

NOTES

The Action of Phosgene on Acetone¹BY MARYAN P. MATUSZAK²

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 1.103₂₀, 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

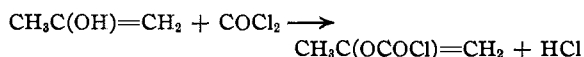


TABLE I

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 ¹⁸	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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RECEIVED APRIL 23, 1934

The Preparation of Some New Alkylphenols¹

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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 prepared² by the condensation of the phenol and fatty acid in the presence of zinc chloride, but more satisfactory results were

(1) The funds for carrying out this work were given by the International Health Division of the Rockefeller Foundation.

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

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 Lohfert⁴ 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 amyhydroquinone 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

(3) Rosenmund and Schnurr, *Ann.*, 460, 56 (1928); Baltzly and Bass, *THIS JOURNAL*, 55, 4292 (1933).

(4) Rosenmund and Lohfert, *Ber.*, 61, 2801 (1928).

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

TABLE I

	Compound	Reaction temp., °C.	Yield, %	B. p., °C.	(Mm.)	M. p., °C.
1	2-Butyryl-6-ethylphenol	120	71	170-175	(1)	91-92
2	2-Butyryl-4-ethylphenol	120	50	112-113	(1)
3	2-Propionyl-6-propylphenol	120	87	164	(3)	78-79
4	2-Propionyl-4-propylphenol	120	61	115-118	(3)	(Phenylhydrazone, 96)
5	2-Butyryl-4,6-dimethylphenol	120	45	121	(2)	(Phenylhydrazone, 168-170)
6	2-Butyryl-4,5-dimethylphenol	120	89	40-41
7	4-Butyryl-2,5-dimethylphenol	25	70	131-132
in C ₆ H ₅ NO ₂						
8	3,3'-Diacetyl-4,4'-dihydroxydiphenyl	120	75	219-219.5
9	3,3'-Dipropionyl-4,4'-dihydroxydiphenyl	120	55	140-141
10	4-Caproylcatechol ^a	140	62	93-94
11	2-Valerylhydroquinone	180	70	174-176	(2)

	Physical form	Solvent for crystallization	Formula	Analyses, %			
				C	Calcd.	H	Found.
1	Colorless plates	Bz-pet. ether	C ₁₂ H ₁₆ O ₂	75.0	8.4	74.9	8.2
2	Oil	C ₁₂ H ₁₆ O ₂	75.0	8.4	74.9	8.6
3	Colorless plates	Pet. ether	C ₁₂ H ₁₆ O ₂	75.0	8.4	74.9	8.4
4	Oil	C ₁₂ H ₁₆ O ₂	75.0	8.4	74.5	8.5
5	Oil	C ₁₂ H ₁₆ O ₂	75.0	8.4	75.1	8.3
6	Colorless prisms	Dil. alc.	C ₁₂ H ₁₆ O ₂	75.0	8.4	75.2	8.7
7	Colorless prisms	Benzene	C ₁₂ H ₁₆ O ₂	75.0	8.4	74.8	8.6
8	Yellow needles	HAc	C ₁₆ H ₁₄ O ₄	71.1	5.2	70.8	5.0
9	Yellow needles	HAc	C ₁₈ H ₁₈ O ₄	72.5	6.1	72.6	6.4
10	Colorless plates	Bz	C ₁₂ H ₁₆ O ₂	75.0	8.4	74.9	8.4
11	Oil	C ₁₁ H ₁₄ O ₂	68.0	7.3	68.4	7.2

^a Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

TABLE II

Compound	B. p., °C.	(Mm.)	M. p., °C.	Yield, %	Analyses, %			
					C	Calcd.	H	Found
2-Butyl-6-ethylphenol	108-112	(2)	46	80.9	10.2	81.0	10.5
2-Butyl-4-ethylphenol	112-118	(5)	31	80.9	10.2	80.5	10.1
2,6-Dipropylphenol ^a	114-116	(5)	63	80.9	10.2	80.8	10.2
2,4-Dipropylphenol ^a	125-126	(10)	34	80.9	10.2	81.0	10.5
2-Butyl-4,6-dimethylphenol	106-108	(3)	80	80.9	10.2	80.5	10.3
2-Butyl-4,5-dimethylphenol	135-140	(8)	43-45	68	80.9	10.2	80.6	10.2
4-Butyl-2,5-dimethylphenol	130-132	(4)	70	80.9	10.2	80.7	10.9
3,3'-Diethyl-4,4'-dihydroxydiphenyl ^b	119-120	55	79.3	7.5	79.3	7.9
3,3'-Dipropyl-4,4'-dihydroxydiphenyl ^b	113-114	35	79.9	8.2	79.9	8.4
4-Hexylcatechol	169	(4.5)	25-26	50	74.3	9.5	74.2	9.8
2-Amylhydroquinone ^c	176-180	(3)	85-86	10	73.3	9.0	73.1	9.0

^a Prepared by Claisen [*Ann.*, **418**, 69 (1919)] by the reduction of the corresponding diallylphenols.

^b White needles from petroleum ether.

^c White plates from benzene.

from 150-170° was obtained consisting mainly of hydroquinone and finally 5 g. (10%) of amyhydroquinone boiling at 176-180° at 3 mm. The reason for this behavior has not been investigated as yet. The physical constants of these phenols are given in Table II.

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RECEIVED JUNE 11, 1934

Isobutyrylformic Acid Phenylhydrazone

BY LYMAN C. CRAIG

In an earlier paper¹ we have reported the isolation of isobutyrylformic acid from the reaction mixture which results on treatment of ergotinine with aqueous alkali. The phenylhydrazone of the ketonic acid was prepared for final identifi-

(1) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **104**, 547 (1934).