A platinum electrode was the anode; for voltammetric studies a wire with an exposed surface area of about 0.15 cm.^{2} was used and a foil electrode (surface area about 6 cm.^{2}) was used for electrolyses. A silver wire coiled in a helix of *ca.* 1.3-cm. diameter and immersed in a solution of silver perchlorate and sodium perchlorate in acetonitrile served as the reference electrode and as the cathode. It was necessary to isolate the silver electrode from the anthracene solution during electrolysis by means of a cylinder fitted with a fine porosity fritted disk to avoid reduction of the electrolysis products to the starting material. All solutions were deaerated for at least 30 min. by bubbling with nitrogen which had been passed through vanadous chloride solution, concentrated sulfuric acid, and finally acetonitrile. An atmosphere of nitrogen was maintained above the solution during electrolysis.

Current–Voltage Curves.—An approximate current–voltage curve (uncorrected for the *iR*-drop in the cell) was recorded on each electrolysis solution over the voltage range: 0 to +3 v. (*vs.* Ag/Ag$^-$). The exact position of the anodic wave was then determined point by point using the potentiostat by setting the platinum electrode potential manually and observing the current. Electrolyses were performed with the anode potential set to a value about 0.1 v. more positive than the half-wave potential determined from the latter current–voltage curve, which was corrected for the *iR*-drop in the cell. The electrolysis was allowed to proceed until the current decreased to a constant value. Magnetic stirring continued throughout the electrolysis.

An acetonitrile solution 0.5 *N* in sodium perchlorate and 0.1 *N* in silver perchlorate and a solution of ethanol in acetonitrile plus supporting electrolyte showed no appreciable current at potentials less anodic than +1.2 v. (*vs.* Ag/Ag$^+$). Anthracene in this solvent is oxidized at potentials more anodic than about +0.88 v. (*vs.* Ag/Ag$^+$).

Properties of the Electrolysis Product.—The compound was not appreciably soluble in absolute ethanol, ether, water, benzene, or chloroform, but could be recrystallized from acetone. On heating it turned brown slowly near 250° and melted to a dark brown liquid at about 275°. Addition of concentrated sulfuric acid to the product caused the formation of a green color; upon standing for less than 1 min. the color became a ruby red. No color change was observed upon heating a solution of the electrolysis product in benzonitrile, anisole, or xylene.

The results of direct elemental analyses for C, H, and O were 87.24, 4.80, and 8.22%, respectively, and are in excellent agreement with those calculated for bianthrone: C, 87.02; H, 4.70; and O, 8.28%. Duplicate molecular weight determinations (cryoscopy in benzene) of 319 and 329 were reported; the low results are attributed to experimental error.

The ultraviolet absorption spectrum of the electrolysis product in absolute ethanol solution showed a peak at 267 mμ (log ϵ 4.39), a shoulder at 300 mμ (log ϵ 3.9), and a minimum at 242 mμ (log ϵ 4.07). The infrared absorption spectrum (potassium bromide pellet) showed strong peaks at 1320 cm.$^{-1}$, 1660 cm.$^{-1}$ (conjugated carbonyl), and peaks of moderate intensity at 1580 cm.$^{-1}$, 690 cm.$^{-1}$, 930 cm.$^{-1}$, and 790 cm.$^{-1}$.

Mass spectra were obtained by introducing the sample directly into the electron beam of the mass spectrometer[11] and showed peaks at *m/e* 193 and 165; at the sample pressures used no peaks were evident at higher *m/e* values.

Chemical Synthesis of Bianthrone.—Bianthrone was prepared chemically by the action of concentrated nitric acid on a suspension of anthracene in glacial acetic acid.[12] The melting point and infrared and ultraviolet spectra of this preparation were identical to those of the electrolysis product. The reactivities with the reagents previously mentioned were also the same for the two preparations. The mass spectrum of this compound when injected directly into the electron beam was identical with that obtained from the electrolysis product.

Acknowledgment.—The authors are grateful to Mr. A. L. Burlingame and to Mr. James A. McCloskey, Department of Chemistry, Massachusetts Institute of Technology, for their interest and for their assistance in obtaining and interpreting the mass spectral data.

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[11] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc. New York, N. Y., 1962, pp. 33, 34.

[12] E. Josephy and F. Radt, "Elsevier's Encyclopedia of Organic Chemistry," Vol. 13, Elsevier Publishing Co., New York, N. Y., 1946, p. 766.

Beckmann Rearrangement of Arylglyoxylonitrile Oxime *p*-Toluenesulfonates[1]

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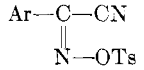
Oxime esters readily undergo the Beckmann rearrangement,[2,3] and references to literature on this subject are available in recent papers.[4,5]

A brief study of the rearrangement of the *p*-toluenesulfonates (I) of five phenylglyoxylonitrile oximes is reported here. Characterization of these oxime tosylates, prepared from the sodium salt of the corresponding phenylglyoxylonitrile oxime[6] and tosyl chloride, is summarized in Table I.[7]

TABLE I

OXIME TOSYLATES (I)



$$\mathrm{Ar{-}C({=}N{-}OTs){-}CN}$$

I, Ar	M.p., °C.	Yield, %	Anal. Calcd. C	Anal. Calcd. H	Anal. Calcd. N	Anal. Found C	Anal. Found H	Anal. Found N
Phenyl	135	64	59.98	4.03	9.33	60.12	4.09	9.01
p-Chlorophenyl	154	66	53.81	3.31	8.37	53.74	3.40	8.18
p-Nitrophenyl	146	34	52.17	3.21	12.27	52.11	3.11	11.98
p-Methoxyphenyl	141	55	58.18	4.27	8.48	58.07	4.43	8.32
Mesityl	152	86	63.14	5.30	8.18	62.99	5.47	8.14

The α-cyano tosyl esters (I) appeared to be much more stable than ordinary oxime tosylates.[2,4] They did not undergo solvolysis in refluxing ethanol, and could be recovered unchanged either after a three-hour period of refluxing in benzene containing an equivalent of aniline or after a pyridine solution was warmed on the steam bath for two hours.[8]

When treated with excess sodium ethoxide in ethanol or with ethanolic potassium hydroxide, the first four tosylates listed in Table I were converted to diethyl

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[1] This research was supported by the Advanced Research Projects gency under Army Ordnance contract no. DA-01-021-ORD-11909.

[2] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948); W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5880, 5972 (1958).

[3] J. C. Craig and A. R. Naik, *ibid.*, **84**, 3410 (1962).

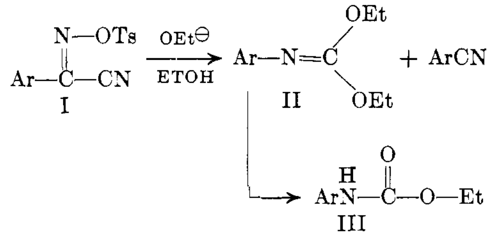
[4] W. Z. Heldt, *J. Org. Chem.*, **26**, 1695 (1961).

[5] J. P. Freeman, *ibid.*, **26**, 3507 (1961).

[6] M. R. Zimmermann, *J. prakt. Chem.*, (2) **66**, 353 (1902).

[7] Although both *syn* and *anti* forms of all the oximes apparently exist,[6] isomeric tosylates were isolated only in the mesityl case (see Experimental). The *anti* configuration of the oxime tosylates indicated in Table I and in the discussion following cannot be considered to have been established; a *syn* configuration also could explain the results obtained here. Since the type of migration observed here corresponds to that usually associated with an *anti* configuration, these oximes tosylates are written in the *anti* configuration.

[8] With I, Ar = *p*-chlorophenyl, some rearrangement probably occurred during chromatography on an alumina column[3] for only 75% recovery of tosylate was possible. Characterization of any rearrangement product was not attempted. Rearrangement of phenylglyoxylonitrile oxime to N-phenyloxamide by phosphorus pentachloride in ether, followed by hydrolysis, has been reported,[6] but the *p*-nitro-, *p*-chloro-, and *o*-chlorophenylglyoxylonitrile oximes were reported to be unaffected by this treatment. We have observed that both the phenyl and *p*-chlorophenyl oximes and phosphorus pentachloride in ether or methylene chloride yield not only some oxamide, but also significant amounts (15–30%) of the α-chloroiminoarylacetonitrile. The results of this study will be reported later.



N-arylimidocarbonates II.[9] A small amount of aryl cyanide also was formed.[7]

To determine the amount of nitrile and imidocarbonate produced in these ethoxide-induced rearrangements, the reaction mixtures were chromatographed on silica gel. It has been shown that diethyl N-arylimidocarbonates are converted cleanly to N-arylurethans (III) during passage through a silica gel column.[10] The results of those experiments are summarized in Table II.

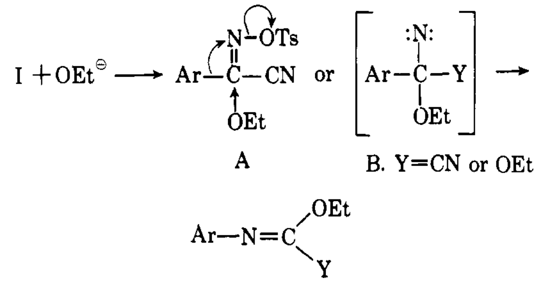
TABLE II

BECKMANN REARRANGEMENT OF α-OXIMINO TOSYLATES (I)

I, Ar	Yield, %[a] Nitrile	Yield, %[a] Urethan
Phenyl, run 1[b]	. .	62
run 2[c]	8.3	60
p-Chlorophenyl, run 1	5.6	64.0
run 2	4.5	63
p-Methoxyphenyl, run 1	6.4	76.7
run 2	6.8	64
p-Nitrophenyl, run 1	8.3	24.9
Mesityl, run 1[d]	Trace	None

[a] Yield of product isolated from the chromatographic column. [b] Run 1 was conducted with about 2.5 equivalents of potassium hydroxide in ethanol at about 60°. [c] Run 2 refers to experiments conducted with about 2.3 equivalents of sodium ethoxide in ethanol at reflux. [d] Cleavage of the tosylate ester and recovery of oxime accounted for about 50% of the reaction products (see Experimental).

The stability of these tosylates indicates that nucleophilic attack of ethoxide ion on the carbon atom of the C=N function, rather than a prior fragmentation,[5] initiates these rearrangements. Although it appears that the rearrangement proceeds either through a concerted process such as that illustrated by A or through an intermediate with an electron deficient nitrogen (B),[7,11] no definitive mechanistic choice can be made at this time. The timing of the cyanide ion displacement is unknown also.



The small amount of nitrile formed may arise from nucleophilic attack at the nitrile function of the cyano tosylate[12]; thus it was of interest to see if the rearrangement of the mesitylglyoxylonitrile oxime tosylate, in which attack at the oxime C=N function was hindered, would lead to mesitonitrile. However, cleavage of the tosylate with regeneration of the oxime appeared to be the main reaction path. This would indicate that attack at the cyano function is not a favorable process with these tosylates, and might be considered additional evidence for their *anti* configuration.[7]

Experimental[13]

The procedure used for the preparation of the first four cyanooxime tosylates listed in Table I is illustrated by the following description.

Preparation of Phenylglyoxylonitrile Oxime *p*-Toluene Sulfonate.—A solution of sodium ethoxide was prepared by dissolving 2.3 g. (0.10 g.-atom) of sodium in 50 ml. of absolute ethanol. This solution was cooled in an ice bath while 11.7 g. (0.10 mole) of phenylacetonitrile and 10.3 g. (0.10 mole) of butyl nitrite was added dropwise. The solution then was stirred at ambient temperature for 45 min. The volume of ethanol was concentrated to 30 ml. at reduced pressure, 30 ml. of ether was added, and the sodium salt of phenylglyoxylonitrile oxime was removed by filtration (9.0 g.). This was suspended in 100 ml. of benzene and 10.2 g. of *p*-toluenesulfonyl chloride was added portionwise. The mixture was refluxed for 2 hr., cooled, and filtered. The filter cake was washed with benzene. The filtrate was washed with water, dried over magnesium sulfate, and evaporated at reduced pressure. The residue 13.9 g., was recrystallized from 95% ethanol. Thus, the tosylate of phenylglyoxylonitrile oxime, 10.2 g. (64% based on sodium salt), m.p. 134–135°, was obtained.

Mesitylglyoxylonitrile Oxime.—The reaction between butyl nitrite and mesitylacetonitrile was conducted as described before except that the ethanol solution was refluxed for 2 hr. The oxime was isolated after chromatography on silica gel and recrystallized from chloroform-hexane, m.p. 113–114°.

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.89. Found: C, 70.14; H, 6.83; N, 14.95.

In subsequent runs, the oxime isolated had a m.p. of 70–77° and was apparently (infrared and analysis) a mixture of *syn* and *anti* forms. No isomerization was observed during recrystallization or chromatography on silica gel, but the isomer of m.p. 113–114° could be separated by chromatography.

Mesitylglyoxylonitrile Oxime *p*-Toluenesulfonate.—A solution of 1.10 g. of the oxime (m.p. 113–114°) and 1.2 g. of *p*-toluenesulfonyl chloride in 20 ml. of acetone was treated dropwise at 0° with 2.5 ml. of 2.6 *N* aqueous sodium hydroxide. After 15 min., 5 ml. of water was added and stirring was continued for 30 min. without the cooling bath. Water (25 ml.) was added, and the precipitate was filtered and washed with water. The tosylate weighed 1.80 g., m.p. 150–152°. It was recrystallized from hexane–chloroform, m.p. 152–153°.

When the tosylate was prepared from the oxime mixture of m.p. 70–77°, the crude product melted at 132–136°.

Anal. Calcd. for $C_{18}H_{18}N_2O_3S$: C, 63.14; H, 5.30; N, 8.18. Found: C, 63.12; H, 5.34; N, 7.99.

The tosylate characterized earlier (m.p. 152–153°) could be obtained by recrystallization of the mixture. The isomeric tosylate

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[9] Rearrangement of the tosylate I, Ar = *p*-nitrophenyl, gave a much more complex product mixture than indicated here, probably due to condensations involving the nitro group. However, some of the expected products were obtained (Table II).

[10] T. E. Stevens, *J. Org. Chem.*, **26**, 3451 (1961). Characterization of several diethyl imidocarbonates and their conversion to urethans are reported here. The infrared spectra of these imidocarbonates have strong C=N absorption at 5.9–6.0 μ, and their presence in the reaction mixtures converted directly to urethans was confirmed by infrared spectral examination of the crude products.

[11] Since mechanism B would not require *anti* migration of the aryl group, the *syn* configuration of the oxime tosylates cannot be ruled out.

[12] Tosylates of arylaldehyde oximes decompose readily to a mixture of nitrile and isonitrile; see E. Müller and B. Narr, *Z. Naturforsch.*, **16b**, 845 (1961).

[13] Melting points are uncorrected.

was obtained as the first fraction elected from a silica gel column, m.p. 149–150°. Its infrared spectrum was quite different from that of the 152° isomer.

Anal. Calcd. for $C_{18}H_{18}N_2O_3S$: C, 63.14; H, 5.30; N, 8.18. Found: C, 63.07; H, 5.40; N, 7.62.

Reaction of Sodium Ethoxide and Phenylglyoxylonitrile Oxime Tosylate.—A mixture of 5.00 g. (16.7 mmoles) of the tosylate and 100 ml. of absolute ethanol was refluxed while 13.9 ml. of 2.60 *N* sodium ethoxide in ethanol was added dropwise. The mixture was refluxed an additional 2 hr. and then the volume of ethanol was reduced to about 25 ml. at reduced pressure. The residue was diluted with water and the product was partitioned between water and methylene chloride. Evaporation of the methylene chloride left 2.49 g. of residue. Distillation of this residue gave diethyl N-phenylimidocarbonate, 1.73 g., b.p. 100° (5 mm.), n^{20}_D 1.5140, infrared spectrum identical with that of an authentic sample.[10]

Diethyl N-(*p*-Chlorophenyl)imidocarbonate.—A solution of 2.0 g. (6 mmoles) of the tosylate of *p*-chlorophenylglyoxylonitrile oxime in 75 ml. of absolute ethanol was stirred at 60° while 13 mmoles of potassium hydroxide in 10 ml. of ethanol was added dropwise. The solution then was stirred overnight at ambient temperature. After the volume of ethanol in the reaction mixture had been concentrated to about 20 ml., water was added, and the mixture was extracted with methylene chloride. The residue obtained on evaporation of the methylene chloride was distilled to give diethyl N-(*p*-chlorophenyl)imidocarbonate, 0.8 g., n^{20}_D 1.5295, b.p. 100° (1 mm.), infrared spectrum identical with that of an authentic sample.[10]

Isolation of Urethans and Nitriles.—The procedures used to obtain the data given in Table II are illustrated.

(A) **Ethanolic Potassium Hydroxide and *p*-Chlorophenylglyoxylonitrile Oxime Tosylate.**—A solution 3.35 g. (10 mmoles) of the tosylate was treated with 22 mmoles of potassium hydroxide in ethanol as described earlier. The 3.0 g. of crude residue obtained was chromatographed on a silica gel column. Pentane in methylene chloride, methylene chloride, and ethyl acetate in methylene chloride were used as successive eluents. The first fraction characterized was *p*-chlorobenzonitrile, 0.077 g. (5.6%), m.p. 92–93°, infrared spectrum identical with that of an authentic sample. The major fraction, eluted by 5% ethyl acetate in methylene chloride, was recrystallized from hexane and gave *p*-chlorophenylurethan, 1.28 g. (64%), m.p. 68–69° (reported[10] m.p. 68–69°).

(B) **Ethanolic Sodium Ethoxide plus *p*-Methoxyphenylglyoxylonitrile Oxime Tosylate.**—A solution of 4.95 g. (15 mmoles) of the tosylate in 100 ml. of hot absolute ethanol was stirred while 30 ml. of 1.19 *N* sodium ethoxide in ethanol (36 mmoles) was added. The mixture was refluxed for 2 hr. The organic product was isolated by extraction with methylene chloride and was chromatographed on a silica gel column. The first fraction characterized was an isonitrile, 0.127 g. (6.4%), m.p. 61–62°, infrared spectrum identical with that of authentic material. The major fraction, *p*-methoxyphenylurethan, weighed 2.27 g. (76.7%). One recrystallization from hexane gave 1.88 g. of urethan, m.p. 65–66° (reported[14] m.p. 66–67°).

(C) **Ethanolic Potassium Hydroxide and Mesitylglyoxylonitrile Oxime Tosylate.**—When 1.7 g. (5 mmoles) of the tosylate of m.p. 152° (presumably of configuration I) was allowed to react with 12 mmoles of potassium hydroxide in 40 ml. of ethanol for 80 min., the only products characterized after chromatography on silica gel were mesitylglyoxylonitrile oxime, 0.38 g. (40%), m.p. 113–114°, and 0.19 g. of an oil that appeared (infrared and analysis) to be mesitylglyoxylonitrile oxime ethyl ether.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.45; N, 12.96. Found: C, 72.06; H, 7.69; N, 14.3.

In another experiment, 2.60 g. (7.6 mmoles), of the mixed tosylates of m.p. 132–136° was allowed to react with 15.1 mmoles of potassium hydroxide in 80 ml. of ethanol at 60° for 3 hr. The product mixture was chromatographed on silica gel to give, in order of elution from the column, 0.24 g. of the supposed O-ethyl oxime, 0.11 g. of mesitonitrile, m.p. 49–51° (reported[15] m.p. 50–52°), and 0.79 g. (55%) of the recovered oxime, m.p. 72–76°.

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Synthesis of Di(methylthiomethyl) Polysulfides

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sym-Dialkyl polysulfides have been known for a long time.[1,2] Some of these have been detected in natural products,[3-5] while others have found industrial applications.[6] Recently, a series of methylthioalkyl isothiocyanates, of which methylthiomethyl isothiocyanate[7] is the lowest member, has been isolated from natural products.[4,8] Symmetrical dialkyl polysulfides, wherein the alkyl moiety contains a sulfur atom, as exemplified by the methylthiomethyl group, have not been described.

$$CH_3{-}S{-}CH_2{-}S_n{-}CH_2{-}S{-}CH_3$$

Methylthiomethyl mercaptan, a key compound in the present investigation, was prepared in good yields by a modification of the method described by Fehér and Vogelbruch.[9] This modification obviated the danger of an explosion. Due to its instability and permeating, garliclike odor, much difficulty was encountered in handling and characterizing this compound. It was found practical not to isolate the mercaptan for preparative work, but to use it in absolute ether solution.

Di(methylthiomethyl) sulfide, included for comparative purposes, was prepared by a new method from chloromethyl methyl sulfide and the hydrate of sodium hydrosulfide (from commercial source) in benzene.

The di- and trisulfides were obtained in substantial amounts as by-products from the reaction used to make the tetrasulfide, namely by treating methylthiomethyl mercaptan and sulfur monochloride in dry benzene in the presence of pyridine at a low temperature—a modification of the general procedure for the synthesis of polysulfides of Patel, *et al.*,[10] who did not obtain the tetrasulfide. The di- and trisulfides were obtained in the pure state by fractional distillation in high vacuum, while the pure tetrasulfide was isolated from the impurities in the residue by extraction with solvents.

In another experiment the same reaction was carried out but in the absence of pyridine. The vacuum fractionation of the reaction product yielded the di- and trisulfides, and an appreciable residue, which could not be distilled. This polysulfidic substance underwent autodesulfuration at room temperature, a behavior

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