Barium Hydroxide.—Three runs were made at 50°, using 0.35 mole of the base with 0.12 mole of the bromide, and 0.15 mole of the hydroxide with 0.07 mole of the bromide. The yields of olefin were 2.2 and 0.8%. The yields of alcohol varied from 91.8 to 97.2%.

In analyzing the distillates from the reaction mixtures for tertiary butyl alcohol, use was made of the indices of refraction of aqueous solutions of that substance given in the "International Critical Tables," Vol. 7, page 68, supplemented by the following new determinations.

TABLE I

REFRACTIVE INDICES OF AQUEOUS TERTIARY BUTYL ALCOHOL SOLUTIONS

t-Butyl alcohol, %	0.857	1.26	1.95	1.96	2.49
n^{25}_{D} reduced to vacuum	1.3336	1.3342	1.3348	1.3349	1.3356
t-Butyl alcohol, %	3.64	3.83	5.33	5.67	6.57
n^{25}_{D} reduced to vacuum	1.3366	1.3367	1.3384	1.3385	1.3397
t-Butyl alcohol, %		7.35	7.63	7.65	9.43
n^{25}_{D} reduced to vacuum		1.3404	1.3407	1.3408	1.3426

The Abbe refractometer was accurate to 0.0002, which in the experiments reported in this paper corresponds to about 0.1 g. of tertiary butyl alcohol. This represents a possible error in analysis of approximately 1.3% in the amount of alcohol reported in the experimental part.

The reactions with tertiary butyl bromide took place much more rapidly than did those with the secondary bromide, and formed the alcohol as the chief product. The maximum yield of butene amounted to but slightly more than 2%, and in the reactions using silver hydroxide at 30°, there was no evidence of olefin formation.

Considerable quantities of butene were formed in all of the reactions with secondary butyl bromide, the yields varying from 13 to 47%. Except in those reactions using silver hydroxide, the amount of olefin produced varied roughly as the concentration of dissolved base. In general, then, the course of the reaction is affected by the concentration of the hydroxide ion, but is little affected by the nature of the metallic ion, although sodium hydroxide gave somewhat lower yields of butene than did potassium hydroxide solutions of the same concentration. Silver hydroxide, however, formed olefin to the extent of 30%, thus approximating the yields from moderately concentrated solutions of potassium hydroxide.

Summary

1. The action of several inorganic hydroxides on secondary and tertiary butyl bromides was investigated, using aqueous solutions in varying concentrations.
2. Olefin was obtained from secondary butyl bromide in yields of from 13 to 47%, the amount varying roughly with the amount of dissolved hydroxide. Silver hydroxide was an exception to this generalization, since it formed relatively large quantities of the olefin.
3. Tertiary butyl bromide gave yields of olefin which varied from 0 (using silver hydroxide at 30°) to 2.2%.

COLUMBIA, MISSOURI RECEIVED JANUARY 25, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Decomposition of Alpha Keto Acids

BY CHARLES D. HURD AND HARRY R. RATERINK

A study was made of the pyrolysis of benzoylformic (phenylglyoxylic) and phenylpyruvic acids to gain further insight into the behavior of α-keto acids. Claisen[1] and later Bouveault[2] found the former to yield benzoic acid and benzaldehyde at 200–250°. Air was not excluded and no study was made of the gaseous reaction products. In the present work (270°) the yields of carbon monoxide and carbon dioxide were about 19 and 49%, respectively; the yields of aldehyde were about 25–15%, and of acid 35–45%. An experiment at 500° resulted in a 62% yield of benzaldehyde.

Phenylpyruvic acid, $C_6H_5CH_2COCOOH$, melts with decomposition. In the present work carbon monoxide, carbon dioxide and phenylacetic acid were established as pyrolytic products. The yield of phenylacetic acid was about 35%. No phenylacetaldehyde was isolable. Phenylpyruvic acid differs from phenylglyoxylic in having a methylene group alpha to the carbonyl. Evidently this —CH_2CO— group sponsored dehydra-

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(1) Claisen, *Ber.*, **10**, 431, 1667 (1877).

(2) Bouveault, *Bull. soc. chim.*, [3] **15**, 1015 (1896).

tion processes during the heating, as indicated by the considerable intractable residue.

Experimental Part

Benzoylformic Acid.—The following modification of Acree's[3] directions was developed in work with R. W. McNamee. Acree oxidized mandelic acid with cold alkaline permanganate and obtained the solid acid by crystallization from carbon disulfide. The crude liquid acid was found to be immiscible with carbon disulfide but the trouble was traced to the presence of water. Drying was readily effected by placing it in a distilling flask with one-third its volume of toluene. Toluene and water are distilled away. The dried liquid residue was then taken up in an equal volume of carbon disulfide, stoppered adequately to exclude moisture and cooled by a mixture of ice and salt. The crystalline benzoylformic acid melted at 58–61°. The yields ranged from 50 to 72%.

Phenylpyruvic Acid.—This acid was prepared by Erlenmeyer's[4] method (from benzyl cyanide, ethyl oxalate and sodium ethoxide *via* ethyl phenylcyanopyruvate) and also by Plöchl's[5] method (from hippuric acid, benzaldehyde and acetic anhydride). Both methods were tedious. In the former method, the ethyl phenylcyanopyruvate (m. p. 123°) was found to hydrolyze to phenylpyruvic acid which melted, after crystallization from benzene, at 146–147° instead of 155°. The purity of the 146–147° acid was confirmed by its neutral equivalent of 165; calcd., 164. Nitrogen was absent by test. The difference in melting points may be due to variations in the method of heating, because it is a decomposition point rather than a true melting point. The 146° material gave a phenylhydrazone with the same melting point as that recorded in the literature, namely, 160–161°.

Pyrolyses[6]

The apparatus used was similar to the one used with mandelic acid.[7] Gas appeared with benzoylformic acid when the bath temperature was 240° and with phenylpyruvic acid at 170°. The temperature used with both was generally about 265–270° because a good separation of benzaldehyde from benzoic acid could be made if this temperature was not exceeded. The aldehyde content of the distillate was confirmed as benzaldehyde phenylhydrazone. The benzoic acid was extracted by alkali from the residue (and also from the distillate if 300° temperature was used). Some sticky red residue failed to dissolve.

Nothing but water distilled from the phenylpyruvic acid. Then, phenylacetic acid was vacuum-distilled from the residue. It was crystallized from water or petroleum ether; m. p. 74–75°. No aldehyde was found. The apparent molecular weight (cryoscopically in benzene) of the resinous, red residue from the vacuum distillation was 330. Data of some of the representative experiments with both acids are collected in Table I.

Flow Method.—A combustion tube, filled with carbon dioxide, was heated electrically to 500°. Then 6.91 g. of molten benzoylformic acid was introduced dropwise. A 62% yield of benzaldehyde was formed (5.65 g. of the phenylhydrazone). Evidently the higher temperature favors the decarboxylation reaction, for this yield of aldehyde far exceeds any in Table I.

TABLE I

PRODUCTS FROM BENZOYLFORMIC ACID

Subs., g.	Bath temp., °C.	Inert gas	CO formed		CO_2 formed		PhCHO		PhCOOH	
			g.	%	g.	%	g.	%	g.	%
1.00	250–300	CO_2	0.0331	18						
1.00	250–300	CO_2	.0367	20						
1.00	250–300	N_2			0.1489	51				
2.00	250–300	N_2			.2777	47			0.91	56
1.20	250–300	N_2			.1650	47			.53	55
4.22[a]	265–270	CO_2					0.28			
5.00[b]	265–270	CO_2					.86	24	1.46	36
5.00[c]	265–270	CO_2					.88	25	1.39	34
4.92[c]	265–270	CO_2					.57	16	1.70	43
PRODUCTS FROM PHENYLPYRUVIC ACID										
							H_2O, g.		$PhCH_2COOH$ g.	%
1.00	260	H_2			0.118	44				
1.00	260	CO_2	0.098	57						
7.5	280	CO_2					1.03		1.96	30
7.0	250	CO_2	.79	66					2.48	43

[a] The heating period was about thirty minutes. [b] Molten benzoylformic acid was dropped rapidly into the hot flask. The dropping funnel was drawn out to a capillary. [c] Same as (*b*) but slower dropping.

Summary

Benzoylformic acid may be dried, prior to crystallization from carbon disulfide, by distilling toluene from it. It and phenylpyruvic acid were pyrolyzed at 250–300°. Benzoylformic acid pro-

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[3] Acree, *Am. Chem. J.*, **50**, 389 (1913).

[4] Erlenmeyer, *Ann.*, **271**, 172 (1892); **333**, 228 (1904).

[5] Plöchl, *Ber.*, **16**, 2815 (1883); Wislicenus, *ibid.*, **20**, 593 (1887).

[6] Preliminary work with benzoylformic acid was performed with Fred E. Smith.

[7] Hurd and Raterink, THIS JOURNAL, **55**, 1543 (1933).

duced more carbon dioxide than carbon monoxide, and more benzoic acid than benzaldehyde. At 500° the benzaldehyde predominated. Phenylpyruvic acid generated slightly more carbon monoxide than dioxide. It yielded also phenylacetic acid and a considerable quantity of intractable dehydration products.

EVANSTON, ILLINOIS RECEIVED JANUARY 26, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Keto Ethers. I. Methoxymethyl Ketones[1]

BY HENRY R. HENZE AND NEIL E. RIGLER

Continuing the investigation in this Laboratory on aliphatic compounds of bifunctional type,[2] attention has now been directed to the synthesis of keto ethers of the type $R{-}CO{-}CH_2{-}O{-}R'$. Of the several methods which have been utilized to prepare alkoxy ketones only those involving the acetoacetic ester synthesis[3] and the Grignard reaction[4] are of general application. By means of the former, James[3] claims to have prepared methoxymethyl *s*-butyl ketone. He treated the ethyl ester of diethylacetoacetic acid with phosphorus pentachloride, obtaining a mixture of mono- and di-chlorodiethylacetoacetic esters. The monochloro compound was converted into the methyl ester of a methoxy derivative which, on hydrolysis, yielded the compound formulated as methoxymethyl *s*-butyl ketone. For it he recorded a boiling point of 130–132° and density of 0.855 at 20°, and stated that it did not form a bisulfite addition product.[5] The Grignard reaction was used by Gauthier[4] to synthesize methyl, ethyl and *n*-propyl methoxymethyl ketones; however, for these keto ethers no physical data other than their boiling points were recorded.[6]

Ten methoxymethyl alkyl ketones, including the four already mentioned, have been synthesized by means of the Grignard reaction and adequately characterized. Secondary or tertiary alkyl had not previously been utilized in the preparation of alkoxyalkyl ketones from nitriles. A critical study of the physical properties of these interesting compounds, which possess valuable solvent properties, will be reported elsewhere.

TABLE I

METHOXYMETHYL ALKYL KETONES, $CH_3{-}O{-}CH_2{-}CO{-}R$

R	B. p. (corr.), °C.	Mm.	d_4^{20}	n_D^{20}	Yield, %
Methyl	114.6	746	0.9491	1.3980	48
Ethyl[a]	133–133.6	757	.9292	1.4063	48.5
n-Propyl[b]	152–153	745	.9139	1.4119	51
s-Propyl	143.5–145	748	.9097	1.4078	44
n-Butyl	167–169	744	.9031	1.4173	34
i-Butyl	163–164	751	.8982	1.4140	30
s-Butyl[c]	164	757	.9047	1.4162	32
t-Butyl	158–159	743	.9091	1.4193	19
n-Amyl	191–191.5	753	.8960	1.4220	46
i-Amyl	185–186	752	.8942	1.4210	71

R	Molecular refractivity		Analyses, %			
			Carbon		Hydrogen	
	Calcd.	Obs.	Calcd.	Found	Calcd.	Found
Methyl	22.21	22.41	54.51	54.73	9.16	9.06
Ethyl	26.83	27.00	58.78	59.19	9.87	10.08
n-Propyl	31.44	31.61	62.02	61.86	10.42	10.40
s-Propyl	31.44	31.47	62.02	62.19	10.42	10.37
n-Butyl	36.06	36.25	64.56	64.59	10.85	10.72
i-Butyl	36.06	36.20	64.56	64.40	10.85	10.72
s-Butyl	36.06	36.05	64.56	64.30	10.85	10.73
t-Butyl	36.06	36.18	64.56	64.51	10.85	10.78
n-Amyl	40.67	40.88	66.61	66.84	11.19	11.12
i-Amyl	40.67	40.88	66.61	66.46	11.19	11.29

[a] In 1933, Maruyama [*Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **20,** 53 (1933)] reported the synthesis of the following ketones, recording the boiling points but no other physical or analytical data: methoxymethyl ethyl ketone, b. p. "about 130°"; methoxymethyl *n*-propyl ketone, b. p. 117° (175 mm.); methoxymethyl *n*-butyl ketone, b. p. 131–132° (173 mm.); methoxymethyl *i*-amyl ketone, b. p. 117° (87 mm.).

[b] Evidence that the b. p. of 142–150° recorded by Gauthier (Ref. 4) is seriously in error.

[c] Proof that James (Ref. 3) did not prepare *s*-butyl methoxymethyl ketone.

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(1) From the thesis of Neil E. Rigler for the M.A. degree, June, 1932. This paper was read in part at the Waco meeting of the Central Texas Section of the American Chemical Society on April 23, 1932.

(2) Henze and Murchison, THIS JOURNAL, **55**, 4255 (1933).

(3) James. *Ann.*, **231**, 240 (1885); Isbert, *ibid.*, **234**, 193 (1886); Fittig and Erlenbach, *Ber.*, **21**, 2138, 2647 (1888); Erlenbach, *Ann.*, **269**, 22 (1892).

(4) Béhal and Sommelet, *Compt. rend.*, **138**, 89 (1904); Sommelet, *Ann. chim. phys.*, [8] **9**, 484 (1906); Gauthier. *ibid.*, [8] **16**, 22 (1909).

(5) Although Sommelet [*Bull. soc. chim.*, [4] **1**, 380 (1907)], in commenting on the reaction as formulated by James, stated that, "The difficulty of interpreting simply this reaction suffices to place in doubt the announced constitution," the compound in question has not previously been resynthesized.

(6) The b. ps. recorded by Gauthier (Ref. 4) are: *n*-propyl methoxymethyl ketone 142–150° (730 mm.), ethyl ketone 130–131° (729 mm.), methyl ketone 114° (732 mm.). Henry [*Rec. trav. chim.*, **23**, 347 (1904)] had synthesized methoxyacetone by a different method and reported b. p. 118° and d^{20} 0.9570.