α-Acetyl-γ-butyrolactone was prepared by the method of Johnson[33] (48% yield), and was converted into 5-chloro-2-pentanone by the procedure of Cannon, *et al.*,[11] in an 18% yield. Ketone VII was prepared by the treatment of 5-chloro-2-pentanone with sodium benzenethiolate (b.p. 125–126°/1.0 mm., n_D^{25} 1.5550, 57% yield). Ketone VIII was prepared as described before (m.p. 69–70.5°, 77% yield). The mixed melting point with previously described ketone VIII (m.p. 68.5–70°) was 67.5–69°.

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.37; H, 6.24. Found: C, 58.09; H, 6.28.

Treatment of cyclopropyl sulfones with acid. Phenyl cyclopropyl sulfone (6.0 g., 0.033 mole) was refluxed for 20 hr. in 20 ml. of 48% hydrobromic acid. The mixture was extracted with chloroform. Distillation of the chloroform extracts yielded 3.3 g. (55% recovery) of phenyl cyclopropyl sulfone (b.p. 124–129°/0.7 mm.). No other products were observed.

Phenyl cyclopropyl sulfone (4.0 g.) was refluxed in 55% hydroiodic acid for 2 hr. The hydroiodic acid was evaporated and the residue yielded 3.9 g. (98% recovery) of starting material (n_D^{21} 1.5496, starting material $n_D^{21.5}$ 1.5516).

Phenyl cyclopropyl sulfone (4.0 g.) was dissolved in 20 ml. of acetic acid and 48% hydrobromic acid[18] was added until the solution became milky. Acetic acid was added to make the mixture homogeneous. The mixture was allowed to stand at room temperature for 3 days and on a steam bath for 1 day. Water was added and the mixture was extracted with ether. Distillation yielded 2.9 g. (72% recovery) of starting material (b.p. 125–130°/1 mm.). The infrared spectrum was identical with phenyl cyclopropyl sulfone.

p-Tolyl cyclopropyl sulfone was treated by the above procedure of Fuson and Baumgartner[18] and starting material was recovered (80%, m.p. 64–65.5°).

Treatment of cyclopropyl sulfones with sodium benzenethiolate and sodium t-butoxide. Phenyl cyclopropyl sulfone (5.0 g., 0.027 mole) was refluxed for 24 hr. in 50 ml. of absolute ethanol which contained 1 g. (0.04 mole) of sodium and 3.0 g. (0.027 mole) of benzenethiol. Most of the ethanol was removed and water was added. An oil was extracted with ether and distilled, yielding 3.7 g. (74% recovery) of phenyl cyclopropyl sulfone (b.p. 136–141°/2 mm.). The infrared spectrum was identical with phenyl cyclopropyl sulfone.

p-Tolyl cyclopropyl sulfone (5.0 g., 0.026 mole) was refluxed for 46 hr. in 25 ml. of ethylene glycol which contained 1.7 g. (0.030 mole) of potassium hydroxide and 2.8 g. (0.025 mole) of benzenethiol. Water was added and crystals formed (3.9 g., 78% recovery of starting material, recrystallized from methanol, m.p. 65–66°).

Phenyl cyclopropyl sulfone (10 g., 0.055 mole) was added to 100 ml. of *t*-butyl alcohol which contained 2.3 g. of sodium and the resulting solution was heated at 70 ± 5° for 60 hr. Water was added and the product was extracted with ether. Distillation yielded 8.9 g. (89% recovery) of phenyl cyclopropyl sulfone (m.p. 33–34°).

Acknowledgment. The authors wish to express their gratitude for the financial support of this study by the Purdue Research Foundation and the National Institutes of Health, Research Grant CY-4536 (Cl).

LAFAYETTE, IND.

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[33] Wm. L. Johnson, U. S. Pat. **2,443,827** [*Chem. Abstr.*, **43**, 678 (1949)].

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[2]]

The Reactions of Thiolsulfinates with Triphenylphosphine, Triphenylarsine, and Triphenylstibine[1]

JOHN F. CARSON AND FRANCIS F. WONG

Received May 31, 1960

Triphenylphosphine reacts smoothly and rapidly with alkyl or aryl thiolsulfinates at room temperature to yield triphenylphosphine oxide and disulfide. Triphenylarsine and triphenylstilbine react similarly with aryl thiolsulfinates to yield disulfide and the corresponding oxide or dihydroxide but require more drastic conditions and the reaction does not occur with alkyl thiolsulfinates.

This study was made with the aim of finding new chemical methods for distinguishing thiolsulfinates and thiolsulfonates from the corresponding disulfides. The reactions of tertiary phosphines and phosphites toward sulfur,[3] episulfides,[4] epoxides,[5] and particularly thiolsulfonates[6] suggested a study of the reactions of the triaryl derivatives of some of the group V elements with thiolsulfinates.

We have found that triphenylphosphine reacts rapidly and smoothly with alkyl or aryl thiolsulfinates at room temperature to yield triphenylphosphine oxide and the corresponding disulfide in nearly quantitative yields. When a solid aryl thiolsulfinate such as phenyl benzenethiolsulfinate or *p*-tolyl *p*-toluenethiolsulfinate is mixed with an equimolar quantity of triphenylphosphine in the solid state, the mixture liquifies in a few minutes with the evolution of heat followed by crystalliza-

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[1] Presented before the Organic Chemistry Division, 136th National Meeting, American Chemical Society, Atlantic City, N. J., Sept. 1959.

[2] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

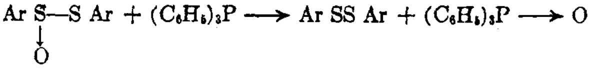
[3] P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

[4] R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958); N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959).

[5] G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955). C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957).

[6] L. Horner and H. Nickel, *Ann.*, **597**, 20 (1955).

tion to give a mixture of triphenylphosphine oxide and disulfide.

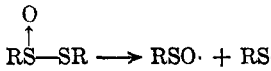


$$\mathrm{Ar\,\underset{\overset{\downarrow}{O}}{S}{-}S\,Ar} + (C_6H_5)_3P \longrightarrow \mathrm{Ar\,SS\,Ar} + (C_6H_5)_3P \longrightarrow O$$

The oxide is easily separated by its insolubility in petroleum ether, and the two products may be isolated in high yields by direct crystallization. Triphenylphosphine also reacts readily with aliphatic thiolsulfinates in which case the reaction is conveniently performed in methanol or benzene solution. Tri-*p*-chlorophenylphosphine also reacted with alkyl or aryl thiolsulfinates in solution to yield the corresponding oxide and disulfide.

Triphenylarsine reacted with aromatic thiolsulfinates to yield the arsine oxide and the disulfide but refluxing in methanol-benzene solution for eighteen hours was required for complete reaction. The reaction does not occur with aliphatic thiolsulfinates. Assuming that the reaction proceeds by a nucleophilic attack of the arsine on a sulfur atom with a partial positive charge, one would expect that tri-*p*-tolylarsine would be more nucleophilic than triphenylarsine and that it might react with aliphatic thiolsulfinates.[7] However, this compound was also unreactive to alkyl thiolsulfinates and required refluxing for reaction with the aromatic derivatives. Similarly, triphenylstibine reacted with phenyl benzenethiolsulfinate and *p*-tolyl *p*-toluenethiolsulfinate to yield triphenylstibine dihydroxide and the corresponding disulfide but no reaction occurred with aliphatic thiolsulfinates. Considerable care was required to establish that the oxide or dihydroxide actually resulted from thiolsulfinate and not from atmospheric oxidation. Triphenylstibine appears to be even more sensitive than triphenylphosphine to air oxidation in the presence of phenyl disulfide.

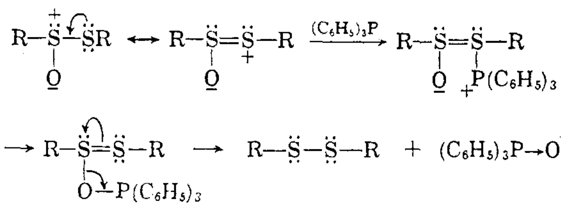
Two possible mechanisms for the reaction with triphenylphosphine may be considered. The thiolsulfinate may dissociate into free radicals:



$$\mathrm{R\overset{\overset{O}{\uparrow}}{S}{-}SR \longrightarrow RSO\cdot + RS\cdot}$$

Capture of oxygen by triphenylphosphine could yield the oxide and combination of RS· radicals would give disulfide. Thiolsulfinates are particularly susceptible to free radial decomposition and the thermal decomposition of these compounds to yield thiolsulfonates and disulfides may proceed by this mechanism.[8]

On the other hand, the possibility of extensive charge separation in thiolsulfinates and the strong nucleophilic activity of triphenylphosphine suggest an ionic mechanism which may be written:



The highly polar sulfoxide group should polarize the adjacent sulfur atom inducing a small positive charge and making it available for attack by the nucleophilic phosphine to yield an intermediate which would readily decompose to disulfide and triphenylphosphine oxide. A similar mechanism could hold for the reaction of thiolsulfonates with triphenylphosphine where two moles of phosphine react with one mole of thiolsulfonate.[6] This mechanism is another example of the general ionic mechanism of organic oxidation just proposed by Levitt.[9]

EXPERIMENTAL

Triphenylphosphine, triphenylarsine, and *triphenylstibine* were Eastman[10] White Label Products and were recrystallized from 95% ethanol before use. Freedom from oxides was assured by infrared spectra.

Tri-p-chlorophenylphosphine was prepared by the procedure of Mann and Chaplin[11] as modified by Bartlett and Meguerian.[3]

Tri-p-tolylarsine was prepared by the procedure of Tarbell and Vaughan.[12]

p-Tolyl p-toluenethiolsulfinate was synthesized by reaction of *p*-thiocresol and *p*-toluenesulfinyl chloride in ether-pyridine solution according to the procedure of Backer and Kloosterziel.[13] The compound was recrystallized twice from petroleum ether (b.p. 30-60°)-chloroform (20:1) at −20° as fine pale yellow needles, melting sharply with decomposition at 102° [Backer and Kloosterziel report 86° as the melting point.] The identity of the compound was established by elemental analyses and by infrared.[14]

Anal. Calcd. for $C_{14}H_{14}S_2O_2$: C, 64.08; H, 5.38; S, 24.44 Found: C, 64.0; H, 5.41; S, 25.0.

Infrared analysis with a potassium bromide disk showed strong absorption at 1093 cm.$^{-1}$ characteristic for S—O vibrations in thiolsulfinates and no absorption between 1163 and 1110 cm.$^{-1}$ showing the absence of thiolsulfonate.

Phenyl benzenethiolsulfinate was prepared by a procedure similar to the previous preparation. The compound melted

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[7] By analogy with the observations of Bartlett and Meguerian (*loc. cit.*) that tri-*p*-tolylphosphine is more reactive and tri-*p*-chlorophenylphosphine is less reactive than triphenylphosphine in nucleophilic attack on S_8.

[8] D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(9) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(10) Mention of commercial name does not imply endorsement by the Department of Agriculture.

(11) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

(12) D. S. Tarbell and J. R. Vaughan, Jr., *J. Am. Chem. Soc.*, **67**, 41 (1945).

(13) H. J. Backer and H. Kloosterziel, *Rec. Trav. Chim.*, **73**, 129 (1954).

(14) Infrared spectra were taken with a Beckman IR-5 recording infrared spectrophotometer (sodium chloride optics).

(15) C. J. Cavallito, J. S. Buck, and C. M. Suter, *J. Am. Chem. Soc.*, **66**, 1952 (1944).

sharply at 70–71°. The absence of thiolsulfonate was established by infrared.

n-Propyl 1-propanethiolsulfinate. The preparation of this compound, based on the procedure of Cavallito *et al.*[15] is described in detail as it was found to give the most reproducible results. A solution of 26 g. (0.173 mole) of *n*-propyl disulfide in 150 ml. of ether and 25 ml. of chloroform in a 1-l., round bottom flask equipped with stirrer and dropping funnel was cooled to 0°. An ethereal solution of monoperphthalic acid, 310 ml. (0.103 g./ml.) (0.175 mole) was added dropwise with stirring at 0° over a 2.5-hr. period. The reaction mixture was left an additional 2 hr. at 0° and filtered from precipitated phthalic acid. The ether solution was diluted with 200 ml. of fresh ether, washed with 300 ml. of 10% aqueous sodium bicarbonate, 150 ml. of distilled water, and then dried over sodium sulfate for 18 hr. at 0°. After filtration, the solution was concentrated with a water aspirator to *ca.* 40 cc. and then concentrated *in vacuo* at 1 mm. to 20 cc. The product was then isolated by evaporative distillation at 0.05 mm. A forerun, 0.9 cc., was obtained by distillation for 1.5 hr. at a bath temperature of 35–45°. Continued distillation for 15 hr. at a bath temperature of 49–51° yielded *n*-propyl 1-propanethiolsulfinate as 11 g. (38%) of colorless liquid. Infrared in the liquid state showed strong absorption at 1090 cm.$^{-1}$ characteristic of thiolsulfinates and no absorption at 1136 cm.$^{-1}$ characteristic for thiolsulfonates. Attempts to obtain additional product by distillation for longer times or at higher temperatures yielded material contaminated with thiolsulfonate.

Ethyl ethanethiolsulfinate was prepared by the same procedure as for the propyl derivative and was isolated by evaporative distillation at 0.05 mm. (bath temp. 41–43°). Infrared showed strong absorption at 1088 cm.$^{-1}$ and very weak absorption at 1127 cm.$^{-1}$

Reaction of triphenylphosphine with p-tolyl p-toluenethiolsulfinate. Triphenylphosphine, 0.6 g. (0.0023 mole), and *p*-tolyl *p*-toluenethiolsulfinate, 0.6 g. (0.0023 mole), were mixed and gently shaken together. In 15 min., the dry mixture liquified to a yellow melt, generating heat, and then rapidly solidified to a white crystalline mass. The product was dissolved in 10 ml. of benzene and then concentrated *in vacuo* to a slush of *ca.* 2 ml. Petroleum ether (b.p. 67–69°) was added and the crystalline mixture kept overnight at 3°. Filtration yielded 0.60 g. of triphenylphosphine oxide (94%) identified by m.p. 155–156° and mixed melting point with an authentic sample. The mother liquor, on concentration to a solid and recrystallization from 80 ml. of 50% ethanol yielded 0.54 g. of *p*-tolyldisulfide (96.%), m.p. 46–47°. When *p*-tolyldisulfide was substituted for thiolsulfinate, no reaction occurred and the starting materials were recovered.

Triphenylphosphine and n-propyl 1-propanethiolsulfinate. Triphenylphosphine, 1.092 g. (0.00416 mole), and the thiolsulfinate, 0.691 g. (0.00415 mole), were dissolved in 50 ml. of methanol and kept overnight under nitrogen at room temperature. The solution was then concentrated *in vacuo* to dryness and the resulting white solid recrystallized from petroleum ether (b.p. 67–69°)–benzene to yield 1.11 g. (95.9%) of triphenylphosphine oxide. When double the amount of triphenylphosphine was used, the yield of oxide isolated was still 1 mole per mole of thiolsulfinate.

Tri-p-chlorophenylphosphine and ethyl ethanethiolsulfinate. A solution of equimolar quantities of tri-*p*-chlorophenylphosphine and ethyl ethanethiolsulfinate in absolute ethanol at 24–26° for 30 hr. gave a 95.6% yield of tri-*p*-chlorophenylphosphine oxide as tiny white needles, m.p. 177–178°; undepressed in m.p. when mixed with authentic oxide prepared by oxidation of tri-*p*-chlorophenylphosphine with hydrogen peroxide. Potassium bromide pellets of this oxide in the infrared showed a strong band at 1193 cm.$^{-1}$ characteristic for P → O stretching.

The reaction of triphenylarsine with p-tolyl p-toluenethiolsulfinate. A solution of 1.18 g. (0.00386 mole) of triphenylarsine and 1.0 g. (0.00381 mole) of the thiolsulfinate in 75 ml. of methanol was boiled under reflux under nitrogen for 24 hr. and then concentrated *in vacuo* to 20 ml. and kept at 0° overnight. *p*-Tolyl disulfide, 0.134 g., m.p. 46–47° was removed by filtration. By concentrating the mother liquor to 10 ml., a second crop, 0.461 g. of the disulfide was obtained, yield 63%. The mother liquor on concentration *in vacuo* to an oil and trituration with 30 ml. of petroleum ether (b.p. 67–69°) yielded 0.92 g. of triphenylarsine oxide (75%), m.p. 194–196°. This was recrystallized from water to yield the typical transparent prisms of the hydrate which on drying *in vacuo* over sulfuric acid became opaque and were converted to the oxide, m.p. 194–195.5° identified by mixed melting point with authentic triphenylarsine oxide.

When triphenylarsine and ethyl ethanethiolsulfinate were treated in the same manner, no oxide was formed and triphenylarsine was recovered in 85% yield.

Tri-p-tolylarsine and phenyl benzenethiolsulfinate. A solution of tri-*p*-tolylarsine, 1.577 g. (0.00453 mole), and phenyl benzenethiolsulfinate, 1.06 g. (0.00454 mole), in 100 ml. of methanol and 50 ml. of benzene—the addition of benzene was necessary for complete solution—was heated under nitrogen in an oil bath at 70–75° for 18 hr. and then concentrated *in vacuo* to a white solid. Solution in 5 ml. of benzene followed by addition of 75 ml. of petroleum ether yielded 1.53 g. of asbestos-like needles, m.p. 130–133°, representing a 93% yield calculated as tri-*p*-tolylarsine oxide. On exposure to air, the product rapidly became sticky and apparently recrystallized as needles to give the hydrate, m.p. 92–93°. This was identical with tri-*p*-tolylarsine dihydroxide (or oxide hydrate) prepared by oxidation of tri-*p*-tolylarsine with hydrogen peroxide in acetic acid by mixed melting point and by comparison of infrared spectra (potassium bromide disc). The principal bands in the infrared were at 3400 cm.$^{-1}$ (strong), 3030 and 2915 (weak), 1087 (strong), 881 strong (shoulder 893), 804, strong (shoulder 810). Attempts to recrystallize the hydrate from ethanol-water as recommended by Vaughan and Tarbell[16] were usually unsuccessful. The compound could be recrystallized by dissolving in 10 parts of dioxane and 15 parts of water followed by concentration *in vacuo* to half volume. Alternately, it could be recrystallized from benzene–petroleum ether (b.p. 67–69°) and the crystalline product allowed to humidify in air.

The mother liquor, after removal of the tri-*p*-tolylarsine oxide, yielded 0.74 g. of phenyl disulfide (75%).

No reaction was observed with aliphatic thiolsulfinates either at room temperature or under refluxing conditions.

Triphenylstibine and phenyl benzenethiolsulfinate. A solution containing 1.65 g. (0.00467 mole) of triphenylstibine and 1.10 g. (0.00469 mole) of phenyl benzenethiolsulfinate in 100 ml. of methanol and 50 ml. of benzene was heated under nitrogen in an oil bath (68–70°) for 39 hr. The solution which was originally yellow became colorless in a few hours. It was concentrated *in vacuo* to 15 ml.; 50 ml. of hexane was added and the solution was again concentrated to 15 cc. when 35 ml. of hexane was added and the solution allowed to crystallize overnight in the absence of air. A crop of 1.04 g. of white powder was obtained, sintering at 210–215°, and a second crop 0.63 g. was obtained to give a combined yield of 92% calculated as triphenylstibine dihydroxide. This material usually obtained amorphous could be crystallized from 10 parts of hot benzene and 40 parts of hot petroleum ether (b.p. 67–69°) as prisms, m.p. 208–210°. The identity as triphenylstibine dihydroxide was established by conversion to the dichloride, m.p. 144–145° by solution in ethanol-hydrochloric acid and by mixed melting point with authentic triphenylstibine dihydroxide prepared by alkaline hydrolysis of triphenylstibine dibro-

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(16) J. R. Vaughan, Jr., and D. S. Tarbell, *J. Am. Chem. Soc.*, **67**, 144 (1945).

mide. A 73% yield of phenyl disulfide was isolated from the mother liquor.

Acknowledgment. We acknowledge the assistance of Mr. Glen Bailey and Mrs. Edith Gong for infrared spectroscopic determinations and Mr. L. M. White and Miss Geraldine Secor for elemental analyses.

ALBANY 10, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND GEOLOGY, CLEMSON COLLEGE AND THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

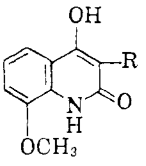
The Furanoquinoline Alkaloids: Synthesis and Reactions of Some Related 4-Hydroxy-2-quinolones

JOHN W. HUFFMAN[1]

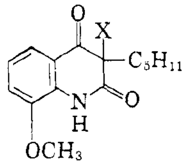
Received October 25, 1960

In the course of efforts directed at the total synthesis of some furanoquinoline alkaloids, 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone (Ib) was prepared. Ib with bromine gave 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4(1H,3H)-quinolindione (IIa) which with base was reduced to Ib. In an effort to investigate the course of this reduction 1-methyl-3-benzyl-4-hydroxy-2-quinolone (VIII) was synthesized and brominated to give IX. This compound was also reduced when treated with base. The possible mechanism of these base catalyzed reductions is discussed.

In the course of efforts directed at the total synthesis of isopropylfuranoquinoline alkaloids, of the lunacrine[2] and balfourodine[3] groups, we attempted to prepare 3-(3-methyl-1-butenyl)-4-hydroxy-8-methoxy-2-quinoline (Ia). It was felt that this compound under appropriate conditions could be cyclized to a derivative of lunacrine. Although we have been unable to effect the synthesis of Ia, the reactions of the expected precursors of Ia appear to be of sufficient interest to warrant their presentation.



Ia. R = $CH{=}CH{-}CH(CH_3)_2$
b. R = $CH_2CH_2CH(CH_3)_2$



IIa. X = Br
b. X = OH

It was proposed to bring about the synthesis of Ia *via* its saturated analog, 3-(3-methylbutyl)-4-hydroxy-8-methoxy-2-quinolone (Ib). Ib was prepared in good yield by the usual synthetic route for 3-alkyl-4-hydroxy-2-quinolones, through the interaction of an alkylmalonic ester and an aniline derivative in a high boiling solvent.[3,4] Diethyl isoamylmalonate[5] with *o*-anisidine in boiling phenyl ether afforded the desired hydroxyquinoline in good yield.

Treatment of Ib with either pyridinium bromide perbromide in acetic acid or *N*-bromosuccinimide in carbon tetrachloride gave a yellow bromo compound, $C_{15}H_{18}BrNO_3$. The infrared spectrum of the bromination product showed a split carbonyl band, with absorption at 5.86 μ and 6.01 μ, rather than the typical 4-hydroxyquinolone absorption exhibited by Ib. The ultraviolet spectrum of the yellow, bromo compound showed high intensity maxima at 235 and 240 mμ, instead of the complex spectrum of the parent compound. On the basis of the elemental analysis, and the rather drastic changes in spectral properties in the bromo compound, it was felt that the bromination product must be 3-(3-methylbutyl)-3-bromo-8-methoxy-2,4-(1H,3H) - quinolindione (IIa). Confirmation of this structure was obtained by the treatment of IIa with zinc–acetic acid, whereby the original 4-hydroxyquinolone was regenerated.

It was supposed that the reaction of IIa with base would afford the desired unsaturated quinolone derivative (Ia). When the bromoquinilindione (IIa) was treated with methanolic potassium hydroxide, the product in 60% yield was, however, the parent quinolone, 3 - (3 - methylbutyl) - 4 - hydroxy - 8-methoxy-2-quinolone. Attempted dehydrohalogenation of the bromo compound with collidine also effected reduction to the hydroxyquinolone. While there is some precedent for the reduction of α-halo ketones to the parent compound on treatment with collidine,[6] there seems to be no precedent for the reduction of an α-halo carbonyl compound by means of hydroxylic base.

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