and 0.97 g (0.0075 mole) of *p*-chlorophenol was heated in a glass tube, which was not closed but formed a long vertical capillary, at 200 ± 8° for 20 hr. IIa and *p*-chlorophenol were distilled under reduced pressure. From the residue which contained much oily part, 0.44 g (13%) of IIIa and 0.32 g (7%) of IVa were obtained after recrystallizations from tetrahydrofuran. Absence of *p*-chlorophenol resulted in the marked change in the yields of IIIa (4%) and IVa (31%).

Reaction of 1-(*p*-Chlorophenyloxycarbonyl)pyrrolidine with IIa.—Reaction of 1-(*p*-chlorophenyloxycarbonyl)pyrrolidine (mp 55–56°) (2.25 g, 0.01 mole) and IIa (1.37 g, 0.01 mole) was carried out as in A at 200 ± 5° for 20 hr. The odor of pyrrolidine was quite pronounced when the reaction tube was opened after cooling. Dry toluene was added to the reaction mixture, and the mixture was submitted to fractional distillation. To the distillate (up to 110°) phenyl isocyanate was added. After removal of toluene and excess phenyl isocyanate by distillation under reduced pressure, a small amount of crystals was obtained, the infrared spectrum of which was identical with that of 1-(N-phenylcarbamyl)pyrrolidine. The distillation residue, after removal of toluene and a part of IIa, consisted almost entirely of unchanged 1-(*p*-chlorophenyloxycarbonyl)pyrrolidine and gave only 0.15 g (5%) of IVa on treatment with ether.

The Reaction of *p*-Nitrostyrene Oxide with Sodiomalonic Ester. II

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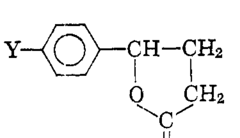
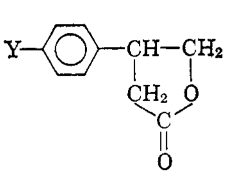
Recent work[1,2] on the reaction of sodiomalonic ester with styrene oxide has made it clear that products result from attack of malonate ester anion on both the α and β atoms of the epoxide, and that earlier reports[3] that only β attack occurs were erroneous. Presumably, the earlier errors were caused by similarities in melting points of the lactones Ia and IIa, which were produced by hydrolysis and decarboxylation of the initial condensation products. Proton magnetic resonance data have now established the structural assignments of both isomeric lactones without question.[1]



Ia, Y = H
Ib, Y = NO_2



IIa, Y = H
IIb, Y = NO_2

Some years ago one of us[4] studied the reaction of *p*-nitrostyrene oxide with sodiomalonic ester and reported that the resulting lactone (after hydrolysis and decarboxylation) had structure Ib, basing our conclusion on the early reports and on the fact that the product was identical with the product of nitration of the presumed Ia. The newer reports[1,2] suggested that our conclusion was in doubt, and was in fact probably incorrect (as turned out to be the case). The purpose of this note is to correct our earlier communication.

β-Phenyl-γ-butyrolactone (IIa), mp 46–47°, was isolated from the reaction of styrene oxide with sodiomalonic ester, as described earlier.[1-3] Its pmr spectrum corresponded with that described by DePuy and coworkers,[1] and we therefore agree[1,2] that α attack by diethyl malonate anion on styrene oxide is of greater importance than β attack. γ-Phenyl-γ-butyrolactone (Ia), mp 37°, was prepared[5] by catalytic reduction of β-benzoylpropionic acid.

When the β-phenyl lactone IIa was nitrated as described earlier,[4] β-nitrophenyl-γ-butyrolactone (IIb), mp 112–113°, was isolated. This had properties similar to those described earlier, and its synthesis and pmr spectrum led to the conclusion that it has structure IIb rather than that (Ib) assigned earlier. Genuine Ib was prepared by nitration of Ia and had mp 76–77°. Its pmr spectrum is described in the Experimental Section.

Repetition of the condensation of sodiomalonic ester with *p*-nitrostyrene oxide with careful scrutiny of intermediates in the reaction confirms the report[4] that only one product is formed in amounts substantial enough to observe. This product leads to IIb on hydrolysis and decarboxylation; it is the result of attack by ethyl malonate anion on the α position of *p*-nitrostyrene oxide. The powerful electron-attracting effect of the *p*-nitro group should enhance markedly the reactivity of the α position in styrene oxide toward nucleophilic attack, as suggested earlier,[4] and this is in fact observed.

Experimental Section

β-Phenyl-γ-butyrolactone (IIa), mp 46–47°, was prepared as described earlier by condensation of sodiomalonic ester with styrene oxide.[1-3] γ-Phenyl-γ-butyrolactone (Ia), mp 37°, was prepared[5] by hydrogenation of β-benzoylpropionic acid over palladium-on-charcoal catalyst.

β-*p*-Nitrophenyl-γ-butyrolactone (IIb), mp 112–113°, was prepared by nitration of Ib with acetyl nitrate, as described earlier.[4] Its pmr spectrum, taken in acetone in the aromatic (downfield) region and in chloroform in the remaining region, was very similar to that reported by DePuy for IIa.[6] A multiplet of about seven peaks assignable to the two dissimilar α-methylene protons was observed in the range τ 6.7–7.7, the benzylic hydrogen was assigned to the doublet of triplets in the τ 5.9–6.7 region, and the γ-methylene protons appear as two triplets in the τ 5.1–5.9 region. Cristol and Helmreich[4] had proven the location of the nitro group by oxidation of IIb to *p*-nitrobenzoic acid. The pmr spectrum confirms this by giving two doublets (J = 9 cps) of equal intensity (two protons each). The one at τ 1.80 is assigned to the protons *ortho* to the nitro group and that at τ 2.35 to those *meta* to the nitro group.

γ-Nitrophenyl-γ-butyrolactone (Ib) was prepared from γ-phenyl-γ-butyrolactone (Ia) by nitration with acetyl nitrate at below 0°, substantially as described for IIb. Chromatography on silica gel, using methylene chloride–chloroform (1:1) as eluting solvent, followed by recrystallization from chloroform-carbon tetrachloride (4:1), gave Ib, mp 76–77°, in 20% yield.

Anal. Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.38. Found: C, 58.04; H, 4.39.

Oxidation with sodium dichromate and sulfuric acid[7] gave *p*-nitrobenzoic acid, mp 236°, proving the position of the nitro group.[7]

Pmr spectra were taken in both acetone and chloroform, and showed great similarity to that reported for Ia. The four methylene protons (α and β to the carbonyl) give a complex

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[1] C. H. DePuy, F. W. Breitbill, and K. L. Eilers, *J. Org. Chem.*, **29**, 2810 (1964).

[2] P. M. J. Bavin, D. P. Hansell, and R. A. W. Spickett, *J. Chem. Soc.*, 4535 (1964).

[3] For discussions and references, see ref 1 and 2.

[4] S. J. Cristol and R. F. Helmreich, *J. Am. Chem. Soc.*, **74**, 4083 (1952).

[5] N. H. Cromwell, P. L. Creger, and K. E. Cook, *ibid.*, **78**, 4412 (1956).

[6] Pmr spectra were obtained using a Varian A-60 nmr instrument using tetramethylsilane (τ 10.00) as internal standard.

[7] The general procedure of O. Kamm and A. O. Mathews, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p 393.

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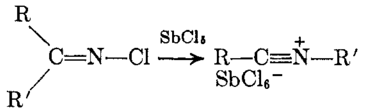
On the basis of a large rate enhancement and the absence of an appreciable kinetic isotope effect it was suggested that the conversion of *syn*-*o*-methylthiobenzaldoxime *o*-iodobenzoate to *o*-methylthiobenzonitrile involved the participation of sulfur.[1] Proton loss from the isothiazolium intermediate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

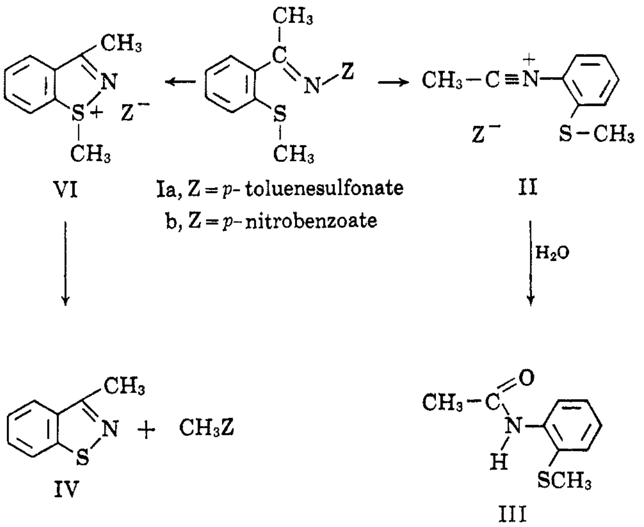
A closely related observation has been described recently by Grob, *et al.*[4] They have isolated nitrilium salts from a Beckmann rearrangement of N-chloroketimines (V), induced by antimony pentachloride or ferric chloride. These salts show a characteristic intense infrared absorption at 2310 cm^{-1}.



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



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).