Evaporation of solvent produced an orange solid. Recrystallization from ethanol yielded 2.50 g (81% yield) of orange plates, mp 114–115°. The ultraviolet spectrum[6] exhibited maxima at 231 mμ (log ε 4.65), 263 sh (3.65), 270 (3.69), 280 (3.65), 314 (3.99), 322 (4.13), 327 (4.22), 335 (4.07), 345 (3.87), and 351 (3.88). The nmr spectrum[7] exhibited an ABC pattern with H_A 7.85, H_B at 7.65, and H_C at 7.50 ppm, $J_{AB} = 2.0$ cps and $J_{AC} = J_{BC} = 8$ cps. The mass spectrum showed a strong molecular ion peak at m/e 308, 310, and 312 (characteristic for the presence of 2-Br) and abundant peaks at 231 and 229 (M − Br), 154, 155, and 156 (M^{2+}), 150 (acenaphthyne, base peak), 123, 122, 111, 110, 100, 99, 98, 87, 86, 85, 76, 75, 74, 73, and 63.

Anal. Calcd for $C_{12}H_6Br_2$: C, 46.5; H, 1.9; Br, 51.7. Found: C, 46.4; H, 2.0; Br, 51.6.

1,2-Dibromoacenaphthylene-5,6-dicarboxylic Acid Di-N,N-dimethylamide (IIb).—Treatment of acenaphthene-5,6-dicarboxylic acid di-N,N-dimethylamide[8,9] with N-bromosuccinimide as described above produced the dibromoacenaphthylene derivative, mp 281–282°, as orange crystals after recrystallization from ethanol. It exhibited a carbonyl peak in the infrared spectrum[10] at 1637 cm^{-1}. The ultraviolet spectrum[6] possessed maxima at 234 mμ (log ε 4.58), 268 sh (3.68), 277 (3.68), 288 sh (3.61), 334 (4.18), and 357 (1.08). The nmr spectrum[7] had an AB pattern for 4 H with H_A at 7.53 and H_B at 7.43 ppm and $J_{AB} =$ 7 cps, a singlet for 6 H at 3.11 and a singlet for 6 H at 2.89 ppm. The steric and electronic hindrance to rotation gives rise to the large separation of the absorption bands for the pairs of N-methyl groups. The mass spectrum shows the expected molecular ion peak at 454, 452, and 450 (characteristic of 2-Br) and abundant peaks at 410, 408, and 406 [M − $(CH_3)_2N$], 314 and 312, 235 (base peak), 207, 206, 191, 190, 179, 178, 146, 145, 105, 99, 98, 86, and 67.

Anal. Calcd for $C_{18}H_{16}Br_2N_2O_2$: C, 47.8; H, 3.5; Br, 35.7; N, 6.0. Found: C, 47.9; H, 3.5; Br, 35.6; N, 5.7.

The diamide was hydrolyzed by refluxing a suspension of 15.0 g (0.0331 mole) in 250 ml of 48% aqueous hydrobromic acid for 45 min. The reaction mixture was cooled in an ice bath and the resultant red solid was removed by filtration. After oven drying (∼80°) for 15 hr, 1,2-dibromoacenaphthylene-5,6-dicarboxylic anhydride weighed 12.2 g (91% yield). Recrystallization from chloroform produced deep red, microscopic needles, mp >350°. The infrared spectrum[10] showed the characteristic anhydride absorption at 1750 and 1710 cm^{-1}. The ultraviolet spectrum[6] exhibited maxima at 223 mμ (log ε 4.23), 251 (3.99), 343 (3.80), 360 (4.03), 368 sh (3.80), and 376 (3.84).

Anal. Calcd for $C_{14}H_4Br_2O_3$: C, 44.3; H, 1.1; Br, 42.1. Found: C, 44.2; H, 1.1; Br, 42.0.

1,2-Dichloroacenaphthylene Derivatives. A. Diacid Chloride V.—To 3.0 g (12.4 mmoles) of carefully dried acenaphthene-5,6-dicarboxylic acid was added 9.0 g (43.2 mmoles) of phosphorus pentachloride and 9.0 ml (98.9 mmoles) of phosphorus oxychloride. The mixture was refluxed for 20 hr during which time all the solid went into solution. After cooling and removal of solvent *in vacuo*, the residue was treated with carbon disulfide. Filtration removed the insoluble solids and evaporation produced 2.97 g (70% yield) of a deep orange compound, mp 228° dec. The acid chloride infrared[10] carbonyl band appeared at 1750 cm^{-1}. The ultraviolet spectrum[11] exhibited maxima at 220 mμ (log ε 4.49), 257 (3.15), 270 (3.12), 285 (3.10), 291 sh (3.04), 336 sh (3.05), and 346 (3.15). The nmr spectrum[12] confirmed the assignment of the symmetrical acid chloride structure by exhibiting only an AB pattern with H_A at 7.97 and H_B at 7.42 ppm, and $J_{AB} = 7$ cps.

B. Dimethyl Ester VII.—A suspension of 118 mg (0.341 mmole) of the acid chloride was refluxed in 12.0 ml of methanol on a steam bath. The solid slowly dissolved and as the reaction proceeded, yellow flakes appeared. Upon cooling and filtration of the beautiful yellow flakes, there was obtained 82 mg (72% yield), mp 166–168°. The ester infrared[10] carbonyl band appeared at 1729 cm^{-1}. The ultraviolet spectrum[6] showed maxima at 236 mμ (log ε 4.50), 265 (3.80), 274 (3.84), 281 (3.75), 330 sh (4.12), 338 (4.22), and 352 sh (3.90). The nmr spectrum[7] exhibited a sharp singlet for 6 H at 3.95 and an AB pattern for 4 H with H_A at 7.97, and H_B at 7.65 ppm, and $J_{AB} = 7$ cps. The mass spectrum showed a molecular ion at m/e 336 with the appropriate isotope peaks as well as abundant absorptions at 305 (M − OCH_3, base peak), 262 (M − $CO_2CH_3CH_3$), 220, 219, 218, and 206 (M − $CO_2CH_3 \cdot 2Cl$).

Anal. Calcd for $C_{10}H_{10}Cl_2O_4$: C, 57.0; H, 3.0; Cl, 21.0. Found: C, 57.0; H, 3.1; Cl, 21.1.

C. Acid Anhydride.—A suspension of 1.00 g (2.89 mmoles) of diacid chloride in 500 ml of moist benzene was refluxed for 5 days under nitrogen. A small amount of a black precipitate remained and was removed by filtration. Evaporation of the solution to dryness *in vacuo* produced 790 mg (100% yield) of dark red-brown powder. Recrystallization from chloroform produced deep red needles, mp 350° dec. The infrared spectrum and analytical data indicate that the anhydride crystallized as a hydrate. The characteristic anhydride doublet appeared in the infrared spectrum[10] at 1760 and 1725 cm^{-1}. The ultraviolet spectrum[6] had maxima mμ (log ε 3.20), 344 sh (3.13), 358 (3.19), and 369 sh (3.02). The nmr spectrum[13] exhibited an AB pattern with H_A at 7.85 and H_B at 7.70 ppm, and $J_{AB} = 7$ cps.

Anal. Calcd for $C_{14}H_4Cl_2O_3 \cdot H_2O$: C, 54.4; H, 1.9; Cl, 23.0. Found: C, 54.8; H, 1.5; Cl, 23.2.

Registry No.—IIa, 13019-33-5; IIb, 13094-92-3; V, 13082-02-5; VII, 13065-24-2; acid anhydride derivative of VII, 13082-03-6; 1,2-dibromoacenaphthylene-5,6-dicarboxylic anhydride, 13019-15-3.

Acknowledgment.—We wish to express our appreciation to the National Institutes of Health (Grant No. GM 13598-01) and the Wisconsin Alumni Research Foundation for support of this work.

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(6) Determined as a solution in ethanol.

(7) Determined as a solution in deuteriochloroform.

(8) B. M. Trost, G. Struve, and D. R. Brittelli, to be published.

(9) *Cf.* L. A. Carpino and S. Gowecke, *J. Org. Chem.*, **29**, 2824 (1964).

(10) Determined as a solution in chloroform.

(11) Determined as a solution in cyclohexane.

(12) Determined as a solution in phosphorus oxychloride.

(13) Determined as a solution in DMSO.

The Hydrolysis of 5-Diphenylmethylene-2(5H)-thiophenone[1]

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Received November 9, 1967

As an extension of the work in which we prepared 5-diphenylmethylene-2(5H)-thiophenone (I),[2,3] we now wish to report the characterization of three of its hydrolysis products.

Treatment of a methanolic solution of I with 0.1 *N* potassium hydroxide solution at room temperature for 5 days led to the isolation of *cis*-5,5-diphenyl-4-mercapto-2,4-pentadienoic acid disulfide (II) in 71% yield. However, when I was refluxed with aqueous 2 *N* potassium hydroxide solution for 24 hr, the isomeric *trans* acid disulfide III was obtained in 39% yield. A third acid which was subsequently shown to be the *trans* mercapto acid IV was isolated in small amounts from the filtrates of III. When I was refluxed with 0.1 *N* potassium hydroxide for 24 hr, the yield of IV was increased to 36%. Reductive cleavage of the *trans* acid disulfide III produced the *trans* mercapto acid IV. However, as might be expected, cleavage of the *cis* acid disulfide II led invariably to isolation of I.

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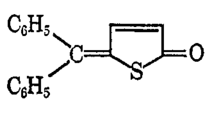
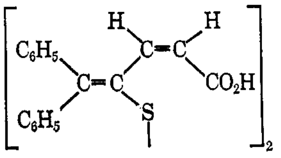
[1] This investigation was supported by Public Health Service Research Grant CA 06774, from the National Cancer Institute.

[2] W. R. Biggerstaff and K. L. Stevens, *J. Org. Chem.*, **28**, 733 (1963).

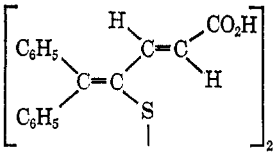
[3] *Cf.* A.-B. Hörnfeldt and S. Gronowitz, *Arkiv Kemi*, **21**, 239 (1963), for spectral studies of closely related compounds.



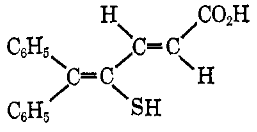
I



II



III



IV

Experimental Section[4]

cis-**5,5-Diphenyl-4-mercapto-2,4-pentadienoic Acid Disulfide (II).**—A solution of 5.00 g (18.9 mmoles) of 5-diphenylmethylene-2(5H)-thiophenone (I)[2] in 420 ml of methanol was prepared by warming the mixture on a steam bath; 1 l. of 0.1 *N* potassium hydroxide was added and sufficient methanol (*ca.* 1 l.) was added with warming to redissolve the precipitated thiolactone. The solution was stirred at room temperature in the presence of air for 5.5 days and was then acidified with 104 ml of 1.0 *N* hydrochloric acid. Water (1 l.) was added and the precipitate was stirred for an additional 2 hr. The solid acid was filtered, vacuum dried, and then stirred with *ca.* 25 ml of carbon disulfide and refiltered. After drying *in vacuo*, 3.80 g (71%) of the *cis* acid disulfide II, mp 207–208.5° dec, was obtained. Several recrystallizations from methanol gave an analytical sample in the form of yellow platelets: mp 210–211° dec; $\tilde{\nu}_{max}^{KBr}$ (cm^{-1}) 3000 (bonded OH),[5] 1693 (α,β-unsaturated carboxylic acid),[6] 1631 (nonaromatic C=C),[7] 460 (tentatively assigned to S–S);[8] λ_{max}^{EtOH} 315 (sh) mμ (log ϵ 4.08). The nmr spectrum determined in tetrahydrofuran-d_8[9] revealed peaks at δ 7.23 and 7.09 (two magnetically dissimilar phenyl groups), doublets centered at δ 6.72 and 5.62 (*cis*-HC=CH) (J_{AB} = 11.5 cps),[10] and a broad, low peak centered at *ca.* δ 6.4 (COOH).[11] Equilibration of the acid with CH_3OD resulted in the disappearance of the peak at δ 6.4.

Anal. Calcd for $C_{34}H_{26}O_4S_2$: C, 72.57; H, 4.66; mol wt, 562.7. Found: C, 72.34; H, 4.69; mol wt, 575.[12]

The methyl ester of the *cis* acid disulfide II was prepared by treating a solution of 1.80 g (3.2 mmoles) of II in 100 ml of 0.1 *N* potassium hydroxide with 2.5 ml of dimethyl sulfate. Upon warming, an orange solid separated which was filtered, washed with water, and dried to give 1.80 g (91%), mp 75–78°, of the methyl ester. Recrystallization from methanol gave an analytical sample: mp 79–80°; $\tilde{\nu}_{max}^{KBr}$ (cm^{-1}) 1730 (α,β-unsaturated ester), 1640 (nonaromatic C=C); λ_{max}^{EtOH} 315 (sh) mμ (log ϵ 4.17). The nmr spectrum determined in carbon tetrachloride showed a singlet at δ 3.43 (CH_3) and doublets centered at δ 5.55 and 6.69 (HC=CH) (J_{AB} = 11.5 cps).

Anal. Calcd for $C_{36}H_{30}O_4S_2$: C, 73.19; H, 5.12; mol wt, 591. Found: C, 73.26; H, 5.06; mol wt, 574.

trans-**5,5-Diphenyl-4-mercapto-2,4-pentadienoic Acid Disulfide (III).**—A mixture of 2.00 g (7.5 mmoles) of thiolactone I and 200 ml of 2 *N* potassium hydroxide was refluxed in the presence of air; after *ca.* 5 hr a deep yellow solution had been attained. At the end of 24 hr, heating was discontinued but stirring was maintained for an additional 15 hr. The solution was then filtered, cooled, and acidified with dilute hydrochloric acid. The resulting finely divided yellow precipitate was filtered and air dried; after further drying *in vacuo*, 1.60 g of a solid acid, mp 153–163°, was obtained. Recrystallization from methanol gave 0.85 g (39.5%) of the *trans* acid disulfide, mp 248–252°. Several additional recrystallizations produced an analytical sample: mp 251–252°; $\tilde{\nu}_{max}^{KBr}$ (cm^{-1}) 3000 (bonded OH), 1692 (α,β-unsaturated carboxylic acid), 972 (C–H out-of-plane deformation, *trans* olefin),[13] 455 (S–S);[8] λ_{max}^{EtOH} 2.39 mμ (log ϵ 4.54), 315 mμ (log ϵ 4.44). The nmr spectrum determined in tetrahydrofuran-d_8 indicated a pair of doublets centered at δ 7.48 and 6.39 (*trans*-HC=CH) (J_{AB} = 15 cps);[10] irradiation of the δ 7.48 doublet caused the doublet centered at δ 6.39 to collapse into a singlet. Two additional peaks were observed, δ 7.23 (two phenyl groups) and a broad, low peak at δ 9.7 (COOH). The latter peak disappeared when the acid was equilibrated with CH_3OD.

Anal. Calcd for $C_{34}H_{26}O_4S_2$: C, 72.57; H, 4.66; mol wt, 562.7. Found: C, 72.60; H, 4.60; mol wt, 554.

The **methyl ester** of the *trans* acid disulfide III was prepared by the method described for the *cis* acid II. The yellow ester was recrystallized from methanol to give a analytical sample: mp 165–166°; $\tilde{\nu}_{max}^{KBr}$ (cm^{-1}) 1718 (α,β-unsaturated $COOCH_3$), 980 (out-of-plane C–H deformation, *trans* olefin),[13] 455 (S–S).[8] The nmr spectrum determined in carbon tetrachloride showed a singlet at δ 3.60 (CH_3) and doublets centered at δ 6.32 and 7.33 (HC=CH) (J_{AB} = 16 cps) and δ 7.12 (C_6H_5–). The integration indicated a ratio of 1:4 (methyl:other protons).

Anal. Calcd for $C_{36}H_{30}O_4S_2$: C, 73.19; H, 5.12. Found: C, 73.11; H, 4.99.

trans-**5,5-Diphenyl-4-mercapto-2,4-pentadienoic Acid (IV).**—A mixture of 1.00 g (3.8 mmoles) of the thiolactone I and 200 ml of 0.1 *N* potassium hydroxide was refluxed for 24 hr in an air atmosphere. The cooled solution was acidified to yield an orange precipitate which was filtered, washed with water, and dried *in vacuo* to give 0.76 g of solid acid, mp 161–169°. Recrystallization from benzene–petroleum ether (bp 30–60°) gave 0.38 g (35.5%) of the *trans* mercapto acid IV, mp 177.5–180°. Repeated recrystallization produced an analytical sample: mp 183.5–184.5°; $\tilde{\nu}_{max}^{KBr}$ (cm^{-1}) 3000 (bonded OH), 1685 (α,β-unsaturated COOH), 2575 (–SH),[14] 975 (C–H out-of-plane deformation, *trans* olefin);[13] λ_{max}^{EtOH} 237 (log ϵ 4.16), 325 (log ϵ 3.97). The nmr spectrum determined in carbon tetrachloride showed a singlet at δ 3.10 (S–H), two doublets centered at δ 6.20 and 7.61 (*trans* HC=CH) (J_{AB} = 15 cps), and a broad singlet at δ 11.1 (COOH).

Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.57; H, 4.66; mol wt, 282.3. Found: C, 72.35; H, 4.96; mol wt, 296.

In another run the suspension of I in 0.1 *N* potassium hydroxide was repeatedly evacuated and nitrogen, which had been passed through a tower packed with hot copper wire,[15] was alternately admitted. Upon working up the hydrolysis product as before, it was found that the yield of mercapto acid IV remained practically unchanged. When the *cis* acid disulfide II was refluxed in 0.1 *N* potassium hydroxide for 24 hr in an atmosphere of purified nitrogen, the mercapto acid IV was produced in 2% yield[16] along with a trace of the *trans* acid disulfide III.

Reduction of *cis* Acid Disulfide II with Sodium Sulfide.—To 1.80 g (3.2 mmoles) of II dissolved in 30 ml of methanol was added an aqueous, saturated solution of 0.7 g (2.9 mmoles) of sodium sulfide and 0.5 g of sodium hydroxide. After warming on the steam bath for 15 min, 12 ml of 1 *N* hydrochloric acid was added; the yellow solid which precipitated was filtered, washed, and dried to give 0.45 g of a yellow solid, mp 111–112.5°. There was no melting point depression when the product was mixed with an authentic sample of thio lactone I and the infrared spectra of the two samples were identical.

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(4) Melting points of samples melting below 200° were determined on a Hershberg apparatus; those melting above 200° were determined on a Kofler micro hot stage and are corrected. Infrared spectra were determined on a Beckman IR-12 spectrophotometer. Ultraviolet spectra were obtained in 95% ethanol solution by means of a Beckman DK-2 spectrophotometer.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 162.

(6) Reference 5, p 168.

(7) Reference 5, p 41.

(8) Reference 5, p 352.

(9) The nmr spectra using tetramethylsilane as an internal reference were recorded on a Varian A-60 spectrometer through the courtesy of the Chemistry Department, University of California at Los Angeles. Tetrahydrofuran-d_8 was obtained from Volk Radiochemical Co., Burbank, Calif.

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, pp 85, 87.

(11) Reference 10, p 112.

(12) Vapor pressure osmometer, Model 301A, Mechrolab, Inc., Mountain View, Calif.

(13) Reference 5, p 45.

(14) Reference 5, p 351.

(15) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1960, p 219.

(16) Disulfide linkages have been cleaved by hydroxide ions; *cf.* A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 608 (1959).

Reduction with Dithiothreitol.[17]—To 100 mg of II dissolved in 15 ml of 0.1 *N* potassium hydroxide (pH 8) was added 30 mg of dithiothreitol. After swirling for 15 min, the turbid suspension was acidified to pH 3 and allowed to stand. The yellow product which separated was filtered and dried to give 63 mg of a solid, mp 93–95°. Recrystallization from methanol gave 28 mg of yellow crystals, mp 108–110°, identical with thio lactone I. A reduction of *trans* acid disulfide III with dithiothreitol led to a product identical with the previously described *trans* mercapto acid IV in *ca.* 50% yield.

Registry No.—I, 13083-98-2; II, 13083-99-3; II (methyl ester), 13084-00-9; III, 13084-01-0; III (methyl ester), 13084-02-1; IV, 13084-03-2.

Acknowledgment.—The authors wish to thank Mrs. Kuen-Lan Chao and Mrs. Shirley Scheidt for valuable technical assistance.

(17) W. W. Cleland, *Biochemistry*, **3**, 480 (1964).

On the Mechanism of Phenanthridine Formation from *o*-Arylbenzophenone Oximes

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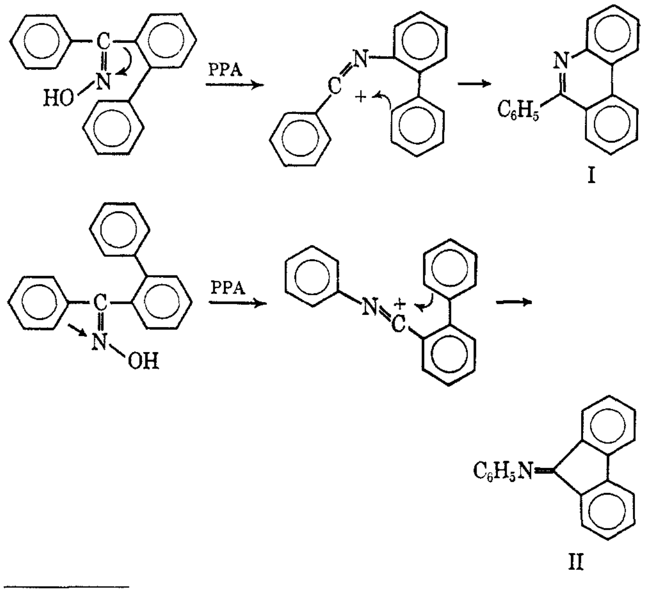
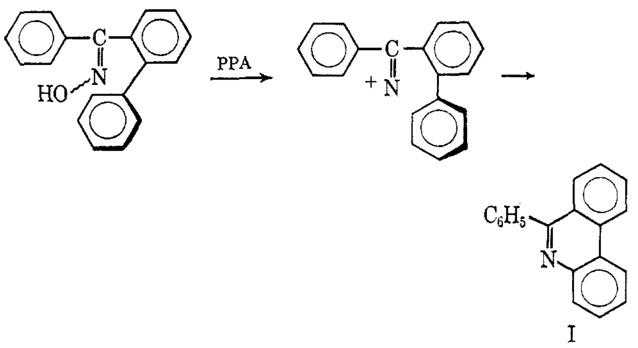
Received February 16, 1967

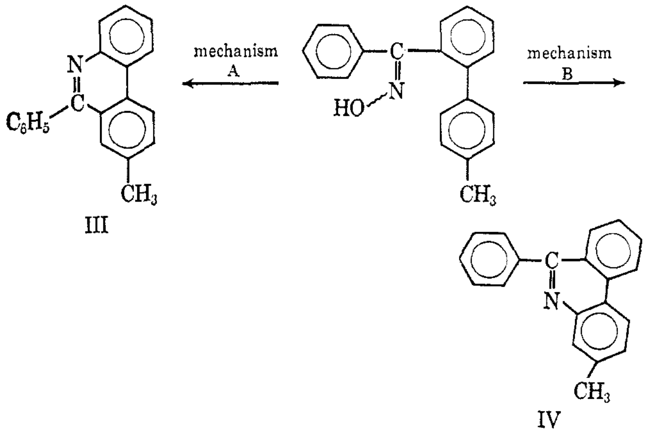
Several years ago, Smith reported[2] that the Beckmann reaction of *o*-phenylbenzophenone oxime in polyphosphoric acid (PPA) produced 6-phenylphenanthridine (I) and 9-fluorenone anil (II) in a 20:80 ratio. It was proposed that aryl migration in the isomeric oxime mixture produced two iminocarbonium ions which subsequently underwent electrophilic aromatic substitution rather than hydrolysis to amides (Scheme I). However, in view of our recent investigations establishing the intermediacy of iminium cations $(>\mathrm{C}{=}\mathrm{N}^+)$ in certain Beckmann reactions,[3,4] it appeared of interest to determine whether electrophilic attack of such species directly on an *o*-aryl group, rather than prior rearrangement to an iminocarbonium ion, might be the actual pathway to I. Although discrete iminium cations in *o*-arylbenzophenone oxime reactions were considered unlikely,[4] it seemed that the question could be neatly resolved by using *o*-(*p*-tolyl)benzophenone oxime, which would give either of two known methyl-6-phenylphenanthridines (III or IV) depending on the mechanism.

Scheme I



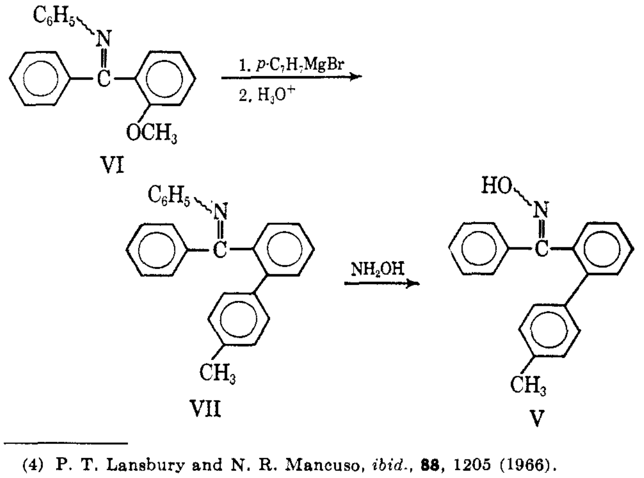


mechanism B



The required ketoxime (V) was prepared from *o*-methoxybenzophenone anil[5] (VI), employing conjugate addition–displacement with *p*-tolylmagnesium bromide to give VII, followed by hydrolysis and oximation, or direct oximation of VII (Scheme II).

Scheme II



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(1) Alfred P. Sloan Foundation Fellow, 1963–1967.

(2) P. A. S. Smith, *J. Am. Chem. Soc.*, **76**, 431 (1954).

(3) P. T. Lansbury, J. G. Colson, and N. R. Mancuso, *ibid.*, **86**, 5225 (1964).

(4) P. T. Lansbury and N. R. Mancuso, *ibid.*, **88**, 1205 (1966).

(5) R. C. Fuson, R. J. Lokken, and R. L. Pedrotti, *ibid.*, **78**, 6064 (1956).