161°. The above-mentioned melting point of the hydrate agrees with that cited earlier,[5] but the present melting point of the anhydrous acid is given for the first time. The acid liberates a considerable amount of heat when placed in contact with water.

Bromomethylphosphonic Acid.—In an attempt to form bromomethylphosphonyl dibromide, formaldehyde and phosphorus tribromide were heated in a sealed vessel precisely as described above for the chloro analog. Very considerable decomposition took place and the only identified products were unchanged phosphorus tribromide and a small amount of methylene bromide. Bromine failed to react after many hours with methylphosphonyl dichloride under ultraviolet irradiation at 120–125°. A similar failure was recorded in a reaction of hydroxymethylphosphonic acid with phosphorus pentabromide, obtained *in situ* by addition of bromine to phosphorus tribromide.

Ford-Moore and Williams,[7] in describing the Arbuzov reaction of triethyl phosphite with methylene bromide, state that: "the reaction is very slow with a poor yield of the diphosphonate, the monophosphonate being almost absent." We carried out this reaction under somewhat drastic conditions and obtained rather satisfactory results. Triethyl phosphite (126 g.) and methylene bromide (162 g.) were heated in an autoclave at 172° for four hours. The resulting mixture was distilled under reduced pressure and yielded 23 g. of diethyl bromomethylphosphonate, b.p. 50° at 0.05 mm., $n^{20}{}_D$ 1.4592, $d^{20}{}_4$ 1.4363, *MR* 43.99 (calcd. *MR* 43.92). The product also boils at 66° at 0.25 mm. The compound was reported previously with b.p. 99° at 1 mm., $d^{20}{}_{20}$ 1.4474, $n^{20}{}_D$ 1.4587.[8]

The ester was hydrolyzed by refluxing for nine hours with 48% hydrobromic acid, the solution was concentrated under reduced pressure and the residue was taken up in water. Re-evaporation under reduced pressure after treatment with charcoal, yielded an uncrystallizable sirup. A small portion of this was seeded with a tiny crystal of chloromethylphosphonic acid; this resulted in rapid crystallization of the product. A small portion of this was then used to seed the main batch. After drying *in vacuo* over phosphorus pentoxide the resulting acid melted at 62°, softening at 54°.

Anal. Calcd. for CH_4O_3BrP: P, 17.71; Br, 45.68. Found: P, 17.96; Br, 44.71.

Iodomethylphosphonic Acid.—Diethyl iodomethylphosphonate was prepared conventionally from methylene iodide and triethyl phosphite; b.p. 61° at 0.01 mm. The ester (23.6 g.) was dissolved in 100 ml. of concentrated hydrochloric acid and 50 ml. of water and refluxed for one day. After the usual treatment with charcoal, evaporation and drying under reduced pressure a brownish product was obtained which contained free iodine. This evidently originated in partial hydrolysis of the halogen and formation of hydriodic acid. The iodine was removed by prolonged evacuation of finely powdered product, which then melted at 75–82°. It was then recrystallized from ethylene chloride and after drying under reduced pressure melted at 89°, softening at 86°.

Anal. Calcd. for CH_4O_3IP: P, 13.96. Found: P, 13.9.

Attempted Preparation of Fluoromethylphosphonic Acid.—Diethyl iodomethylphosphonate (25 g.) was added to 40.3 g. of thoroughly dried silver fluoride and the mixture was slowly heated in a distillation apparatus to 125° over five hours at about 30 mm. The distillate (2.3 g., b.p. 89–93° at 20 mm.) was redistilled, yielding a product which boiled at 91–92° at 21 mm. The physical constants and a qualitative examination showed this to be diethyl methylphosphonate, formed apparently by a reductive process from the iodo derivative. This was the only recoverable product from the reaction.

Hydroxymethylphosphonic Acid.—This acid is readily prepared by the method outlined by Page.[9] Its purification is a rather tedious process. Crystallization from alcohol-ethyl acetate mixture proposed by Page is rather wasteful of the product. We noted that this acid has a negative coefficient of solubility in ethyl acetate with temperature. It dissolves quite readily in dry ethyl acetate at about −15° and separates from it in the form of fine crystals on warming to room temperature. After thorough drying the product melts at 99–100°. Previously reported highest melting point is 98–99°.[10]

Page[9] stated that in qualitative tests run in the cold this acid inhibits the precipitation of the yellow phosphomolybdate precipitate from solutions containing phosphates. We examined this effect under the normally used conditions of analytical procedure (hot solution in the presence of much ammonium nitrate) and found that such inhibition does not take place under these conditions.

Determination of Apparent Dissociation Constants.—Both the procedure of the determinations and the method of calculation were precisely the same as reported in the previous paper.[1] In all cases the locations of the breaks in the titration curves agreed excellently with the calculated values; no evidence of cleavage of the carbon–phosphorus link in the trichloromethyl acid was observed The approximate locations of the breaks, which may be of interest for titrations with visual indicators were as follows: hydroxymethylphosphonic acid *p*H 5 and 9.5; chloromethylphosphonic acid 4.5 and 8.5; dichloromethylphosphonic acid 4 and 8.5; trichloromethylphosphonic acid 3.5 (very slight) and 7.5; bromo- and iodomethylphosphonic acids 4.5 and 9.

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(8) A. Ya. Yakubovich, V. A. Ginzburg and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 303 (1950).

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The Preparation of Ethyl *o*-Cyanocinnamate and *o*-Carbethoxycinnamonitrile

By James W. Curry[1,2]

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Interest in the anomalous conversion of *p*-quinonemonoxime to *p*-azoxyphenol brought about by treatment with benzenesulfonyl chloride in pyridine and subsequent heating[3–5] suggested an examination of the behavior of the isomeric oximes of 1,2-naphthoquinone under the same conditions. It was possible to obtain the benzenesulfonic esters of 1,2-naphthoquinone-1-oxime and 1,2-naphthoquinone-2-oxime when these oximes were treated with benzenesulfonyl chloride and pyridine, followed by isolation through aqueous dilution of the reaction mixture, and recrystallization from a nonhydroxylic solvent. When attempts were made to recrystallize the benzenesulfonic esters from 95% ethanol, smooth conversions were effected to products which did not contain sulfur. Microanalysis indicated that the isomeric products had the composition $C_{12}H_{11}NO_2$, and infrared analysis showed the presence, in both compounds, of conjugated $C{\equiv}N$ and conjugated ester $C{=}O$ groupings. On the basis of the participants in the conversions and analyses of the products, structure III, ethyl *o*-cyanocinnamate, can be assigned to the product, m.p. 76–77°, obtained from the benzenesulfonic ester of 1,2-naphthoquinone-1-oxime (I). Simi-

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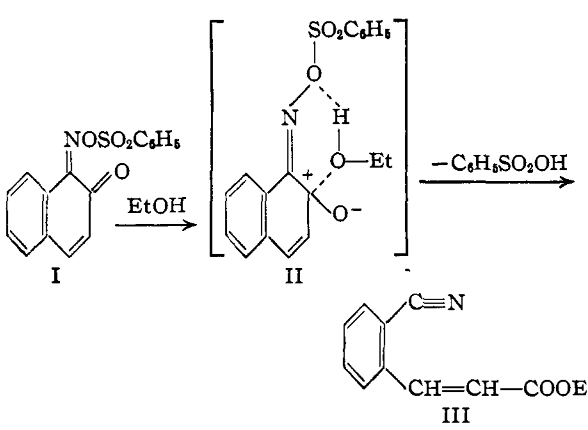
(1) U. S. Atomic Energy Commission Predoctoral Fellow, 1951–1952.

(2) Dow Corning Corporation, Midland, Michigan.

(3) N. J. Leonard and J. W. Curry, *J. Org. Chem.*, **17**, 1071 (1952).

(4) R. A. Raphael and E. Vogel, *J. Chem. Soc.*, 1958 (1952).

(5) E. Beckmann and O. Liesche, *Ber.*, **56**, 1 (1923).



larly, the product, m.p. 45–46°, from the benzenesulfonic ester of 1,2-naphthoquinone-2-oxime, is *o*-carbethoxycinnamonitrile.

The assignment of structure III is consistent with the finding of Werner and Piguet[6] that *trans*-*o*-cyanocinnamic acid was formed by treating 1,2-naphthoquinone-1-oxime (I) with benzenesulfonyl chloride in pyridine solution, followed by acidification of the reaction mixture with dilute sulfuric acid. Also, the product obtained by Beckmann and Liesche,[5] when they subjected 1,2-naphthoquinone-2-oxime to similar reaction conditions, has been identified as *o*-carboxycinnamonitrile.[7] A logical mechanism for the facile ethanolysis of the benzenesulfonic ester of 1,2-naphthoquinone-1-oxime (I) probably involves a cyclic six-membered transition state (II), and a similar transition state can be pictured to account for the formation of *o*-carbethoxycinnamonitrile. One might expect *cis* products to result from these conversions, but isomerization to the *trans* compounds is readily possible in the acidic medium (liberation of benzenesulfonic acid) either at the transition stage or on equilibration of the product. On the basis of the infrared evidence, it is probable that the *trans* forms of both esters were obtained.[8] The spectrum of ethyl *o*-cyanocinnamate showed a band at 967 cm.$^{-1}$, and the same band, though less intense, was found in the spectrum of *o*-carbethoxycinnamonitrile. In neither spectrum was there a band indicative of a *cis* configuration.[9]

Experimental[10]

Benzenesulfonic Ester of 1,2-Naphthoquinone-1-oxime.—A mixture of 12.6 g. (0.073 mole) of 1,2-naphthoquinone-1-oxime[11] and 12.9 g. (0.073 mole) of benzenesulfonyl chloride in 70 ml. of pyridine was allowed to stand until the heat of reaction had subsided. The reaction mixture was diluted to 500 ml. with water, and the precipitate which formed was filtered, washed with water and dried. The product was recrystallized from chloroform–carbon tetrachloride as yellow needles which possessed two melting points. The material melted at 86.5–89°, almost immediately resolidified and melted again at 139.5–141.5° (dec.), (reported[12] for the benzenesulfonic ester of 1-nitroso-2-naphthol, 124–125° and 141°); yield 5.8 g. (26%).

Anal. Calcd. for $C_{16}H_{11}NO_4S$: C, 61.35; H, 3.54; N, 4.37. Found: C, 60.45; H, 3.63; N, 4.31.

The infrared spectrum showed an absorption band at 1648 cm.$^{-1}$, indicating the presence of conjugated C=O.

Benzenesulfonic Ester of 1,2-Naphthoquinone-2-oxime.—This compound was prepared from 1,2-naphthoquinone-2-oxime[13] in the same manner as was the benzenesulfonic ester of the 1-oxime. The material was recrystallized as yellow platelets from carbon tetrachloride, m.p. 118–121° (dec.); yield 12.3 g. (54%).

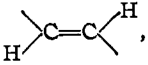
Anal. Calcd. for $C_{16}H_{11}NO_4S$: C, 61.35; H, 3.54; N, 4.37. Found: C, 61.27; H, 3.79; N, 4.56.

Absorption bands at 1685 and 1592 cm.$^{-1}$ in the infrared spectrum indicated the presence of conjugated C=O and conjugated C=N, respectively.

Ethyl *o*-Cyanocinnamate.—To 150 ml. of 95% ethanol was added 5.0 g. (0.016 mole) of the benzenesulfonic ester of 1,2-naphthoquinone-1-oxime. The mixture was boiled until all the material had gone into solution, then for five minutes longer. The solution was decolorized with Norite, filtered and poured into a large excess of cold water. The mixture was cooled to crystallization and the product was separated by filtration. Recrystallization from dilute ethanol gave colorless needles, m.p. 76–77° (reported[8] 57°); yield 2.6 g. (82%).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.41; H, 5.42; N, 6.91.

The infrared spectrum showed absorption bands at 2220, 1714, 1636, and 967 cm.$^{-1}$, indicative of conjugated C≡N, conjugated ester C=O, conjugated C=C, and *trans*

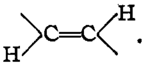


, respectively.

***o*-Carbethoxycinnamonitrile.**—This ester was obtained from 5.0 g. (0.016 mole) of the benzenesulfonic ester of 1,2-naphthoquinone-2-oxime by the procedure described above for the synthesis of ethyl *o*-cyanocinnamate. Recrystallization from dilute ethanol gave colorless needles, m.p. 45–46°; yield 2.5 g. (79%).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.78; H, 5.78; N, 7.16.

The infrared spectrum showed the presence of conjugated C≡N (2212 cm.$^{-1}$), and conjugated ester C=O (1712 cm.$^{-1}$). There was also a weak band at 967 cm.$^{-1}$, indicative of *trans*



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Ruthenium Isotope Abundances[1]

BY LEWIS FRIEDMAN AND A. P. IRSA

RECEIVED JUNE 17, 1953

Mass spectrographic investigations of the abundances of the ruthenium isotopes have been carried out by Aston[2] and Ewald.[3] Ewald's work, which has been tentatively accepted by the N.R.C. Subcommittee on Nuclear Constants,[4] involved a photographic plate calibration using cadmium abundance data which subsequently have been

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(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

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