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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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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

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

Pittsburgh, Pa. Received April 23, 1934

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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[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).

[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).

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 in $C_6H_5NO_2$	70	.....	...	131–132
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, % Calcd. C	H	Found. C	H
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	$C_{12}H_{16}O_3$				
11	Oil		$C_{11}H_{14}O_3$	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, % Calcd. C	H	Found C	H
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 amylhydroquinone 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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Isobutyrylformic Acid Phenylhydrazone

BY LYMAN C. CRAIG

In an earlier paper[1] 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-

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

cation. Although the analytical figures obtained with this derivative were satisfactory, its melting point (152°) proved to be higher than that recorded in the literature (128°[2] and 143°[3]). In order to clear up this discrepancy, we have since prepared the phenylhydrazone of synthetic isobutyrylformic acid. The latter melts at 152°, thus confirming our observation on the substance obtained from ergotinine. A mixed melting point showed no depression.

The method of synthesis was essentially that reported by Tschelinzeff[4] with a slight variation in the method of hydrolysis of the intermediate isobutyryl cyanide. It was found necessary to heat the cyanide on the steam-bath for two hours in 1:1 hydrochloric acid in order to effect hydrolysis. The hydrolysis mixture was extracted with ether, the ether extract dried with sodium sulfate and evaporated to a sirup. If this sirup is used to prepare the hydrazone it does not crystallize. However, if the sirup is shaken with a little water, in which it is not completely soluble, and the aqueous layer used to prepare the hydrazone, the product crystallizes nicely. Repeated recrystallizations from dilute alcohol failed to raise the melting point above 152°.

Anal. Calcd. for $C_{11}H_{14}O_2N_2$: C, 64.08; H, 6.84; N, 13.59. Found: C, 64.15; H, 6.74; N, 13.66.

FROM THE LABORATORIES OF
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NEW YORK, N. Y.

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[2] D. Tschtschenke, *Bull. soc. chim.*, [4] **37**, 623 (1925).

[3] E. Abderhalden and E. Rossner, *Z. physiol. Chem.*, **163**, 261 (1926).

[4] W. Tschelinzeff and W. Schmidt, *Ber.*, **62**, 2210 (1929).

COMMUNICATIONS TO THE EDITOR

ORGANIC REACTIONS WITH LIQUEFIED HYDROGEN CHLORIDE

Sir:

Information is accumulating in our laboratories relative to the reaction of liquefied hydrogen chloride with various types of organic compounds. In the majority of cases the reactions proceed rapidly indeed, partly because of the fact that the liquefied hydrohalides, in particular hydrogen chloride, are excellent solvents for a wide range of compounds. Many of the resulting solutions are good conductors of electricity.

The reactions observed so far are additions to multiple bonds, dehydration, or both; acidolysis appears not to be as frequent as might be anticipated. Reactions of hydrohalides as exemplified by our experiments are interesting in view of theoretical considerations concerned with addition to multiple bonds. As example of these reactions the following are typical: (1) vinyl acetate reacts with liquid hydrogen chloride at atmospheric pressure forming α-chloroethyl acetate in 50 to 70% yields. The literature contains two boiling points for this compound, 119–121° (740 mm.[1]) and 113–116° (740 mm.[2]); different preparations resulted in products which boiled at either one or the other of the two points. This is being investigated. (2) Allyl alcohol (b. p. 96.5–97.5°) is converted to allyl ether (b. p. 91–93°) with a high yield. (3) Acetaldehyde yields α,α'-dichloroethyl ether boiling at 112.5–114° in yields of 70%, n_D^{25} 1.4186, d_4^{25} 1.106. This compound was identified by hydrolysis to acetaldehyde in the presence of *p*-nitrophenylhydrazine and isolation of the hydrazone. (4) Good yields of ethylene chlorohydrin are obtained from the reaction of ethylene oxide with liquefied hydrogen chloride.

A mixture of one mole of isopropyl acetate and one mole of *n*-butyl alcohol was treated with liquid hydrogen chloride at atmospheric pressure, from which was isolated some isopropyl alcohol and butyl acetate. This is being investigated on a series of such compounds with the purpose of obtaining data relative to negativity of the groups tested.

A number of cases have been found in which no action takes place. Cinnamic acid is a typical example. This work is being extended. A complete report will be made later.

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[1] Descade, *Ann. chim.*, [7] **29**, 488 (1903).

[2] Ulich and Adams, THIS JOURNAL, **43**, 660 (1921).