acid-concentration and running a series of small-scale extractions with diisopropylcarbinol using the indicated amount of sodium aluminate and varying amounts of added aluminum nitrate. The yield as a function of added aluminum nitrate was determined within 10% by alpha-counting a plate upon which an aliquot of the resulting carbinol had been evaporated and strongly heated to remove polonium. A more precise determination of the yield could be obtained by alpha pulse analysis[4] of this plate or by adding Pa^{233}, a 27.4-day beta emitter, as a tracer to determine the chemical yield. The addition of Pa^{233} to the fluoride solution before the addition of aluminum ion should result in rapid and complete exchange.

The organic and aqueous phases were kept thoroughly mixed while the aluminum salts were added, because the extractability of protactinium decreases rapidly with time after the fluoride is complexed. It is believed that following liberation from the fluoride complex, the protactinium undergoes a fairly rapid hydrolysis to form polymerized, non-extractable species. After one wash of the carbinol with 3.0 *M* nitric acid and re-extraction of the protactinium into a 10% hydrogen peroxide solution whose volume was 5% of the carbinol volume, a product containing primarily calcium and uranium and about 4% protactinium by weight was obtained.

The remaining uranium was removed by exhaustive extraction with diethyl ether from a solution 0.1 *M* in nitric acid and 10 *M* in ammonium nitrate. Further purification was accomplished by the precipitation of insoluble hydroxides from this aqueous solution, thorough washing to remove salts, and dissolution in oxalic acid. The protactinium was then precipitated as the tannate by the addition of tannic acid and adjustment of the *p*H to 6–7 by the addition of alkali. The resulting tannate was dissolved cautiously in concentrated nitric acid and heated until all the organic matter had been destroyed.

Protactinium was then extracted with an equal volume of diisopropyl ketone[5] from an 8 *M* nitric acid solution, the extract washed with 6 *M* nitric acid, and the protactinium re-extracted with slightly acid hydrogen peroxide. This gave material containing 98% protactinium by weight. Final purification was achieved by extraction with diisopropyl ketone from a 6 *M* hydrochloric acid solution.[6] The resulting ketone contained protactinium in which no impurity could be detected by spectrochemical analysis[7] and no alpha activity other than protactinium by alpha pulse analysis.[3] To date, 35 mg. of pure material has been obtained by this procedure.

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[4] For a description of this instrument see A. Ghiorso, A. H. Jaffey, H. P. Robinson, and B. B. Weissbourd, "The Transuranium Elements," National Nuclear Energy Series, Div. IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, Paper No. 19.2. J. Mech of this laboratory kindly performed this and many more analyses essential to this work.

[5] E. K. Hyde and M. J. Wolf, *National Nuclear Energy Series*, Div. IV, **17B**, Paper No. 3.12.

[6] The distribution coefficient of Pa between diisopropyl ketone and 8 *M* HNO_3 is about 2 and between diisopropyl ketone and 6 *M* HCl is slightly greater. However, by recycle of the organic phase more than 95% of the protactinium can be recovered.

[7] We are indebted to J. Faris of this Laboratory for this analysis done by the copper spark method; see Mark Fred, N. Nachtrieb and Frank Tomkins, *J. Optical Soc. Am.*, **37**, No. 4, 279 (1947).

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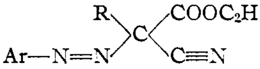
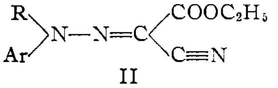
Preparation and Attempted Rearrangement of Phenylazobenzylmalonitriles

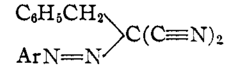
BY DAVID Y. CURTIN[1a] AND CHARLOTTE S. RUSSELL[1b]

Favrel[2] observed that certain derivatives of ethyl cyanoacetate when treated with aryldiazonium salts in buffered solution gave not only the expected azo compound (I) but also the isomeric hydrazone (II). The reaction products were isolated by letting the reaction mixtures stand for a number of weeks until crystallization occurred. Favrel did not report the rearrangement of purified I to II. It was the purpose of the present work to prepare and attempt to effect the rearrangement of certain azo compounds which were easier to isolate than those prepared by Favrel.


I


II

For this reason phenylazobenzylmalonitrile (III), *p*-nitrophenylazobenzylmalonitrile (IV), and *p*-xenylazobenzylmalonitrile (V) were prepared.


$$\begin{matrix}C_6H_5CH_2 \\ ArN{=}N\end{matrix}\!\!>\!C(C{\equiv}N)_2$$

III, Ar = C_6H_5
IV, Ar = p-NO_2-C_6H_4
V, Ar = p-$C_6H_5C_6H_4$

That these compounds were azo compounds and not the rearranged hydrazones is shown by the spectra (Figs. 1 and 2.)

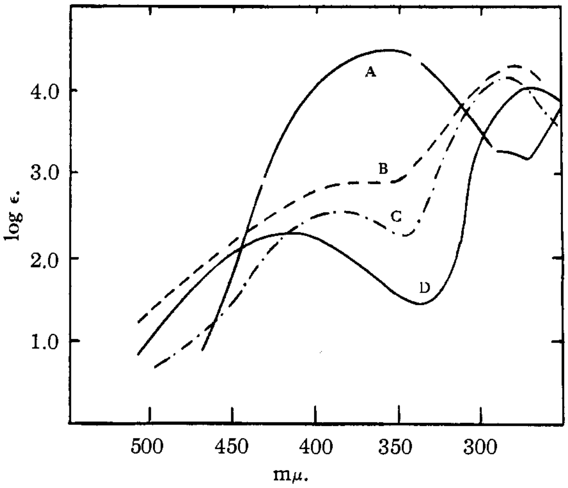


Fig. 1.—A, mesoxalonitrile phenylhydrazone; B, *p*-nitrophenylazobenzylmalononitrile (IV); C, phenylazobenzylmalonitrile (III); D, 1-phenylazo-1-phenylcyclohexane.

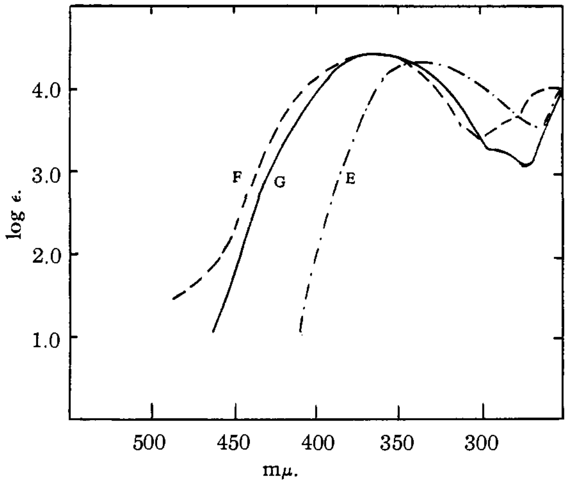


Fig. 2.—Spectra in ethanol of: E, benzaldehyde methylphenylhydrazone; F, diethylmesoxalate *p*-xenylhydrazone; G, mesoxalonitrile phenylhydrazone.

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[1b] Taken from the Ph.D. dissertation submitted to Columbia University by Charlotte S. Russell.

[2] G. Favrel, *Bull. soc. chim. France*, **47**, 1290 (1930).

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).

[5] P. Grammaticakis, *Bull. soc. chim. France*, 438 (1947).

[6] B. Lythgoe, A. R. Todd and A. Topham, *J. Chem. Soc.*, 315 (1944).

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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MARCH 19, 1951

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[1] E. Ureta, Dissertation, Escuela nacl. cienc. biol., 1949.

[2] (a) J. Erdos, *Anales escuela nacl. cienc. biol. Mex.*, **4**, 387 (1947); (b) N. Erdos and G. Carvajal, *ibid.*, **5**, 113 (1948); (c) R. E. Gonzalez, Dissertation, Escuela nacl. cienc. biol., 1947.

[3] J. Erdos, *Mikrochemie ver. Mikrochim. Act.*, **361** (1948).