NOTES

The Action of Phosgene on Acetone[1]

By Maryan P. Matuszak[2]

The product isolated by microfractionation from a reaction mixture of 70 cc. of acetone and 7 cc. of liquid phosgene, after half an hour at room temperature, was a colorless, unsaturated, strongly lachrymal compound having a sharp, unpleasant, irritating odor, a boiling point of 93° corr. (746 mm.), a specific gravity of 1.103^{20}_{20}, and a chlorine equivalent of 119. These properties correspond more closely to those expected of the hitherto undescribed isopropenyl chloroformate than to those of other possible products, indicating that the reaction involves the enol form of acetone

$$CH_3C(OH){=}CH_2 + COCl_2 \longrightarrow CH_3C(OCOCl){=}CH_2 + HCl$$

Table I

Properties of Possible Products

Compound	Boiling point, °C.	Specific gravity	Chlorine equivalent
Isopropenyl chloroformate	100 (est.)	1.10 (est.)	120.5
Acetoacetyl chloride	134 (est.)	1.23 (est.)	120.5
2,2-Dichloropropane	69.7	1.0925^{20}	56.5
Monochloroacetone	119	1.162^{16}	92.5
Dichloroacetone	120	1.236^{21}	63.5

No dichloroacetone[3,4] was found. On long standing the reaction mixture also formed water and mesityl oxide, by condensation of acetone.

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[3] Wroblevsky, *Z. Chem.*, [2] **4**, 565 (1868).

[4] Kempf, *J. prakt. Chem.*, [2] **1**, 414 (1870).

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The Preparation of Some New Alkylphenols[1]

By R. W. Stoughton, R. Baltzly and A. Bass

During a systematic study of alkylphenols as anthelmintics, a number of new phenols were prepared by the Fries rearrangement of the proper ester to the hydroxy ketone and subsequent Clemmensen reduction. Ketones of dihydric phenols have been prepared[2] by the condensation of the phenol and fatty acid in the presence of zinc chloride, but more satisfactory results were obtained in the case of catechol and hydroquinone derivatives by subjecting equimolecular quantities of the free phenol and its di-ester to the action of aluminum chloride. In most cases the ketones were reduced easily to the alkyl derivatives but with valerylhydroquinone the yield was low and considerable amounts of hydroquinone and valeric acid were isolated from the reaction mixture.

Experimental

The esters were prepared by allowing a 10% excess of the acid chloride to stand overnight with the phenol. Usually they were purified by vacuum distillation or recrystallization but probably this was unnecessary as good results were obtained in some cases by sucking off the excess acid chloride under a vacuum and using the product directly.

Fries Rearrangement.—The monohydric phenolic esters were treated with aluminum chloride according to the general directions of Rosenmund and Schnurr.[3] In the case of the dihydroxybenzenes one mole of the free phenol was added to its di-ester and the mixture heated with 2.2 moles of aluminum chloride. This is essentially the procedure of Rosenmund and Lohfert[4] except that better results were obtained by avoiding the use of nitrobenzene as a solvent and heating at 140–80°. Considerable difficulty was encountered in obtaining the valerylhydroquinone in a pure state as it would not crystallize and seemed to oxidize easily to the quinone and quinhydrone. A list of the ketones prepared and their physical constants is given in Table I.

Reduction of Ketones.—The ketones were reduced using the detailed procedure of Coulthard, Marshall and Pyman.[5] A mixture composed of one part ketone, three parts amalgamated zinc, six parts 6 *N* hydrochloric acid and two parts alcohol was refluxed for twelve to eighteen hours. The solution was diluted with water, extracted with ether and the product vacuum distilled. In the preparation of amylhydroquinone about 15 g. of a forerun boiling below 100° at 3 mm. was obtained. This was shown to consist largely of ethyl valerate, identified by saponification and Duclaux constants. A second fraction boiling

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[2] Nencki and co-workers, *J. prakt. Chem.*, **23**, 147, 546 (1881).

[3] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928); Baltzly and Bass, This Journal, **55**, 4292 (1933).

[4] Rosenmund and Lohfert, *Ber.*, **61**, 2601 (1928).

[5] Coulthard, Marshall and Pyman, *J. Chem. Soc.*, **280** (1930).