



takes place. A condenser is sometimes employed for absorbing this energy. It is much simpler, however, to dissipate this energy through a closed circuit as shown in the accompanying sketch. A low resistance relay, say 20 ohms, is connected in series with a high resistance,  $R$  (about 1500 to 1800 ohms) and these in turn are connected to the lighting circuit as indicated. The resistance  $R$  is set so that enough current flows to operate the relay. The contacts of the regulator,  $A$ , are connected across the relay. When the contact is made the relay is short-circuited and its armature released. The energy of the relay coil is thereby dissipated through the closed contact instead of through the open contact and the hot inductive spark eliminated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]  
**PREPARATION OF BENZYL ESTERS OF SOME HIGH-BOILING ACIDS**

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The therapeutic value<sup>2</sup> of certain benzyl esters has recently increased the interest in their preparation. A number of methods have been used with more or less success. The one discussed in this paper is a modification of that used by Bischoff and A. von Hedenstrom<sup>3</sup> by which the ester is made directly from the acid and the alcohol without the use of a catalyst. In all, 8 esters of benzyl alcohol and acids have been prepared with yields varying from 60% in some cases to 90% in others, depending upon the acid.

This method can be used only when the alcohol and acid boil without decomposition at a temperature above the boiling point of water. The apparatus used is very simple.

### General Discussion

A Pyrex tube 1 cm. in diameter, varying in length according to the

<sup>1</sup> Abstract of the thesis presented by Gerald J. Leuck in partial fulfillment of the requirements for the degree of Master of Science in the University of Nebraska.

<sup>2</sup> Macht, *J. Am. Med. Assoc.*, **73**, 599 (1919).

<sup>3</sup> Bischoff and von Hedenstrom, *Ber.*, **35**, 4078 (1902).

demands of the experiment, is inserted in the mouth of a 150cc. Pyrex flask and the joint sealed by a cork stopper. Molecular amounts of benzyl alcohol and the acid are introduced into the flask, the condenser is fitted in place and the flask heated with a free flame so that the vapors of the alcohol and acid reach its top. The heat is controlled so that the vapors of neither the acid nor alcohol escape from the condenser tube. The alcohol and acid soon begin to react to form ester and water, as evidenced by the sputtering noise made when the water comes in contact with the higher-boiling acid and alcohol. Inasmuch as the water vapor is thus not permitted to condense in the flask, it is forced up and out of the tube, and by means of the layer of vapor of alcohol and acid beneath it is prevented from reaching and hydrolyzing the higher boiling ester. The reaction is completed when the sputtering ceases and water vapor no longer issues from the tube.

The height which the alcohol and acid reaches in the condenser tube is a very important consideration. This can usually be determined from the ring of condensing vapor formed by benzyl alcohol as well as by some of the acids. In case this is impossible, a thermometer suspended in the

TABLE I  
EXPERIMENTAL RESULTS

Substance	Length of tube Cm.	Time of reaction	Yield
		Hours	%
Dibenzyl succinate <sup>4</sup> .....	25	1/4	90-95
Benzyl maleate and fumarate <sup>5</sup> .....	25	1/4	75
Benzyl benzoate <sup>6</sup> .....	90	6	85
Dibenzyl phthalate <sup>7</sup> .....	50	5	60
Benzyl butyrate <sup>8</sup> .....	90	5	85
Benzyl valerate.....	90	8	85
Benzyl caproate.....	90	5	88
Benzyl caprylate.....	50	4	80

condenser tube will indicate by the temperature the height of the alcohol and acid vapors and will also show when the temperature at the upper end of the condenser is above the vaporization point of water.

Pure benzyl alcohol must be used. The slightest trace of benzaldehyde or other impurities decreases the yields very markedly.

<sup>4</sup> Del Zanna and Guareschi, *Gazz. chim. ital.*, **11**, 256 (1881). Ref. 3. R. Meyer and K. Marx, *Ber.*, **41**, 2460 (1908). Gomberg and Buchler, *THIS JOURNAL*, **42**, 2059 (1920).

<sup>5</sup> Ref. 3. *Ber.*, **35**, 40, 89-91 (1902).

<sup>6</sup> Claisen, *ibid.*, **20**, 646 (1887). Earl of Berkeley, *J. Chem. Soc.*, **109**, 522 (1910). Tischtschenko, *J. Russ. Phys. Chem. Soc.*, **38**, 355 (1906). Gomberg and Buchler, *THIS JOURNAL*, **42**, 2059 (1920).

<sup>7</sup> Meyer, *Ber.*, **28**, 1577 (1895). Meyer and Jugilewitsch, *ibid.*, **30**, 780 (1897). Ref. 3, p. 4092. Bischoff, *ibid.*, **36**, 160 (1903).

<sup>8</sup> Conrad and Hodgkinson, *Ann.*, **193**, 317 (1878).

The amount of substances used in each case was small and no attempt was made to check the method using large quantities. The method seems to be limited to the preparation of the esters of benzyl alcohol since other high-boiling alcohols were tried and gave unsatisfactory results. Two of the benzyl esters, benzyl phthalate and benzyl butyrate, required that the method be varied.

In the case of dibenzyl phthalate the condenser tube was surrounded with a jacket through which steam was passed while the pressure within the condenser tube was maintained at 200 mm. below atmospheric pressure. In the preparation of benzyl butyrate, it was necessary to apply nearly 1200 mm. pressure before the reaction took place.

Each ester was saponified and the acid and alcohol identified by the usual standard methods.

### Summary

A modification of a standard method of esterification has been worked out, and applied to the preparation of esters of benzyl alcohol and acids with boiling points above the boiling point of water. The advantages of this method are three: (1) it is simple and very easily applied; (2) the product is formed in a relatively high state of purity; (3) the yield is greater in most cases than yields obtained by other methods.

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## THE PREPARATION OF PHENYLIMIDO-PHOSGENE, AND THE CHLORINATION OF FORMANILIDE

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Phenylimido-phosgene, because of its toxic lachrymatory properties, was used by the Germans as a war gas during the last four months of 1917. A sudden temporary revival of its use was noted again in April, 1918, which was ascribed to a clearing out of old chemical stock rather than to a change of military policy in regard to this substance. Although studied by the Allies, phenylimido-phosgene was never adopted or used by them as a weapon. The physiological symptoms are mainly those

<sup>1</sup> The work represented in that portion of this paper dealing with the preparation of phenylimido-phosgene, and thiocarbonyl, as well as some preliminary experiments on the chlorination of formanilide, was carried out in Organic Offense Research Unit No. 3, C. W. S., U. S. A., 1918, by G. A. Perkins, H. A. Shonle and G. A. Taylor. Chloro-phenylimido-phosgene was apparently formed but this was not definitely proved, as the emphasis in the investigation was for the moment elsewhere. The subject has been further studied by W. Lee Lewis and R. S. Bly at Northwestern University. The earlier results are included with the permission of the C. W. S., General Amos A. Fries, Director.