and 69.5 g. (0.57 mole) of *m*-hydroxybenzaldehyde[10] was heated under reflux for 90 minutes. The product was distilled with steam, extracted with ether and finally extracted into 10% sodium bisulfite solution. The bisulfite addition complex was destroyed by acid and the product was extracted into ether. The solution was dried and distilled to yield 29.3 g. (38%) of *m*-methoxybenzaldehyde, b.p. 126–127° (25 mm.).

Other Reagents.—The other reagents used in the condensation reactions were redistilled or recrystallized commercial products, or they were synthesized by well-known methods given in the Organic Synthesis Series. The triethylamine was Sharples anhydrous grade. The tripropylamine was kindly donated by Sharples Chemicals, Inc.

Condensation Reactions.—Equimolar amounts of the benzaldehyde and the phenylacetic acid were mixed with from three-fourths to equal molar portions of the trialkylamine in 3–5 molar portions of acetic anhydride. The reaction mixture was either heated on a steam-bath or boiled under reflux. The reaction mixture was then heated with benzene, and in most cases a solution was obtained. This solution was extracted with portions of hot 10% sodium hydroxide until no more acidic material could be obtained. The combined basic extracts were acidified with hydrochloric acid to yield the crude acid. Crystallization from a suitable solvent, including any necessary treatment with decolorizing charcoal, completed the preparation.

The mother liquors from the crystallization gave no appreciable amounts of the isomeric acids as by-products. The benzene solutions of the original reaction mixtures yielded only tarry residues, which resisted purification, after the acids had been extracted.

In two of the preparations, α-phenylcinnamic acid and 3-phenylcoumarin, the reaction mixtures were freed of steam-volatile impurities by steam distillation. When cooled, the residues deposited crude crystals of the products which were then recrystallized. Such a method of product isolation has been described before for this type of reaction.[11]

The results of these condensation reactions are presented in Table I.

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(10) R. B. Woodward, *Org. Syntheses*, **25**, 55 (1945).

(11) R. E. Buckles, *J. Chem. Education*, **27**, 210 (1950).

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Isolation of Protactinium from a New Source[1]

BY R. ELSON, G. W. MASON, D. F. PEPPARD, P. A. SELLERS AND M. H. STUDIER

In the past, pure protactinium has not been readily available. The isotope of interest, Pa^{231}, occurs naturally only in uranium deposits. The weight ratio of Pa^{231} to uranium is fixed by the relative half-lives and has a theoretical value of 3×10^{-7}. Workers at this and other laboratories have isolated small quantities of protactinium of varying purity by a variety of methods.[2] The following procedure differs from previously reported procedures for the isolation of protactinium in that concentration and preliminary purifications are accomplished by a liquid–liquid extraction technique. The source material exists in large quantities and is capable of yielding gram quantities of protactinium. The equipment requirements of the process are simple and the time and labor involved are small.

An aqueous waste stream of the Mallinckrodt process for the extraction of uranium from pitchblende concentrate was used as a source material.[3] This aqueous waste is a concentrated nitrate solution of essentially all the acid-soluble gross components of the ore concentrate except uranium and contains between 25 and 50% of the protactinium originally present.

This source solution was contacted with tributyl phosphate. The tributyl phosphate extract was then contacted with hydrofluoric acid, which precipitated fluoride-insoluble impurities and left the protactinium in solution in the aqueous supernatant as the fluoride complex. The aqueous extract contained an average of 0.2 mg. of protactinium and 1 to 10-g. quantities of other elements (primarily calcium, rare earths and iron) per liter.

As protactinium cannot be extracted into organic solvents in the presence of fluoride ion it was necessary to complex all of the fluoride. It was found that diisopropylcarbinol was a suitable solvent for those solutions and the optimum acidity was found to be about 0.5 *M*. Protactinium was therefore extracted from the fluoride solution with diisopropylcarbinol after the fluoride was complexed with aluminum ion and the acidity adjusted with sodium aluminate. The carbinol extract was washed, and the protactinium re-extracted into aqueous hydrogen peroxide. Hydrogen peroxide was used, as protactinium forms an insoluble compound in the presence of peroxide in low acid solutions. By proper adjustment of the acidity, the protactinium could be removed quantitatively from the organic phase with a very small volume of peroxide resulting in a product containing primarily uranium and calcium and 4% protactinium. Further purification consisted of removal of uranium by ether extractions, precipitation of protactinium with tannic acid, and solvent–extraction cycles with diisopropyl ketone.

The over-all yield of protactinium obtained in this process was quite low, 5–35% of the content of the original source solution. This low yield was due primarily to the poor extractability of the protactinium from the Mallinckrodt waste into the tributyl phosphate. However, these low yields resulted from operations under conditions far from optimum for the extraction of protactinium, as the primary purpose of this step was the obtainment of elements other than protactinium. Proper adjustment of acidity and salt strength and removal of complexing ions such as sulfate and fluoride would improve the yield considerably. The yields in subsequent steps were quite good; the diisopropylcarbinol extraction yields were 70–90%, and subsequent operations were nearly quantitative.

Sodium aluminate was selected as the neutralizing agent in the carbinol extraction step because of its low equivalent weight, low heat of reaction and the complexing action afforded. Aluminum hydroxide or other alkaline reagents with low heat of reaction could be used in place of sodium aluminate. Preliminary investigations indicated that other solvents could be used in this step in place of diisopropylcarbinol; the most promising were thenoyltrifluoroacetone dissolved in benzene or other appropriate solvent and diisopropyl ketone. Other reagents to complex fluoride were investigated but proved less satisfactory than aluminum ion.

Experimental

Each sample of Mallinckrodt waste stream was contacted for about two hours with 5% of its volume of tributyl phosphate in a 55-gallon contactor. The tributyl phosphate extract was removed and contacted with one-fourth of its volume of 0.5 *M* hydrofluoric acid to precipitate fluoride-insoluble impurities. The aqueous fluoride supernatant solution contained 95–99% of the extracted protactinium and was 3–4.5 *M* in acid and approximately 0.2 *M* in fluoride.

Protactinium was extracted from this fluoride solution by contacting it with about 40% of its volume of diisopropylcarbinol. The acidity was adjusted to 0.5–0.8 *M* by the addition of sodium aluminate, and the fluoride was complexed by the addition of sufficient aluminum nitrate to give a final aluminum concentration approximately 0.6 *M* in excess over a 3:1 molar ratio of aluminum to initial fluoride.

The amounts of neutralizing and complexing agents to be added were determined easily and rapidly by titrating an aliquot of the solution to be processed to determine the total

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(1) The subject of this paper is discussed in greater detail in Argonne National Laboratory Reports ANL-4176, 4411 and 4469.

(2) A. von Grosse, *Nature*, **120**, 621 (1927), and G. Graue and H. Kading, *Angew. Chem.*, **47**, 650 (1934), used residues from pitchblende as their source of protactinium, while R. Thompson and co-workers, National Nuclear Energy Series, Div. IV, Vol. 17B, Paper No. 6.4, used the carbonate residue obtained from treatment of the acid solution of uranium ore with excess sodium carbonate. See also L. Katzin, *et al.*, THIS JOURNAL, **72**, 4815 (1950).

(3) This process for the extraction of uranium differs from those previously described in that a carbonate precipitation is not made.

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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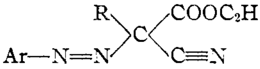
Preparation and Attempted Rearrangement of Phenylazobenzylmalonitriles

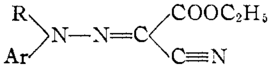
BY DAVID Y. CURTIN[1a] AND CHARLOTTE S. RUSSELL[1b]

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.



$Ar{-}N{=}N{-}C(R)(COOC_2H_5){-}C{\equiv}N$

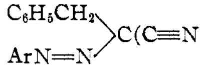
I



$(R)(Ar)N{-}N{=}C(COOC_2H_5){-}C{\equiv}N$

II

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



$(C_6H_5CH_2)(ArN{=}N)C(C{\equiv}N)_2$

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.)

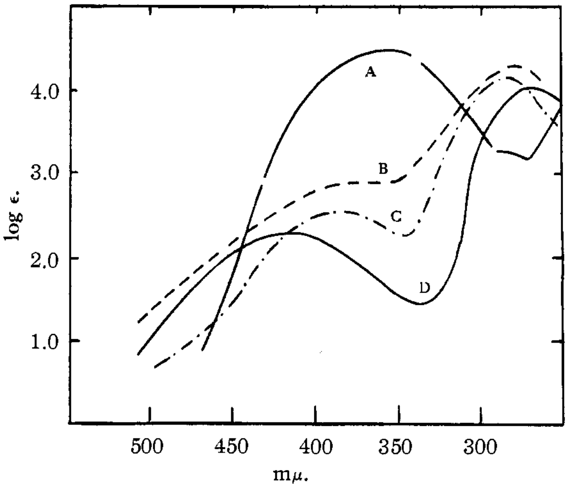


Fig. 1.—A, mesoxalonitrile phenylhydrazone; B, *p*-nitrophenylazobenzylmalononitrile (IV); C, phenylazobenzylmalonitrile (III); D, 1-phenylazo-1-phenylcyclohexane.

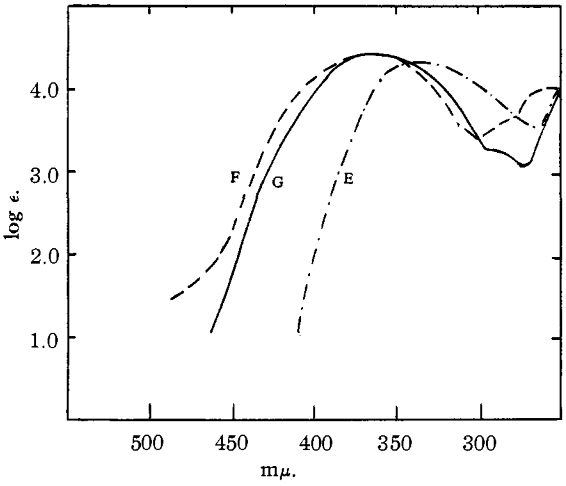


Fig. 2.—Spectra in ethanol of: E, benzaldehyde methylphenylhydrazone; F, diethylmesoxalate *p*-xenylhydrazone; G, mesoxalonitrile phenylhydrazone.

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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).