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.

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

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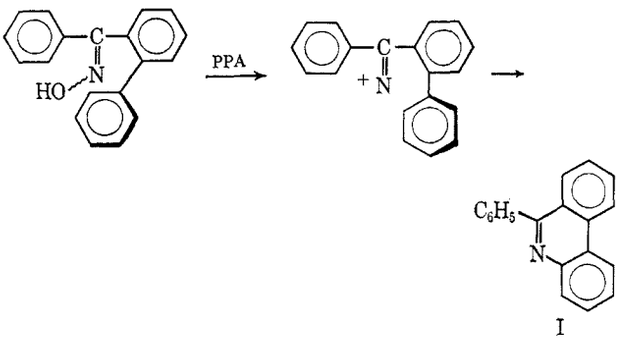
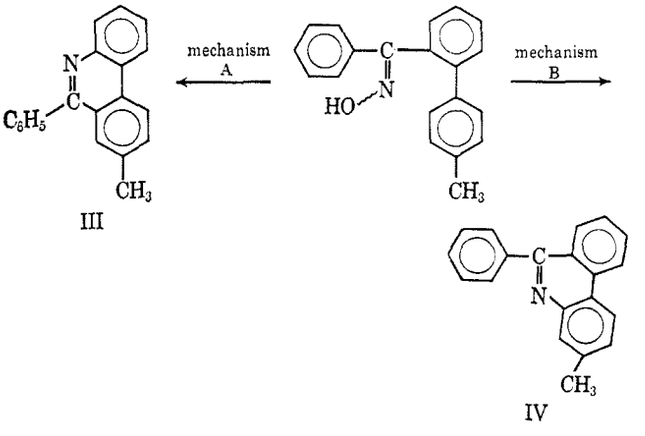
Several years ago, Smith reported[2] that the Beckmann reaction of *o*-phenylbenzophenone oxime in polyphosphoric acid (PPA) produced 6-phenylphenanthridine (I) and 9-fluorenone anil (II) in a 20:80 ratio. It was proposed that aryl migration in the isomeric oxime mixture produced two iminocarbonium ions 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 (>C=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



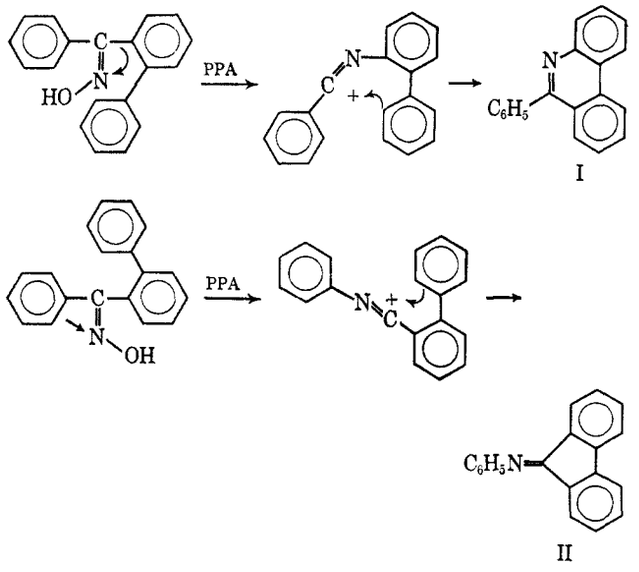
mechanism B

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.

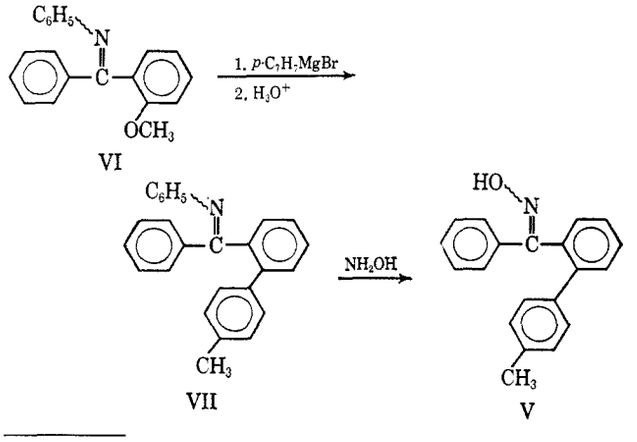


The required ketoxime (V) was prepared from *o*-methoxybenzophenone anil[5] (VI), employing conjugate addition–displacement with *p*-tolylmagnesium bromide to give VII, followed by hydrolysis and oximation, or direct oximation of VII (Scheme II).

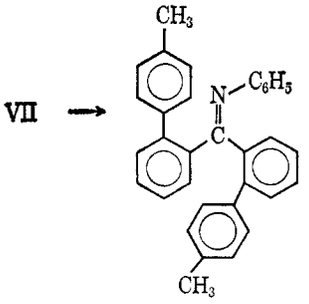
SCHEME I



SCHEME II



(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).



VIII

A side reaction in the preparation of VII was the further conjugate addition of *p*-tolyl Grignard reagent to VII, providing what appears to be 2,2′-di(*p*-tolyl)-benzophenone anil (VIII), on the basis of elemental analysis and nmr spectroscopy. The methyl groups in VIII are magnetically nonequivalent ($\Delta\nu$ = 4.3 Hz at 60 HMz) at room temperature, but the signals coalesce upon heating the sample, since facile *syn–anti* interconversion produces identical environments for both methyl groups. Cooling the sample to room temperature produced the original pair of methyl singlets. The coalescence temperature is 53°, at which k is calculated[6] to be 9.6 sec^{-1}, corresponding to $\Delta F^*_{326°} \sim 18$ kcal/mole. The inversion rate for VIII is similar in magnitude to recent data of Curtin, *et al.*,[7] on *p,p′*-dimethoxybenzophenone anil ($k_{62°}$ = 10.9 sec^{-1}).

When V was heated in PPA,[2] a mixture of 2-methyl-9-fluorenone and 8-methyl-6-phenylphenanthridine (III) was obtained in a ratio of *ca.* 8:1. Since III has mp 90° and III picrate has mp 280°, whereas 3-methyl-6-phenylphenanthridine (IV) melts at 119° and IV picrate has mp 245°,[8] it was not difficult to show that III was the correct structure for the phenanthridine product. Thus, the pathway to these products is that in which the oxime polyphosphates[3,4] rearrange with simultaneous aryl migration to give iminocarbonium ions (mechanism A) as postulated by Smith.[2] There is no evidence that iminium ions are formed from V. Since Smith's *o*-phenylbenzophenone oxime was a mixture of stereoisomers of unknown composition,[2] as was probably the case with V, which melted over a 10° range, it is not possible to say whether the fluorenone anil–phenanthridine ratios reflect the oxime isomer distribution (assuming stereospecific *trans* migration) or whether oxime isomerization occurs prior to rearrangement. However, the preponderance of fluorenone anils does seem to be consistent with the preferred *anti*-phenyl conformations of *ortho*-substituted benzophenone oximes.[9]

Experimental Section[10]

o-(p-Tolyl)benzophenone Anil (VII).—An ether solution (100 ml) of *p*-tolylmagnesium bromide, prepared as usual from *ca.* 0.06 mole each of *p*-bromotoluene and magnesium was added dropwise to a solution of 4.0 g (14 mmoles) of *o*-methoxybenzophenone anil[5] (VI) in 100 ml of benzene. The nitrogen-flushed reaction mixture was refluxed for 20 hr, cooled, and hydrolyzed with aqueous ammonium chloride solution. The product was extracted into ether, dried, and concentrated to an amorphous residue. Chromatography over alumina, using petroleum ether–benzene (with gradually increasing portions of the latter), afforded initially the expected *o*-(*p*-tolyl)benzophenone anil (VI) in 63% yield, mp 113–4° (from petroleum ether), as pale yellow crystals, ν_{max} 1634 cm^{-1} (>C=N–).

Anal. Calcd for $C_{26}H_{21}N$: C, 89.9; H, 6.1. Found: C, 89.8; H, 6.2.

Further elution yielded 2,2′-di(*p*-tolyl)benzophenone anil (VIII), mp 167–168° (ethanol), whose nmr spectrum showed the expected 21:6 integration ratio of aromatic (6.3–7.2 ppm) to methyl (2.2, 2.3 ppm) proton signals.

Anal. Calcd for $C_{33}H_{27}N$: C, 90.6; H, 6.2; N, 3.2. Found: C, 90.0; H, 6.4; N, 3.6.

o-(p-Tolyl)benzophenone Oxime (V).—A solution of 2.03 g of VII in 16 ml of hydrochloric acid and 100 ml of ethanol was refluxed for 1.5 hr, during which time the bright yellow color faded. Upon cooling and quenching in ice water, a white precipitate (1.48 g, 93%) of the parent ketone, mp 79–80° (ethanol), was obtained. A carbonyl band appeared in the infrared spectrum at 1667 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 87.8 H, 5.9.

The oxime (V) was prepared in the usual manner using ethanol pyridine as solvent and a 24-hr reflux period. The oxime of mp 151–161° (and –OH band at 3280 cm^{-1} together with disappearance of >C=O stretching) was used for the PPA reaction. An analytical sample, mp 164.5–165.5°, was obtained upon recrystallization from methanol.

Anal. Calcd for $C_{20}H_{17}NO$: C, 83.6; H, 6.0; N, 4.9. Found: C, 83.7; H, 6.0; N, 5.1.

Beckmann Reaction of V in Polyphosphoric Acid.—A mixture of 1.63 g of oxime V and 45 g of PPA was heated at 125–140° for 15 min, then cooled and poured into 250 g of ice water. The solution was made alkaline with ammonium hydroxide and extracted with benzene. The benzene solution was then extracted with concentrated hydrochloric acid and the latter solution neutralized to give an oil, which was chromatographed on alumina. Elution with 1:1 petroleum ether–benzene gave 0.14 g of 8-methyl-6-phenylphenanthridine, mp 91.5–92° (lit.[8] mp 90°), which formed a picrate having mp 280.5–281.5° (lit.[8] 280°). The remaining benzene solution was dried over magnesium sulfate and evaporated to yield 0.88 g of 2-methylfluorenone, mp 92° (lit.[11] mp 92.5–93.5°), which showed carbonyl absorption at 1721 cm^{-1} (Nujol) and $\lambda_{max}^{CH_3OH}$ 405 mμ (lit.[11] $\lambda_{max}^{i\text{-}PrOH}$ 400 mμ).

Registry No.—V, 13124-60-2; V (parent ketone), 13124-61-3; VII, 13124-62-4; VIII, 13135-42-7.

(6) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 63.

(7) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966).

(8) R. H. B. Galt and J. D. Loudon, *J. Chem. Soc.*, 885 (1959).

(9) P. A. Smith and E. P. Antoniades, *Tetrahedron*, **9**, 210 (1960).

(10) Melting points were taken on a Mel-Temp capillary tube apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-5A spectrometer, using Nujol mulls. Elemental analyses were by Dr. A. Bernhardt, Mülheim, Germany. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 spectrometer equipped with a variable-temperature probe and an A-6040 temperature controller. Column chromatography was done using Merck alumina and 30–60° petroleum ether.

(11) G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962).

The Synthesis of Oximes. II[1]

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The successful conversion of various 2-chloromethylpyridines to the corresponding 2-pyridine aldoximes by direct reaction with hydroxylamine prompted us to

(1) Part I: F. A. Daniher, B. E. Hackley, Jr., and A. B. Ash, *J. Org. Chem.*, **31**, 2709 (1966).