

poor yields of 4-hydroxycoumarins are then obtained.

The new method would appear to be of industrial significance for the production of 4-hydroxycoumarin which is a key intermediate for the synthesis of a number of leading anticoagulant drugs, like dicoumarol and tromexan, and also for the synthesis of modern anticoagulant rodenticides, warfarin and fumarin.

Small quantities of diaryl malonates were often isolated from the reaction product. The possibility of formation of diaryl malonates *in situ* and their further cyclization under the conditions of our method was, however, unlikely since no appreciable quantity of 4-hydroxycoumarins could be obtained when diaryl malonates such as diphenyl malonate were heated with a mixture of anhydrous zinc chloride and phosphorus oxychloride under the usual conditions of the new method.

We have condensed successfully by our method phenols such as phenol, thiophenol, *o*-, *m*-, and *p*-cresols, 2,5-xylene-1-ol,  $\alpha$ - and  $\beta$ -naphthols, and resorcinol, with malonic acid to give, in most cases, good yields of the corresponding known 4-hydroxycoumarins. Thymol and *p,p'*-dihydroxydiphenyl with malonic acid yielded respectively 5-methyl-8-isopropyl-4-hydroxycoumarin, m.p. 223–224°, (*Anal.* Calcd. for  $C_{13}H_{14}O_3$ : C, 71.54; H, 6.47. Found: C, 71.45; H, 6.19) and 4,4'-dihydroxy-6,6'-dicoumarin m.p. > 360°, difficult to combust and characterized through the diacetyl derivative, m.p. 229–230° (*Anal.* Calcd. for  $C_{22}H_{14}O_8$ : C, 65.03; H, 3.47. Found: C, 65.50; H, 3.77). We have also successfully condensed substituted malonic acids, such as *n*-propyl-, *n*-butyl-, *n*-hexyl-, and phenylmalonic acid with phenol to give good yields of the corresponding known 3-substituted 4-hydroxycoumarins. *n*-Octylmalonic acid with phenol yielded 3-*n*-octyl-4-hydroxycoumarin, m.p. 143–144° (*Anal.* Calcd. for  $C_{17}H_{22}O_3$ : C, 74.42; H, 8.08. Found: C, 74.76; H, 8.21).

The following preparation of 4-hydroxycoumarin is typical: A mixture of phenol (225 g.), malonic acid (247.5 g.), anhydrous zinc chloride (979 g.), and phosphorus oxychloride (657 ml.) was heated with stirring at 60–65° for 35 hr., cooled and de-

composed with ice and water and allowed to stand. The resulting crude 4-hydroxycoumarin was collected, dissolved in 10% sodium carbonate and acidified. At about the neutral point some oily by-product separated out and was removed. Acidification of the remaining solution gave 4-hydroxycoumarin of m.p. 201–203° in 64% yield. On recrystallization from water or dilute alcohol pure 4-hydroxycoumarin of m.p. 209–210° was obtained.

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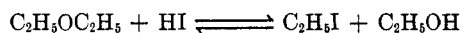
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### Convenient Method for Splitting Diethyl Ether

*Sir:*

During the course of investigation of methods for the preparation of lanthanon iodides in which we were attempting to use diethyl ether as a solvent we discovered an unusual reaction. Anhydrous hydrogen iodide reacts immediately with diethyl ether at room temperature to produce ethyl alcohol and ethyl iodide.



A two layer system is obtained which can be separated by means of a separatory funnel. Undoubtedly hydrogen iodide reacts further with some of the ethyl alcohol to produce more ethyl iodide and some water.

Though we have not conducted a detailed investigation of this reaction it appears that it may be quite superior to the usual method of refluxing ethers with aqueous solutions of hydrogen iodide to split them. We have suggested that a student at another university study the general application of this reaction as a method for splitting ethers.

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