

method was unsatisfactory, because of the slowness of the change of one solid form into the other, and also because there occurs appreciable sublimation of the sulfone above about 80°. We fell back, therefore, upon the solubility method, which was applied as follows.

A three-necked 500-cc. flask, containing a saturated solution of the sulfone in 45% aqueous acetic acid in contact with a large excess of the solid, was heated in a four-liter water-bath provided with a coil of perforated copper pipe. The water in the bath was kept in motion by air bubbles forced through pin-holes in this pipe, while the contents of the flask were agitated by a motor-driven glass stirrer. With the flask contents and bath liquid in vigorous agitation, the temperature of the solution in the flask was raised to 90°, and was then allowed to fall slowly, samples being removed at 76, 70.5, 66, and 60.5°. After this, the temperature was gradually raised again and samples taken at 80, 85, 90, and 92.5°. This procedure was adopted in order to ensure saturation and to facilitate the attainment of

equilibrium. The samples were blown out of the flask by air pressure, through a preheated tube containing a plug of cotton wool to filter out any crystals, into tared bottles. The weights of liquid and solid were determined by evaporation to dryness, and the solubilities calculated on the basis of grams of solid per 100 g. of solvent. Eight determinations were made, with temperatures so chosen as to bring the transition point about halfway between the extremes. The graph shows these experimental results, with the transition point at 74.8°.

Summary

1. Diphenylsulfone exists in two reciprocally convertible allotropic forms, one melting at 128°, and the other at 124°.
2. The conditions are explained under which one form can be changed into the other, the transition temperature being about 74.8°.
3. Some of the confusion in the literature on this subject is thus explained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

The Condensation of 2-Butanone with Aldehydes of the Type RR'CHCHO^{1,2}

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It has been shown that certain straight-chain aldehydes react with 2-butanone under the influence of alkaline condensing agents to form ketols of the type RCHOHCH(CH₃)COCH₃.³ On the other hand, Thoms and Kahre found that with isobutyraldehyde the ketol (CH₃)₂CHCHOHCH₂COC₂H₅ was obtained.⁴ It seemed therefore desirable to investigate the behavior of other aldehydes of the type RR'CHCHO.

2-Butanone was treated with methylethylacetaldehyde, diethylacetaldehyde, and ethyl-*n*-butylacetaldehyde in the presence of dilute potassium hydroxide. In each case the resulting ketol was dehydrated to the unsaturated ketone; this was

reduced to the saturated secondary alcohol and this in turn oxidized to a mixture of acids as described in previous papers.^{3c,3d,5} The water-insoluble acids obtained were then investigated and in each case the acid of the type RCH₂COOH (where the aldehyde in each instance is designated as RCHO) was found and in no case could the acid of the type RCOOH be identified, showing that the secondary alcohols were of the type RCH₂CH₂CHOHC₂H₅ and not RCH₂CH(CH₃)COCH₃, and that these aldehydes, like isobutyraldehyde, had reacted with the methyl group of the 2-butanone. The identity of the acids was established by a comparison of their piperazonium salts with those prepared from known samples of the acids which might be formed. Of the acids required for purposes of comparison β -ethylenanthic and γ -ethylcaprylic acids could not be found described in the literature and their preparation is given in detail. The other acids were

(1) Presented before the Division of Organic Chemistry at the San Francisco meeting of the American Chemical Society, August, 1935.

(2) Based upon a thesis submitted by Maynard M. Baldwin in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Washington.

(3) (a) U. S. Patent 981,668; (b) Salkind, *J. Russ. Phys.-Chem. Soc.*, **37**, 484 (1905); (c) Powell, *THIS JOURNAL*, **46**, 2514 (1924); (d) Powell, Murray and Baldwin, *ibid.*, **55**, 1153 (1933).

(4) Thoms and Kahre, *Arch. Pharm.*, **263**, 241-252 (1925).

(5) Powell and Secoy, *THIS JOURNAL*, **53**, 765 (1931).

either purchased or prepared by standard methods.

Experimental Part

Methylethylacetaldehyde.—This was prepared by the dehydrogenation of *s*-butylcarbinol with a copper-chromium-barium oxide catalyst.⁶ The *s*-butylcarbinol was made by the fractionation of the technical product obtained from the Eastman Kodak Company. The fraction boiling at 127–128° was used and its purity was tested by preparing the 3,5-dinitrobenzoate and comparing it with that of pure *s*-butylcarbinol and with that of isoamyl alcohol, the most likely impurity.

Diethylacetaldehyde.—One portion of this was prepared by the method of Darzens' from diethyl ketone and ethyl chloroacetate. The other portion was prepared from ethylmagnesium bromide and ethyl ethoxyacetate.⁸

Ethyl-*n*-butylacetaldehyde.—This was purchased from the Carbide and Carbon Chemicals Corporation under the name of "octyl aldehyde." The material was dried and distilled and the fraction boiling at 161–162° retained for use.

The Saturated Alcohols.—In Table I are listed some of the properties of the saturated secondary alcohols obtained by reducing the unsaturated ketones formed when the ketols were dehydrated.

Alcohol	B. p., °C.	Mm.	<i>n</i> _D	<i>d</i> ₄
1 6-Methyl-3-octanol	81–83	15	1.4372 (28°)	0.8320 (28°)
2 6-Ethyl-3-octanol	90–92	20	1.4371 (24°)	.8396 (24.5°)
3 6-Ethyl-3-decanol	119–120	18	1.4435 (28°)	.8364 (28°)

	Calcd.		Found	
	C	H	C	H
1	74.92	13.98	75.02	13.55
2	75.87	14.02	75.37	13.76
3	77.33	14.07	76.99	13.67

β-Ethylenanthic Acid.—Ethyl-*n*-butylacetaldehyde was reduced to 2-ethyl-1-hexanol and this was converted into the bromide by treatment with phosphorus tribromide. The crude bromide was treated with sodium cyanide and the nitrile hydrolyzed in the usual manner with sodium hydroxide. The acid boiled at 135° (25 mm.) and at 236° (760 mm.).

(6) Connor, Folkers, and Adkins, *THIS JOURNAL*, **54**, 1139 (1932).
 (7) Darzens, *Compt. rend.*, **139**, 1214 (1904).
 (8) Béhal and Sommelet, *Bull. soc. chim.*, [3] **31**, 300 (1904).

Anal. Calcd. for C₉H₁₈O₂: C, 68.29; H, 11.47. Found: C, 68.41; H, 11.79.

2-Ethyl-1-hexanol.—The reduction of the ethyl-*n*-butylacetaldehyde was carried according to the method described for the preparation of 1-heptanol⁹ using iron and acetic acid, and also by the use of sodium and moist ether. While the second method was inferior to the first in the matter of yield it was superior to it from the standpoint of convenience and time consumption. A solution of 5 g. of magnesium sulfate in 600 cc. of water, 500 cc. of ether, and 64 g. (0.5 mole) of the aldehyde were placed in a two-liter flask fitted with a condenser and dropping funnel. Sixty grams of sodium was then added in small portions through the condenser and at the same time acetic acid was added from the dropping funnel at such a rate that a slight precipitate of magnesium hydroxide was always present; yield 45%.

γ-Ethylcaprylic Acid.—This was prepared in the usual manner from 2-ethyl-1-bromohexane and ethyl malonate. The acid boiled at 253–256° (760 mm.).

Anal. Calcd. for C₁₀H₂₀O₂: C, 69.70; H, 11.71. Found: C, 69.67; H, 11.66.

The Piperazonium Salts.—The method of Pollard, Adelson, and Bain¹⁰ was used for the preparation of these salts. Table II gives the properties of the piperazonium salts of the acids actually found among the water-insoluble oxidation products of the saturated alcohols. Although γ-ethylcaprylic acid was not among these, it is included in the table because it is a hitherto unknown acid.

Piperazonium salt of	M. p., °C.	Neut. equiv.		Nitrogen, %	
		Calcd.	Found	Calcd.	Found
β-Methylvaleric acid	129	318.2	316.2	8.79	8.85
γ-Methylcaproic acid	109	346.3	343.8	^a	
β-Ethylvaleric acid	134	346.3	343.6	8.08	7.78
β-Ethylenanthic acid	100	402.2	398.4	6.96	7.14
γ-Ethylcaprylic acid	110	430.4	433.6	6.51	6.56

^a Not enough of the salt was available to carry out both determinations.

Summary

Methylethylacetaldehyde, diethylacetaldehyde, and ethyl-*n*-butylacetaldehyde react with the methyl group of 2-butanone under the influence of alkaline condensing agents.

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(9) Clarke and Dreger, "Organic Syntheses," Coll. Vol. I, p. 298.
 (10) Pollard, Adelson and Bain, *THIS JOURNAL*, **56**, 1759 (1934).