, *Gazz. chim. italiana*, **31**, ii, 256 (1901).

(2) Barnett, Cook and Driscoll, *J. Chem. Soc.*, **123**, 503 (1923).

(3) Schönberg and Ismail, *ibid.*, 1374 (1940).

and were then titrated with 0.1 N arsenite using a polarized platinum-platinum electrode as indicator. The results are shown in Table I.

It will be seen that both methods yielded quantitative iodine consumption values and that in the presence of pyridine, the iodine uptake was five times that in the presence of acetate.

A repetition of the above experiment using monochlorohydroquinone, dichlorohydroquinone, and tetrachlorohydroquinone gave 8, 6, and 2 milliequivalents of iodine consumed per millimole of substance. This result indicates that the excess iodine consumption in the presence of pyridine is due to the oxidation of the ring hydrogen atoms of hydroquinone.

By titrating iodide with silver nitrate solution it was shown that all the iodine consumed was reduced to iodide.

This reaction has been incorporated into a scheme of analysis for phenol, catechol and hydroquinone soon to be published.

Summary

1. The reaction between hydroquinone, iodine and pyridine has been extended to the preparation of a dipyridinium and a tripyridinium betaine.

2. The reaction products have been isolated as reineckeate, picrate, and cadmium iodide salt.

3. The analytical features of the reaction have been shown.

BETHESDA, MD. RECEIVED MAY 28, 1945

[CONTRIBUTION FROM THE UNIVERSAL OIL PRODUCTS COMPANY]

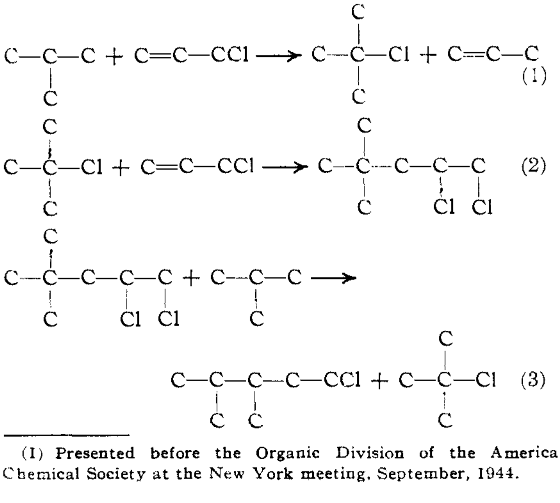
Condensation of Saturated Hydrocarbons with Haloölefins. I. The Reaction of Isobutane with Vinyl Chloride and Allyl Chloride[1]

BY LOUIS SCHMERLING

Investigation of the condensation of saturated hydrocarbons with haloölefins has led to a new method for the preparation of saturated halohydrocarbons as well as to an insight into the mechanism of the reactions. The present communication describes the results obtained by the interaction of isobutane with vinyl and allyl chlorides in the presence of aluminum chloride.

A 35–40% yield of 1-chloro-3,4-dimethylpentane and a 13–15% yield of 1,2-dichloro-4,4-dimethylpentane were obtained by the reaction of isobutane with allyl chloride at about −10°. The structure of the chloroheptane was determined by converting it to the corresponding alcohol, which yielded derivatives identical with those prepared from synthetic 3,4-dimethylpentanol. The structure of the dichloroheptane was established by conversion to 4,4-dimethyl-1-pentene by reaction with zinc and alcohol.

The following hypothesis is presented as the probable mechanism of the reaction. It is analogous to that recently proposed for the alkylation of isoparaffins with olefins.[2]



$$C{-}\underset{\substack{|\\ C}}{C}{-}C + C{=}C{-}CCl \longrightarrow C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}Cl + C{=}C{-}C \quad (1)$$

$$C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}Cl + C{=}C{-}CCl \longrightarrow C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}C{-}\underset{\substack{|\\ Cl}}{C}{-}\underset{\substack{|\\ Cl}}{C} \quad (2)$$

$$C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}C{-}\underset{\substack{|\\ Cl}}{C}{-}\underset{\substack{|\\ Cl}}{C} + C{-}\underset{\substack{|\\ C}}{C}{-}C \longrightarrow C{-}\underset{\substack{|\\ C}}{C}{-}\underset{\substack{|\\ C}}{C}{-}C{-}CCl + C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}Cl \quad (3)$$

The t-butyl chloride formed by eq. 3 starts a new cycle by reacting with allyl chloride as in eq. 2. The reaction indicated in eq. 1 is assumed to occur only as the initiating step. Although it is assumed that propene is formed in negligible amounts, it was not isolated under the reaction conditions used. The propene apparently reacts either with isobutane (*via* t-butyl chloride) to yield heptane[2] or with the catalyst to form the so-called lower layer complex.

That the reaction of eq. 2 can occur is shown by the fact that 1,2-dichloro-4,4-dimethylpentane may be prepared in 48% yield by the condensation of t-butyl chloride with allyl chloride at −20 to −10° in the presence of aluminum chloride.[3]

Evidence in support of eq. 3 was obtained by showing that 1-chloro-3,4-dimethylpentane and t-butyl chloride are produced by the reaction of the dichloroheptane with isobutane in the presence of aluminum chloride. The rearrangement of the carbon skeleton which occurs is readily explained by Whitmore's[4] "common basis of intramolecular rearrangements." It differs somewhat from the previously described rearrangements in that migration of the methyl group is preceded by migration of one of the methylene hydrogens of the neopentyl group.

Increasing the temperature at which the reaction of isobutane with allyl chloride was carried out resulted in a decrease in the yield of chlorinated products, the decrease being due to the conversion of the chlorides to paraffins. Thus, for example

---

(1) Presented before the Organic Division of the American Chemical Society at the New York meeting, September, 1944.

(2) L. Schmerling, THIS JOURNAL, **66**, 1422 (1944).

(3) To be described in a forthcoming publication.

(4) F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).