pattern centering at τ 7.37 (range τ 6.9–7.7), while the benzylic proton appears as a triplet (two overlapping doublets, J = 7 cps) centering at τ 4.33 (range τ 4.1–4.5). The key difference between the spectra of IIb and Ib is the position of this benzylic proton which in Ib is shifted downfield (compared with IIb) by approximately 2 ppm by the lactonic oxygen. The aromatic protons appear as two peaks, the one at τ 1.86 representing the two protons *ortho* to the nitro group and that at τ 2.33 corresponding to the protons *meta* to it.

Condensation of Sodiomalonic Ester and *p*-Nitrostyrene Oxide.—The condensation was carried out as described earlier[4] and was sampled at the α-ethoxycarbonyl-β-nitrophenyl-γ-butyrolactone stage without crystallization. The pmr spectrum of this crude material had no absorption in the τ 4–5 region where the resonance of the benzylic proton of the γ-nitrophenyl isomer might be expected to appear. Hydrolysis and decarboxylation of this unpurified material as described earlier[4] gave a chloroform extract, which, after treatment with 25 mg of activated charcoal, was evaporated to dryness. A pmr spectrum of the residue in deuterated chloroform was identical with that of pure IIb, and, in particular, no peak at τ 4.33 ascribable to Ib could be detected. The sample of IIb rapidly crystallized and melted at 107–110° without purification. A mixture melting point with pure IIb, mp 112–113°, was 108–110°.

An Isothiazole and a Nitrilium Salt from the Reaction of *syn*-Methyl *o*-Methylthiophenyl Ketoxime Esters

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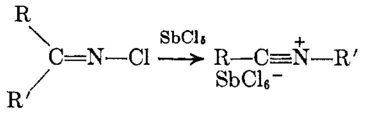
On the basis of a large rate enhancement and the absence of an appreciable kinetic isotope effect it was suggested that the conversion of *syn*-*o*-methylthiobenzaldoxime *o*-iodobenzoate to *o*-methylthiobenzonitrile involved the participation of sulfur.[1] Proton loss from the isothiazolium intermediate results in nitrile formation.

It was thus of interest to examine the reaction of Ia wherein proton loss is blocked. The corresponding acetophenone oxime derivatives were synthesized and their reactions were investigated. Treatment of the sodium salt of *syn*-methyl *o*-methylthiophenyl ketoxime with *p*-toluenesulfonyl chloride at 0° gave a yellow crystalline substance which underwent exothermic decomposition at 20°. The infrared spectrum of this compound at 0° displayed a very intense band at 2330 cm^{-1} in the region characteristic of triple-bond stretching.[2]

The infrared spectra of several types of carbon–nitrogen triple bond compounds were examined. The spectrum of benzonitrile in chloroform exhibits a strong band at 2230 cm^{-1}, and that of phenyl isocyanide at 2130 cm^{-1}. The infrared spectra of N-phenylacetonitrilium hexachloroantimonate prepared from treatment of the acetonitrile–antimony complex and methyl chloride, and of N-phenylbenzonitrilium hexachloroantimonate from the action of antimony pentachloride on N-phenylbenzimidoyl chloride, have been reported by Gordon and Turrell[3] as displaying a strong band at 2400 and 2300 cm^{-1}, respectively. The yellow substance, stable only below room temperature, would thus appear to be a nitrilium salt.

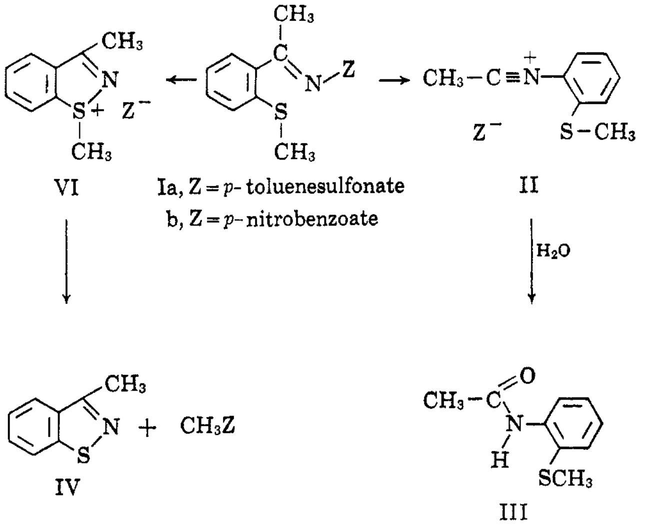
A closely related observation has been described recently by Grob, *et al.*[4] They have isolated nitrilium salts from a Beckmann rearrangement of N-chloroketimines (V), induced by antimony pentachloride or ferric chloride. These salts show a characteristic intense infrared absorption at 2310 cm^{-1}.



V

The possibility that the nitrilium ion produced is II can be confirmed in that *o*-methylthioacetanilide (III) should be produced on hydrolysis (Scheme I).

Scheme I



VI; Ia, Z = *p*-toluenesulfonate; b, Z = *p*-nitrobenzoate; II; IV; III

Upon working up the solution of Ia, three components were isolated. These were subsequently identified as 3-methylbenzisothiazole (32%, IV), the amide III (23%), and *o*-methylthioacetophenone, the latter produced by the hydrolysis of unrearranged oxime.

Attempts to prepare a stable crystalline oxime ester were successful upon treating the sodium salt of the ketoxime with *p*-nitrobenzoyl chloride. Rearrangement of Ib in tetrachloroethane produced 3-methylbenzisothiazole (IV, 60% yield) and methyl *p*-nitrobenzoate (68%).

The 3-methylbenzisothiazole was identified by microanalysis, nmr, and conversion to its previously reported hydrochloride.[5]

The isolation of IV from the reaction of *syn*-methyl *o*-methylthiophenyl ketoxime *p*-nitrobenzoate provides unequivocal evidence for *ortho* sulfur participation. The ketoxime ester reacts with participation to form a

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(1) R. J. Crawford and C. Woo, *Can. J. Chem.*, **43**, 3178 (1965).

(2) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Mathesen and Co. Ltd., London, 1954, p 223.

(3) L. E. Gordon and G. C. Turrell, *J. Org. Chem.*, **24**, 269 (1959).

(4) C. A. Grob, H. P. Fisher, W. Raudenbusch, and J. Zergenyi, *Helv. Chim. Acta*, **47**, 1003 (1964).

(5) A. Ricci and A. Martani, *Ric. Sci., Rend.*, **B2**, 177 (1962); *Chem. Abstr.*, **58**, 11340c (1963).

sulfonium intermediate VI, which in the presence of a good nucleophile such as the *p*-nitrobenzoate anion gives IV and methyl *p*-nitrobenzoate.

A similar behavior has been observed in the acetolysis of *o*-methoxyneophyl *p*-toluenesulfonate.[6] This system ionizes with anchimeric assistance involving *o*-methoxy participation. The final products are the hydrobenzofuran and methyl *p*-toluenesulfonate.

Compound Ia gives rise to a mixture of products, a nitrilium salt as an intermediate in the Beckmann rearrangement and the isothiazole IV. The more stable *p*-nitrobenzoate ester produces only the isothiazole as a result of sulfur participation. The nitrilium salt reported herein is the first observed under mild conditions which have previously been suggested to give rise to imidate ester formation.[4]

Experimental Section

All melting points and boiling points are uncorrected. The infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer, equipped with grating optics. The nmr spectra were measured using a Varian Associates A-60 spectrometer, with tetramethylsilane as an internal standard. The ultraviolet spectra were obtained on a Cary Model 14M spectrophotometer.

***o*-Methylthioacetophenone.**—Using essentially the method of Bowman,[7] a mixture of magnesium (9.7 g, 0.4 g-atom), 30 ml of dry benzene, and 5 ml of dry ethanol was placed in a three-necked flask fitted with a funnel and reflux condenser. After addition of a crystal of iodine and 2 ml of carbon tetrachloride, a small portion of a solution of ethyl malonate (64 g, 0.4 mole) and dry ethanol (19 ml, 0.45 mole) in 80 ml of dry benzene was added and the mixture was heated until a vigorous reaction set in; then the remainder was added at a convenient rate. The mixture was refluxed until the dissolution of the magnesium was completed. The mixture was then distilled slowly to remove most of the free ethanol as the azeotrope with benzene (until the temperature reached 70°). The residue in the flask consisted of ethanol-free ethoxymagnesium malonic ester in benzene solution.

o-Methylthiobenzoyl chloride (31 g, 0.20 mole) was dissolved in 100 ml of benzene and then added, with stirring and cooling, to the benzene solution of the ethoxymagnesium malonic ester. The resulting mixture was stirred overnight. The cooled mixture was added, with stirring, to a beaker containing 100 g of crushed ice and 350 ml of 10% sulfuric acid. The benzene solution was dried, and benzene and excess of malonic ester were removed under reduced pressure on a water bath up to 100°.

Propionic acid (120 g) was added to the crude acyl malonate along with 2.0 g of sulfuric acid, and the mixture was refluxed for 3 hr. A vigorous evolution of gas occurred in the early stages. Then 75 ml of 4 *N* sulfuric acid was added to the slightly cooled reaction mixture, and refluxing was continued until no further gas was evolved.

The reaction product was poured into 500 ml of water containing 500 g of ice. The mixture was neutralized by aqueous sodium hydroxide. The ketone separated was filtered and recrystallized from Skelly B; 23 g (83%) of *o*-methylthioacetophenone, mp 45–47°, was isolated. The infrared spectrum in chloroform shows a strong band at 1664 cm^{-1}. The nmr spectrum in carbon tetrachloride shows two sharp singlets at τ 7.45 and 7.66 and the aromatic protons at τ 2.05–2.88 in a ratio of 3:3:4.

Anal. Calcd for $C_9H_{10}OS$: C, 65.0; H, 6.02. Found: C, 65.0; H, 6.00.

***syn*-Methyl *o*-Methylthiophenyl Ketoxime.**[8]—The oxime was prepared as described previously[1] for other oximes: mp 121–123°.

Anal. Calcd for $C_9H_{11}NOS$: C, 59.7; H, 6.07; N, 7.74. Found: C, 59.8; H, 6.19; N, 7.84.

***syn*-Methyl *o*-Methylthiophenyl Ketoxime *p*-Nitrobenzoate (Ib).**—The ester was prepared by a method described previously:[1] mp 94–96°. The infrared spectrum in chloroform shows a strong band at 1747 cm^{-1}. The nmr spectrum in deuteriochloroform shows four singlets at τ 1.60, 2.60, 7.42, and 7.50 with an integrated intensity of 4:4:3:3.

Anal. Calcd for $C_{16}H_{14}N_2O_4S$: C, 58.2; H, 4.24; N, 8.49. Found: C, 58.1; H, 4.29; N, 8.21.

Aceto-*o*-methylthioacetanilide (III).—*o*-Thioaniline was methylated using sodium hydroxide and dimethyl sulfate. Methyl *o*-aminophenyl sulfide, bp 137–140° (15 mm), was isolated in 93% yield [lit.[9] bp 133–134° (15 mm)].

A solution of 1 g of acetyl chloride in 10 ml of benzene was added slowly to a cooled solution of 2 g of methyl *o*-aminophenyl sulfide in 20 ml of benzene. The mixture was warmed on a steam bath for 10 min; the solution was washed successively with 10 ml of water, 10 ml of 5% hydrochloric acid, 10 ml of 5% sodium hydroxide, and 10 ml of water. The benzene was evaporated and the residue was recrystallized from 95% ethanol to give 2 g (77%) of colorless needles, mp 104–106° (lit.[9] mp 102–103°). The infrared spectrum in chloroform shows strong bands at 1675 and 3340 cm^{-1}. The nmr spectrum in deuteriochloroform shows two methyl singlets at τ 7.65 and 7.81, a doublet at τ 1.80, and the aromatic protons spread from τ 2.5 to 3.0 in an area ratio of 3:3:1:4.

Reaction of *syn*-Methyl *o*-Methylthiophenyl Ketoxime and *p*-Toluenesulfonyl Chloride (Ia).—The ethereal solution from the reaction of the sodium salt of *syn*-methyl *o*-methylthiophenyl ketoxime (0.80 g, 3.9 mmoles) and *p*-toluenesulfonyl chloride (0.70 g, 3.7 mmoles) in 45 ml of dry ether was allowed to stand in the refrigerator at −24° for about 3 hr, whereupon 30 ml of water was added. The mixture was stirred until all the ether had evaporated. The residue was extracted with 20 ml of chloroform and dried, the solvent was evaporated, and 0.50 g (40%) of the reaction product was redissolved in a few milliliters of chloroform and chromatographed through a short alumina column using 150 ml of chloroform–hexane mixture as eluent. Successive 5-ml portions of the eluent were collected, the solvent was evaporated, and the residue was identified. The first 70 mg eluted was a yellow oil that proved to be 3-methylbenzisothiazole (IV, 32%): hydrochloride mp 116°.[5] The second product, 60 mg (23%), was identified as the amide III by mixture melting point analysis with an authentic sample. The third fraction (24%) was then identified as *o*-methylthioacetophenone by its infrared and nmr spectra.

Infrared Spectra of the Reaction Products of Ia.—The reaction was carried out as described in the preceding section; however, after standing overnight at −24° the ether solution was lyophilized, and the resulting yellow crystals were taken up in chloroform at 0°. The infrared spectrum showed intense absorption at 2310 cm^{-1}. It was not possible to let the crystals come to room temperature for they were transformed into a brown intractable syrup at about 20°.

Reaction of Ib to Produce IV.—A solution of *syn*-methyl *o*-methylthiophenyl ketoxime *p*-nitrobenzoate (1.6 g, 4.8 mmoles) in 20 ml of tetrachloroethane was refluxed for 3 hr. The mixture was cooled and chromatographed over alumina as before. Two compounds were isolated. The 3-methylbenzthiazole (60% yield) was found by microanalysis to have a molecular formula of C_8H_7NS.[10]

Anal. Calcd for C_8H_7NS: C, 64.5; H, 4.70; N, 9.40. Found: C, 64.2; H, 5.12; N, 9.77.

The second compound (component 5, 68% yield) was identical with an authentic sample of methyl *p*-nitrobenzoate in all respects—infrared and nmr spectra, melting point, and mixture melting point.

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(8) The *syn* configuration has been assigned to these compounds on the basis of the rearrangement products and that they are pure isomers from their nmr spectra.

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