III, IV and V decomposed at their melting points with the evolution of gas. At room temperature they were unstable over long periods of time. Numerous attempts to rearrange these compounds to the corresponding hydrazones (including conditions comparable with those under which Favrel obtained rearranged products) failed. In every case, either starting material was recovered or there was extensive decomposition.

1-Phenylazophenylcyclohexane was also prepared but could not be made to undergo rearrangement to a hydrazone.

Experimental[3]

Phenylazobenzylmalonitrile (**III**) was prepared by adding to a solution of phenyldiazonium chloride prepared from 2.9 g. (0.032 mole) of aniline to a solution of 5.0 g. (0.0321 mole) of benzylmalonitrile[4] and 30.3 g. (0.037 mole) of sodium acetate in 54 cc. of water and 90 cc. of ethanol with vigorous stirring at 0° for two hours. The yellow solid was collected by filtration. A yield of 7.1 g. (84%) of III, m.p. 74.5–77.2°, was obtained after recrystallization from alcohol. Further recrystallization from ethanol gave m.p. 75.8–76.4°.

Anal. Calcd. for $C_{16}H_{12}N_4$: C, 73.9; H, 4.6; N, 21.5. Found: C, 73.9; H, 4.4; N, 21.5.

III, after several months standing in an amber bottle, decomposed to a gummy red mass which could not be crystallized. It was unchanged by four hours treatment with boiling hexane, by five days in refluxing ether under nitrogen, or 50 hours of standing in glacial acetic acid, sodium acetate and water. The last conditions were chosen to approximate those under which rearrangement was obtained by Favrel.

_p_-Nitrophenylazobenzylmalonitrile (IV) was prepared by the same method as was used for III, above.

IV was obtained in 87% yield and melted at 132–133° (dec.) after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{16}H_{11}N_5O_2$: C, 63.0; H, 3.6; N, 23.0. Found: C, 63.0; H, 3.5; N, 22.7.

When IV was heated in glacial acetic acid for one hour and the solvent removed by distillation under reduced pressure a 19% yield of benzylmalononitrile was obtained as shown by m.p. and mixed m.p. No other product could be isolated. IV could be recovered from acetic acid and sodium acetate after eight days of standing at room temperature.

_p_-Xenylazobenzylmalonitrile (V) was prepared in 87% yield by the method used for III and melted after recrystallization from aqueous ethanol at 100–102° (dec.).

Anal. Calcd. for $C_{22}H_{16}N_4$: C, 78.6; H, 4.8; N, 16.7. Found: C, 78.6; H, 5.0; N, 16.7.

1-Phenylazophenylcyclohexane was prepared by the method of Grammaticakis.[5]

Diethyl mesoxalate _p_-xenylhydrazone was prepared in 50% yield by treating diethyl malonate with *p*-xenyldiazonium chloride under conditions similar to those used for the preparation of III. After recrystallization it melted at 97–98° (dec.).

Anal. Calcd. for $C_{19}H_{20}N_2O_4$: C, 67.1; H, 5.9; N, 8.3. Found: C, 66.9; H, 5.7; N, 8.3.

Ultraviolet spectra were obtained with a Beckman DU quartz spectrophotometer. A hydrogen arc was the light source in the range 270–320 mμ, and a tungsten lamp for higher wave lengths. All spectra were measured in ethanol at concentrations of from 0.001 to 0.00001 molar.

Mesoxalonitrile phenylhydrazone, m.p. 139–145° (dec.), was prepared by the method of Lythgoe, Todd and Topham.[6]

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(3) All melting points are corrected. Microanalyses were performed by the Clark Microanalytical Laboratories, Urbana, Illinois, and Dr. Francine Schwarzkopf, Elmhurst, New York.

(4) Our m.p. was 87–89°, in fair agreement with J. C. Hessler, *Am. Chem. J.*, **22**, 169 (1899).

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Vapor Phase Esterification with Chlorosulfonic Acid as Catalyst[1]

BY JOSÉ ERDOS AND ERNESTO URETA

We have used chlorosulfonic acid as an esterification catalyst in the liquid phase with marked success,[2] and have now investigated the use of this catalyst in the vapor phase esterification of acetic acid by ethyl alcohol. The effect of temperature, vaporization velocity, reactant proportions and amount of catalyst have been studied. Of these, temperature and reactant proportions are the most important.

Reactions were carried out in an apparatus designed for work in the vapor phase[3] using pumice stone as a catalyst bed. Using 0.5 mole of acetic acid, 1.0 mole of alcohol, 0.015 mole of chlorosulfonic acid and a rate of addition of 2.5 cc. of acetic acid per minute, the results shown in Table I were obtained.

TABLE I

Temperature, °C.	Yield, %
50–90	80–83
90–130	83–89
130–300	89–91
325	78.5
350	74.5

At 170° with 2 moles of acetic acid, 3 moles of alcohol and 0.015 mole of chlorosulfonic acid, variation in the rate of addition between 2.5 and 20 cc. of acetic acid per minute did not affect the yield. The yield at this temperature was likewise unaffected by a fivefold increase in the ratio of reactants to catalyst. The effect of the molar proportions of reactants at a temperature of 170° using 0.015 mole of chlorosulfonic acid and an addition rate of 10–15 cc. of acetic acid per minute is shown in Table II.

TABLE II

Molar ratio ethyl alcohol/acetic acid	Yield, %
1	71.5
1.25	77.0
1.5	91.0
2.0	91.3
4.0	94.5

A comparison of chlorosulfonic acid with sulfuric acid as a catalyst for this esterification is given in Table III.

TABLE III

Temp., °C.	Yield, %	
	Sulfuric acid	Chlorosulfonic acid
70	71.3	82.2
130	80.0	88.7
200	86.2	90.6
250	87.4	91.0

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