4. Iodine in potassium iodide solution reacts with dihexinyl mercury giving a 22% yield of butyl iodoacetylene and a large quantity of addition products. Iodine in liquid ammonia reacts with the same compound, giving a 54% yield of butyl iodoacetylene without a trace of addition products.

5. The bis alkinyl mercuries either solid or in solution react with hydrogen sulfide giving mercury sulfide.

6. Diamyl and dibutyl acetylenes are rearranged at 210° by sodamide in mineral oil to decyl and octyl acetylenes.

7. Hexyl, octyl, and decyl iodoacetylenes have been prepared and some of their physical properties recorded.

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A Phase Rule Study of Mixed Derivatives of Alcohols

BY WM. E. CALDWELL AND K. R. MACLEAN

The determination of the percentage of one alcohol mixed with another has been approximated on the basis of gradation of some physical property of the alcohols as mixed. Mixtures of alcohols have even been oxidized to their respective acids and estimated according to variation of the properties of the mixed acids.[1,2,3] A study of the physical properties of mixtures of other derivatives of alcohols might lead to methods for determination of percentage of one alcohol mixed with another. Melting points of solid alcohol derivatives when mixed might offer possibility of determination of relative proportions of the alcohols. If the solid derivatives are relatively easily prepared in the presence of water, the method might be applied to the determination of proportions of mixed alcohols in water solution. Accordingly a phase rule study has been made upon mixed solid derivatives of alcohols.

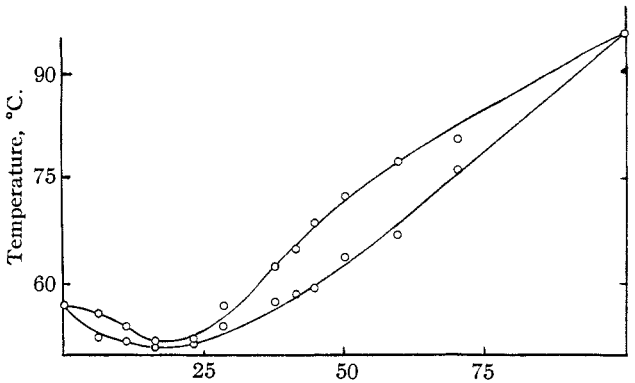
Compounds Prepared.—The following alcohol derivatives were made and carefully purified.

	Melting point, °C.
Methyl *p*-nitrobenzoate	96.0– 96.5
Ethyl *p*-nitrobenzoate	57.0– 57.5
Methyl 3,5-dinitrobenzoate	106.5–107.0
Ethyl 3,5-dinitrobenzoate	91.5– 92.0
Butyl 3,5-dinitrobenzoate	63.3– 63.3

The various nitrobenzoates were chosen because of their ease of prepara-

(1) Werkman and Osburn, *Ind. Eng. Chem.*, **3**, 387 (1931).
(2) Archibald and Beamer, *ibid.*, **4**, 18 (1932).
(3) M. Johnson, *ibid.*, **4**, 20 (1932).

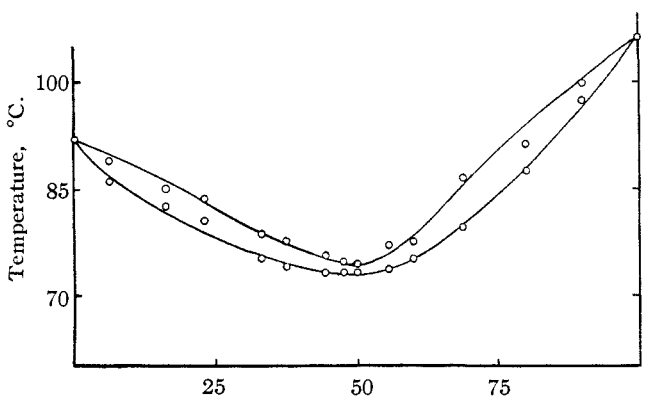
tion, ease of purification and solubility considerations. These listed melting points agree very closely with those obtained by other workers.[4]



Percentage of methyl *p*-nitrobenzoate by weight with ethyl *p*-nitrobenzoate.

Fig. 1.

Mixed Melting Point Studies.—Mixtures were made of ethyl *p*-nitrobenzoate and methyl *p*-nitrobenzoate by weighing varying quantities of these two compounds together and thoroughly mixing when grinding the mix in an agate mortar. Large melting point tubes were filled with the



Percentage of methyl 3,5-dinitrobenzoate by weight with ethyl 3,5-dinitrobenzoate.

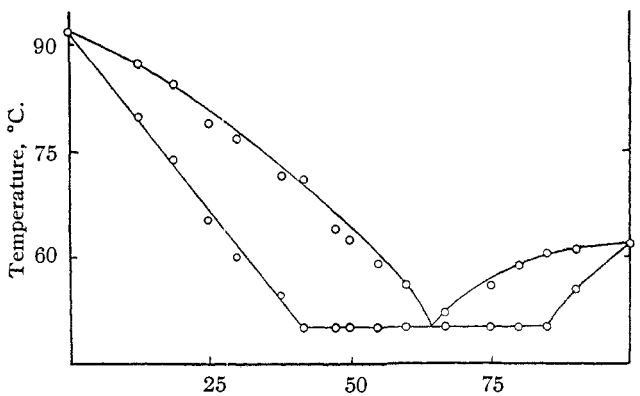
Fig. 2.

different mixes and the temperatures recorded as first appearance of melting was seen and the temperature of clearance as the last morsel of solid disappeared. Heating was slowly carried on in Thiele tubes. Results have been plotted in Fig. 1. The temperature range between tem-

(4) Malone and Reid, THIS JOURNAL, **51**, 3424 (1929).

peratures of first and last melting is small for the pure compounds and for the composition of minimum melting temperature. The curve indicates the formation of a continuous system of mixed crystals in the solid phase and a minimum melting temperature of 52° for the mixture of about 20% methyl *p*-nitrobenzoate with about 80% ethyl *p*-nitrobenzoate.

When the system ethyl 3,5-dinitrobenzoate and methyl 3,5-dinitrobenzoate is studied in similar manner, a like system is evidenced. Results are shown in Fig. 2; a minimum melting temperature of 73° for about equimolar mixture is indicated. A few of the points of first melting within 5% on either side of the mid-point are almost on a line, which may indicate some small range of insolubility in the solid state and an invariant point or true eutectic.



Percentage of butyl 3,5-dinitrobenzoate by weight with ethyl 3,5-dinitrobenzoate.

Fig. 3.

When the system ethyl 3,5-dinitrobenzoate and butyl 3,5-dinitrobenzoate is studied a true eutectic is exhibited with a fairly definite range of insolubility in the solid state. Figure 3 is a plot of results of study on the first and last melting temperatures of mixtures of these two alcohol derivatives. The eutectic would seem to be about 64% butyl 3,5-dinitrobenzoate and near 51°. The range of solubility in the solid state is also approximated by the curve.

Summary

1. Temperature–composition phase diagrams have been established for methyl *p*-nitrobenzoate and ethyl *p*-nitrobenzoate, methyl and ethyl 3,5-dinitrobenzoates and ethyl 3,5-dinitrobenzoate and butyl 3,5-dinitrobenzoate.

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