[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

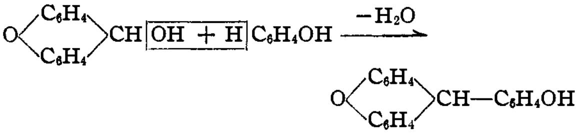
Monohydroxyphenylxanthanes[1]

BY JOSEPH B. NIEDERL AND WILLIAM F. HART[2]

In the course of the systematic investigation of the condensation of alcohols with phenols[3,4] the reaction of xanthydrol with phenols was studied using glacial acetic acid, sulfuric acid or anhydrous aluminum chloride as condensing agent. The phenolic products obtained in each case were the corresponding hydroxyphenylxanthanes. The method employing glacial acetic acid was found to be most satisfactory, indicating the extreme reactivity of the hydroxyl group in xanthydrol. This fact had been noticed previously also by Fabre, Fosse and Robyn,[5] who condensed the three dihydroxybenzenes (resorcinol, catechol and hydroquinone) and their derivatives with xanthydrol and obtained the respective mono and dixanthyl compounds.

This reaction was extended to include phenol (I), *p*-chlorophenol (II), *p*-hydroxyacetophenone (III), α - naphthol (IV), *p* - *t* - (2′ - phenyl)-butylphenol (V), and *p*-*t*-(2′-phenyl)-amylphenol (VI). Condensation was effected in each case and crystalline products were obtained also in cases where conventional methods for obtaining crystalline derivatives had failed. Such phenols were the *p* - *t* - (2′ - phenyl) - butylphenol and *p* - *t*-(2′-phenyl)-amylphenol.[6] These compounds were first condensed with xanthydrol and then methylated to yield the crystalline 1-methoxy-2-xanthyl-4-(2′-phenyl)-butylbenzene (V) and 1-methoxy - 2 - xanthyl - 4 - (3′ - methyl - 2′-phenyl)-butylbenzene (VI), respectively.

The reaction in all these condensations appears to involve the elimination of one mole of water between the hydroxyl group of xanthydrol with either the ortho or para hydrogen atom of the respective phenol, as follows



$$O\langle{}^{C_6H_4}_{C_6H_4}\rangle CH\boxed{OH + H}C_6H_4OH \xrightarrow{-H_2O} O\langle{}^{C_6H_4}_{C_6H_4}\rangle CH—C_6H_4OH$$

The products obtained by condensing phenol itself with xanthydrol (I), as well as its methyl ether (Ia), were found to be identical with 4-hydroxyphenylxanthane and 4-methoxyphenylxanthane, respectively, prepared by Gomberg and co-workers.[7]

Of interest is the observation that compounds in the xanthyl group (xanthydrol, xanthone, etc.) in general, and also the relatively non-toxic xanthylphenols described above, the phenol coefficient of which is less than one,[8] appear to produce in adult ovariectomized rats and mice physiological symptoms which are usually associated with feeble estrogenic substances.

Experimental

Condensation Method.—Four grams (0.02 mole) of xanthydrol was dissolved in 6 cc. of glacial acetic acid and the mixture warmed gently on the water-bath to effect solution. To this solution was added 2 g. (0.04 mole) of phenol, whereupon the solution turned red. The condensation flask was stoppered and allowed to stand for twenty-four hours at room temperature. Excess of water was then added to wash out acetic acid and unreacted phenol. If the phenol employed was not water soluble the condensation product was washed further with ammonium hydroxide of sufficient concentration (usually 10%) to dissolve that particular phenol. The condensation product was then dissolved in benzene and this solution was extracted three times with Claisen solution (50% potassium hydroxide plus an equal volume of methanol). The Claisen solution insoluble fraction contained unreacted xanthydrol, xanthone and other products not yet identified. The combined Claisen solution extracts were washed with benzene, diluted with water and acidified with dilute hydrochloric acid (10%). This acid solution was extracted with ethyl acetate or ether, the solvent removed and the residue recrystallized from an appropriate solvent, such as methanol or benzene. Decolorizing carbon was used to remove highly colored impurities. When the phenolic product obtained was difficult to crystallize, its methyl ether was prepared by methylation with dimethyl sulfate.

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(1) Presented at the New York meeting of the American Chemical Society, April, 1935. (Original manuscript received April 4, 1936.)

(2) Abstracted from Part II of the thesis presented by William F. Hart to the Faculty of the Graduate School of New York University in partial fulfilment for the degree of Doctor of Philosophy, April 1, 1936.

(3) Niederl and co-workers, THIS JOURNAL. **53**, 3390 (1931); **55**, 284, 4549 (1933); **57**, 2625 (1935).

(4) J. B. Niederl, U. S. patent 2,029,539 (1936).

(5) R. Fabre, *Ann. chim.*, [9] **18**, 49 (1922); Fosse and Robyn, *Compt. rend.*, **146**, 813 (1908); **160**, 1538 (1923).

(6) McGreal and Niederl, THIS JOURNAL, **57**, 2625 (1935); Zimmerman, M.Sc. Thesis, New York University, 1936; B. Gutchin, M.Sc. Thesis.

(7) Gomberg and co-workers, THIS JOURNAL, **34**, 1529 (1912); **47**, 198 (1925).

(8) The authors wish to thank Dr. Wm. A. Feirer of Sharp and Dohme, Inc., Philadelphia, for determining the phenol coefficients of these compounds.

	Compound	Formula	M. p., °C.	Analyses, %			
				Calcd.		Found	
				C	H	C	H
I	4-Hydroxyphenylxanthane	$C_{19}H_{14}O_2$	150	83.19	5.15	83.63	5.80
	(a) Methyl ether	$C_{20}H_{16}O_2$	112–113	83.28	5.56	83.15	5.64
	(b) Benzoate	$C_{25}H_{18}O_3$	183–184	82.51	4.79	82.17	4.32
II	5-Chloro-2-hydroxyphenylxanthane	$C_{19}H_{13}O_2Cl$	132	73.89	4.24	74.38	4.42
III	2-Hydroxy-5-acetylphenylxanthane	$C_{21}H_{16}O_3$	189	79.71	5.09	79.77	5.03
IV	α-Hydroxy-*x*-xanthylnaphthalene	$C_{23}H_{16}O_2$	195	85.15	4.97	84.91	5.10
V	1-Methoxy-2-xanthyl-4-(2′-phenyl)-butylbenzene	$C_{30}H_{28}O_2$	210	85.66	6.71	85.19	6.95
VI	1-Methoxy-2-xanthyl-4-(3′-methyl-2′-phenyl)-butylbenzene	$C_{31}H_{30}O_2$	202	85.71	6.91	85.95	7.05

The same phenolic condensation products were obtained when using sulfuric acid as the condensing agent. In this case 0.02 mole of sulfuric acid was added to 0.02 mole of xanthydrol and 0.04 mole of phenol. The initial condensation was carried out at 0° and was worked up as described above. Anhydrous aluminum chloride was also employed as a condensing agent; in this instance benzene was used as inert solvent and the reaction mixture was refluxed for eight hours.

Summary

A number of new monohydroxyphenylxanthanes were prepared by simple condensation methods. The physical, chemical and some physiological properties of these crystalline condensation products have been described.

NEW YORK, N. Y. RECEIVED FEBRUARY 23, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

"Hydro-polymerization"[1]

BY V. N. IPATIEFF[2] AND V. I. KOMAREWSKY[2]

In our study of catalytic hydrogenation, it was of great importance to investigate whether olefinic hydrocarbons could be hydrogenated by hydrogen *in statu nascendi*, obtained by decomposing water with iron in the presence of different salts as promoters.[3] For this purpose amylene and isobutene were heated (300°) in a rotating autoclave in the presence of water, reduced iron and magnesium chloride. The results were negative, although a sufficient amount of hydrogen was formed under this condition. In order to see whether magnesium chloride may act as a poison for amylene hydrogenation, a usual hydrogenation of amylene was made with hydrogen, using iron as catalyst in the presence of magnesium chloride. The hydrogenation took place,[4] but an additional new phenomenon was observed, namely, simultaneous polymerization and hydrogenation which produced *decane.* Therefore, investigation was made of other polymerization agents, such as aluminum chloride, zinc chloride and phosphoric acid,[5] in combination with different hydrogenating catalysts (Fe·NiO). In the presence of such mixed catalyst two reactions were found to take place simultaneously: (1) polymerization of the olefin hydrocarbon; (2) hydrogenation of the polymer formed. It is suggested that this reaction be called "hydropolymerization."

As is evident from the experiments, magnesium chloride and zinc chloride alone do not act as polymerizing agents under the conditions mentioned. However, in the presence of hydrogenating catalysts, polymerization takes place. It is possible that the energy given off during hydrogenation is sufficient to cause the polymerization of olefins by the weak polymerizing catalyst.

(1) Thus, amylene and isobutene, when treated at 300° and under 80 atm. hydrogen pressure in the presence of reduced iron as catalyst, produced pure pentane and isobutane.

(2) Amylene, under the same conditions, in the presence of magnesium chloride alone did not polymerize.

(3) Amylene and isobutene, under the same conditions, in the presence of a mixed catalyst iron and magnesium chloride containing water, produced decanes and octanes.

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(1) Presented before the Division of Organic Chemistry at the 92nd Meeting of the American Chemical Society in Pittsburgh, Pa., September 7–11, 1936.

(2) Research and Development Laboratories, Universal Oil Products Co., Riverside, Illinois.

(3) Benzene, under similar conditions, could not be hydrogenated (Ipatieff, unpublished results).

(4) V. Ipatieff and A. V. Grosse showed the possibility of hydrogenating the olefins in the presence of aluminum chloride (unpublished work).

(5) V. Ipatieff and V. Komarewsky, unpublished work.