[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Chlorinolysis of Sulfur–Carbon Bonds in Aryl–Alkyl Sulfides

BY HAROLD KWART AND ROBERT K. MILLER[1]

RECEIVED APRIL 6, 1956

Chlorine in acetic acid solution containing a small amount of water constitutes a very effective reagent for determining the nature and position of attachment of complex groups bonded to sulfur in aryl–alkyl sulfides. The results of several selected cases suggest a mechanism by which the products and stereochemistry of the reaction can be predicted. A chlorosulfonium ion intermediate is assumed to undergo substitution of the sulfur bond in a fashion analogous to previous observations on the solvolytic reactivity of sulfonium ions.

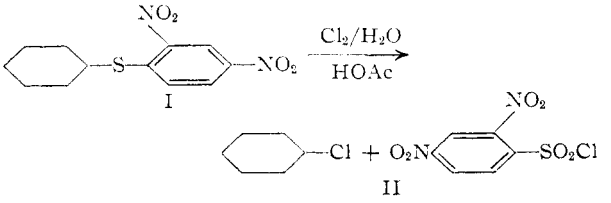
Comparatively little work has been reported on the application of chlorinolysis of sulfur–carbon bonds. In a review of reactions leading to cleavage of such bonds Tarbell and Harnish[2] have indicated that, at the time, cleavage of dialkyl sulfides by chlorinolysis was thought to be impractical due to substitution by chlorine. Other reports[3] tend to establish that compounds of the type RSY (where Y represents a variety of groups including –H, $-SO_3Na$ and $-C(=NH)NH_2\cdot HX$) can be readily converted by treatment with chlorine in aqueous solution to sulfonyl chlorides. There are only a few instances, however, where both products of a reaction of the type

$$RSR' + 3Cl_2 + 2H_2O \longrightarrow RSO_2Cl + R'Cl + 4HCl$$

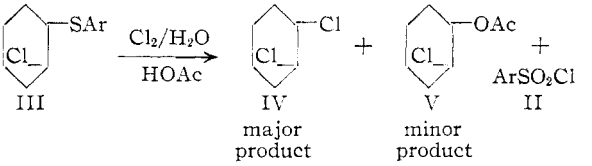
have been clearly identified.[4]

Our objective in the present work was to demonstrate chlorinolysis conditions which could be used as a diagnostic reaction. More specifically it was necessary to show that alicyclic aryl sulfides undergo cleavage with formation of predictable products and that polysubstitution of the non-aromatic moiety does not occur to a significant extent under these conditions. Furthermore, in order that chlorinolysis be applicable for determination of configuration at a carbon center, certain aspects of the mechanism and stereochemical course of reaction had to be ascertained. In this report we examine the results of a few selected cases designed to meet these objectives.

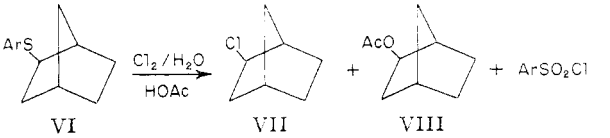
Cyclohexyl 2,4-Dinitrophenyl Sulfide (I).—Chlorinolysis under a standard set of conditions (*ca.* 92% acetic acid, room temperature) afforded an excellent yield of 2,4-dinitrobenzenesulfonyl chloride (II), identified by conversion to both the thiol and sulfonamide. Failure to observe any contamination by cyclohexylsulfonyl chloride confirmed that the course of reaction is consistent with the equation



trans-**2-Chlorocyclohexyl 2′,4′-Dinitrophenyl Sulfide (III).**—The possible influence of neighboring groups and substituents was under consideration when this compound was subjected to standard chlorinolysis conditions. The reaction resulted in a fair yield of *trans*-1,2-dichlorocyclohexane (IV). The sulfonyl chloride group ended up entirely as the aromatic product. The remainder of the cyclohexyl product was the *trans*-1,2-chloroacetate (V), as evidenced by chlorine and elemental analysis, positive hydroxamic acid (ester) test[5] and by the identity of its infrared spectrum with that of a pure (known) sample. The configuration of the carbon atom at the seat of cleavage is preserved in the new alkyl chloride bond of both the dichloride product and the chloroacetate.



exo-**Norbornyl *p*-Tolyl Sulfide (VI).**—Cristol and Brindell[6] first reported the preparation and identification of this substance which we subjected to chlorinolysis in the interests of determining whether neighboring carbon[7] could participate in the chlorinolysis mechanism. The reaction gave an excellent yield of a bicyclic halide (VII), which was in every way identical with known *exo*-norbornyl chloride. As was the case with the cyclohexene adduct III the chlorinolysis of VI also gave a small amount of a higher boiling substance VIII. This was probably *exo*-norbornyl acetate. Thus, the *exo*-configuration of the sulfur–carbon bond in the starting substance is maintained in the chlorinolysis reaction as shown in the equation. The material balance again confirmed that only aryl sulfonyl chloride is obtained by chlorinolysis of aryl–alkyl sulfides.



Discussion and Interpretation.—Tarbell and Harnish have considered earlier suggestions[8] that

(1) National Science Foundation Predoctoral Fellow, at the University of Delaware, 1954 and 1955.

(2) D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 17 (1951).

(3) C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **16**, 621 (1951).

(4) (a) S. W. Lee and G. Dougherty, *J. Org. Chem.*, **5**, 81 (1940); (b) E. Campaigne and W. B. Reid, Jr., *ibid.*, **12**, 807 (1947); (c) J. M. Stewart and H. P. Cordts, THIS JOURNAL, **74**, 5880 (1952).

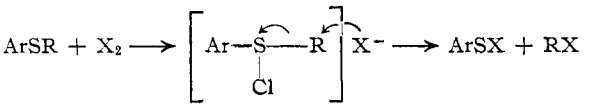
(5) "A Guide to Qualitative Organic Analysis," Revised Edition by D. Davidson and D. Perlman, Brooklyn College Book Store Press, Brooklyn, N. Y., 1954, p. 28.

(6) S. J. Cristol and G. D. Brindell, THIS JOURNAL, **76**, 5099 (1954).

(7) See for example, S. Winstein and O. S. Trifan, *ibid.*, **71**, 2953 (1949).

(8) See reference 2, p. 37–38.

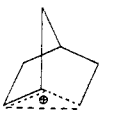
the reaction of halogen with sulfide involves the intermediacy of a halogen addition product, which may be formulated as a sulfonium compound and which decomposes according to the equation



They considered that the intermediate is decomposed by SN2 (rearward) displacement by chloride ion, of the sulfur. Several examples[9] appear to bear out this picture. Our results, however, indicate that this is not an entirely acceptable basis for predicting the course of reaction with variation in Ar and R groups.

Thus, we would have anticipated that, if SN2 displacement by chloride ion was alone the product determining factor, increasing substitution by nitro groups on the aryl moiety should tend to favor nucleophilic attack on the aromatic ring. Ordinarily, in fact, sulfur may be displaced readily from nitro-substituted aromatic rings by nucleophilic reagents. The reaction of 2-hydroxyethyl 2,4-dinitrophenyl sulfide with hydroxide ion is a good case in point.[10] Furthermore, in the instance of I not only is the nitro-substituted ring a preferred site for SN2 displacement, but also the cyclohexyl ring is very resistant to nucleophilic attack, being of the same order of unreactivity in SN2 displacement by iodine ion as the unsubstituted benzene ring (in chlorobenzene).[11] A more likely interpretation of this reaction would suggest that the breaking of the carbon–sulfur bond in the sulfonium intermediate is the controlling factor and that a nitro-substituted aryl group linked to the sulfur provides assistance for this bond-breaking step. This effect may be likened to the influence of α-halogen in promoting SN1 reactivity[12] or the accumulated influence of nitro groups promoting the ionization of the carbon–bromine bond in bromotrinitromethane.[13] The bond-breaking assistance afforded by nitro is particularly effective here when the alkyl group has structural features that would stabilize a carbonium ion developed at the seat of reaction. The exclusive formation of *trans* product resulting from chlorinolysis of III can be interpreted as involving the formation of an intermediate cyclic chloronium ion similar to that postulated by Lucas and Gould[14] to maintain configuration in the conversion of 3-chloro-2-butanols to 2,3-dichlorobutanes.

Further indications of a carbonium ion intermediate may be deduced from the chlorinolysis of VI. The bridged ion structure



commonly written[7] as an intermediate in the solvolytic reactivity of the norbornyl ring system, must also obtain in the chlorinolysis reaction to account for maintenance of configuration in the major product. Another interesting aspect of this reaction is the fact that the carbonium ion has been readily formed even though the aryl ring is *para* substituted by electron-releasing methyl, a change (from nitro) that would not be expected to assist breaking of the sulfur bond to alkyl. Clearly the driving force of reaction is not derived from nucleophilic bond making by chloride ion but rather from the stability of the bridged ion and the anchimeric[15] assistance to ionization. The formation of acetate side product must also be construed as evidence of a carbonium ion intermediate; the intervention of solvents of even extremely low nucleophilicity in the product-determining step is often observed in reactions involving a cationic intermediate.[16]

The work reported here has been used as a basis for the method applied to the determination of structure of the adducts of sulfenyl halides and norbornene.[17] The results are entirely consistent with the mechanistic picture proposed here. That work, furthermore, has shown unequivocally that the acetate side products in chlorinolysis reactions have the same configuration as the major product; it has also been pointed out[17] that the formation of ester (only) by SN2 reaction is unlikely.

The results of the chlorinolysis reaction of sulfur–carbon bonds are distinctly parallel to those we would expect on the assumption of a rapidly formed intermediate sulfonium ion. Studies such as those of Ingold and his collaborators[18] on the solvolytic behavior of sulfonium ions therefore provide a basis for prediction of the chlorinolysis product composition, if we make the assumption that the product is formed in accord with the reactivity of sulfonium ions in the displacement (substitution)[19] reaction. Ingold[19] has made the statement that alkyl sulfonium ions tend to go over from the bimolecular to the unimolecular substitution mechanism at an earlier point in the reaction series than do alkyl halides. We might, therefore, expect an enhanced tendency for chlorinolysis to result in reaction products deducible from a mechanism of SN1 substitution on the chlorosulfonium intermediate.

We are now examining these and other inferences of the analogy to sulfonium ion reactivity in kinetic studies of the chlorinolysis reaction.

(9) See reference 4c and R. H. Baker, R. M. Dodson and B. Riegel, THIS JOURNAL, **68**, 2636 (1946).

(10) G. M. Bennett and E. M. Whincop, *J. Chem. Soc.*, **119**, 1860 (1921).

(11) See J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 158 and 160, and particularly references 47 on p. 157 and 51 on p. 160.

(12) See examples and discussion by J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951).

(13) E. Schmidt, A. Ascherl and W. von Knilling, *Ber.*, **59**, 1876 (1926).

(14) H. J. Lucas and C. W. Gould, Jr., THIS JOURNAL, **63**, 2541 (1941).

(15) S. Winstein, C. R. Lundegren, H. Marshal and L. L. Ingraham, *ibid.*, **75**, 148 (1953).

(16) For example see the discussion of polar reactions of the double bond in reference 11, p. 202 *et seq.*

(17) H. Kwart and R. K. Miller, THIS JOURNAL, **78**, in press.

(18) For example, J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 236 (1935); E. D. Hughes and C. K. Ingold, *ibid.*, 1571 (1933).

(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII and particularly p. 339.

Experimental[20]

Cyclohexyl 2,4-Dinitrophenyl Sulfide.—Several attempts to prepare cyclohexanethiol by various procedures gave mixtures of the thiol and cyclohexanol. It was possible to use the crude product, however, in the preparation of the desired sulfide. Thus, crude cyclohexanethiol, prepared from cyclohexanol (189 g., 1.89 moles) by the procedure of Frank and Smith,[21] was dissolved in 400 ml. of ethanol and 70 ml. of 28% potassium hydroxide added. The resulting solution was poured into a warm solution of 2,4-dinitrochlorobenzene (70 g., 0.345 mole) in 300 ml. of ethanol. The mixture was stirred and heated on the steam-bath for about 10 minutes, then cooled to room temperature and filtered. The residue was washed repeatedly by slurrying with boiling water until no more chloride ion was extracted. The air-dried, yellow cyclohexyl 2,4-dinitrophenyl sulfide weighed 60.8 g. (11.4% of the theoretical based on cyclohexanol) and had m.p. 140–145°. Repeated recrystallization from carbon tetrachloride raised the m.p. to 146–147° (lit.[22] m.p. 148°). Hydrogen peroxide oxidation of a sample of this product gave a sulfone of m.p. 170–172° (lit. m.p. 172°).

2-Chlorocyclohexyl 2′,4′-Dinitrophenyl Sulfide.—2,4-Dinitrobenzenesulfenyl chloride (50 g., 0.213 mole) and 80 ml. of cyclohexene were mixed and heated. After an initial sudden vigorous boiling, during which all the halide dissolved, the mixture refluxed smoothly and the product began to crystallize from the boiling solution. Refluxing was continued for 30 minutes, after which the mixture was cooled to ice-bath temperature, and the product filtered off; 65 g. (96.3%) of sulfide, m.p. 115–118°, resulted. Recrystallizations from carbon tetrachloride gave a constant m.p. of 118–119° (lit.[23] m.p. 117–118°).

Degradation of 2-Chlorocyclohexyl 2′,4′-Dinitrophenyl Sulfide. (a) **2-Chlorocyclohexyl 2′,4′-Dinitrophenyl Sulfone.**—Cyclohexene adduct (10 g., 0.032 mole), 80 ml. of glacial acetic acid, and 15 ml. of 30–35% hydrogen peroxide were heated together on a boiling water-bath for 2.5 hours. The solution was allowed to stand overnight, and then the crystals which had deposited were filtered off and air-dried; 9.1 g. (82.7%) of 2-chlorocyclohexyl 2′,4′-dinitrophenyl sulfone, m.p. 129–131°, was obtained. Recrystallization from ethanol increased the m.p. to 130–131°.

Anal. Calcd. for $C_{12}H_{13}ClN_2O_6S$; S, 9.19. Found: S, 9.21, 9.22.

(b) **1-Cyclohexenyl 2′,4′-Dinitrophenyl Sulfone.**—2-Chlorocyclohexyl 2′,4′-dinitrophenyl sulfone (5 g., 0.014 mole) dissolved in 50 ml. of benzene was dehydrochlorinated by adding 3 ml. of triethylamine and letting the mixture stand at room temperature. Triethylamine hydrochloride began to separate almost immediately; after standing for 5 days 1.90 g. (96.3% of theory) of the hydrochloride was filtered off. The filtrate was washed with 50 ml. of water, then with three 50-ml. portions of 1:2 hydrochloric acid, and finally with three 50-ml. portions of water. The benzene solution, on dilution to twice its volume with low boiling petroleum ether, gave a crystalline precipitate which was filtered off. Evaporation of the mother liquor to small volume and addition of petroleum ether gave additional solid. The combined crude yield (4.21 g., 94.0%) was recrystallized from benzene–petroleum ether to give 3.27 g. of pale yellow, coarsely crystalline olefin sulfone of m.p. 156–160°. Its infrared spectrum showed strong absorption at 6.11 μ, characteristic of the carbon–carbon double bond. Instead of attempting to further purify this compound, it was oxidized to adipic acid to complete its identification.

(c) **Adipic Acid.**[24]—To a stirred solution of 1-cyclohexenyl 2′,4′-dinitrophenyl sulfone (3 g., 0.0096 mole) in 100 ml. of acetone and 5 ml. of water was added, portionwise, powdered sodium permanganate. The reaction rapidly generated heat; by cooling under tap water the temperature was maintained in the range 25–35°. When 5.11 g. of the oxidizing agent had been added the permanganate color was no longer discharged and the oxidation was considered complete. Water and sodium bisulfite were added in portions until the mixture was clear. The solution was then diluted to 600 ml. with water and passed through Amberlite IR-120 to remove cations. Evaporation of water in a stream of warm air gave a mass of yellow oily crystals which were transferred to a filter and washed with a few drops of water. The residue was charcoaled while being recrystallized from hot water to yield 0.50 g. (35.7%) of adipic acid, m.p. 148.5–150.5° (lit.[25] m.p. 149–150°), mixed m.p. with authentic adipic acid, 148.5–150°.

***exo*-Norbornyl *p*-Tolyl Sulfide.**—*p*-Toluenethiol was added to norbornene by the procedure of Cristol and Brindell.[6] The product had the b.p. 107–108° (0.8 mm.), $n^{20}D$ 1.5756 (lit.[6] b.p. 175–176° (11 mm.), $n^{20}D$ 1.5758).

***exo*-Norbornyl Chloride.**—The method of Schmerling[26] was used to prepare an authentic sample of this compound. A large excess of hydrogen chloride was added to a Dry Ice–acetone cooled solution of norbornene (50 g., 0.532 mole) in 120 ml. of petroleum ether (30–60°). The mixture was allowed to stand for a day, washed with water, sodium bicarbonate solution, and again with water, dried over calcium chloride, and distilled. After removal of solvent, 49.25 g. (70.8% yield) of *exo*-norbornyl chloride, b.p. 54–55.5° (16 mm.), $n^{20}D$ 1.4842, was obtained (lit.[26,27] b.p. 97° (100 mm.), 52° (11 mm.), $n^{25}D$ 1.4823, $n^{20}D$ 1.4849).

Chlorinolysis of Cyclohexyl 2,4-Dinitrophenyl Sulfide. 2,4-Dinitrobenzenesulfonyl Chloride.—Cyclohexyl 2,4-dinitrophenyl sulfide (10 g.) suspended in a mixture of 80 ml. of glacial acetic acid and 3 ml. of water reacted as described for the chlorinolysis of *endo*-3-chloro-*exo*-norbornyl 2,4-dinitrophenyl sulfide.[17] Pouring the reaction mixture over ice produced a yellow solid which, on recrystallization from benzene–petroleum ether, had a m.p. 97–98°. This product was insoluble in boiling water, but easily dissolved in warm 5% sodium hydroxide. The sodium hydroxide solution, when prepared by gentle warming, gave no precipitate with barium chloride. Prolonged boiling of a sodium hydroxide solution followed by acidification gave a precipitate of 2,4-dinitrobenzenethiol, and the solution, after filtering off the thiol, gave a strong test for sulfate ion. This behavior is characteristic of 2,4-dinitrobenzenesulfonyl chloride.[28]

Since the melting point of the product obtained here is somewhat lower than that reported in the literature,[29] the sulfonyl chloride was converted to its sulfonamide by treating it with aqueous ammonia. The product, after recrystallization from water, had the m.p. 152–152.5° (lit.[29] m.p. 156–157°).

Chlorinolysis of 2-Chlorocyclohexyl 2′,4′-Dinitrophenyl Sulfide.—Cyclohexene adduct (81.5 g., 0.258 mole) was subjected to chlorinolysis in the usual manner in a solution of 250 ml. of glacial acetic acid and 10 ml. of water.[30] Removal of solvent from a petroleum ether extract followed by two distillations through a small Vigreux column afforded a 29.8% yield of *trans*-1,2-dichlorocyclohexane, b.p. 53.2–54.0° at 6 mm., $n^{20}D$ −1.4896 (lit.[31] b.p. 88–89° and 30 mm., $n^{20}D$ 1.4904). Identification was completed by infrared spectrum comparison with the published data of Stevens and Grummitt.[32] From the high boiling residue was obtained, after two distillations, a 15% yield of *trans*-1-acetoxy-2-chlorocyclohexane, b.p. 78.2–81.0° at 5 mm. (lit.[33] b.p. 98.0–98.5° at 12 mm.).

Identification of this *trans*-chloroacetate was completed by infrared spectral comparison with that of a known sample which was prepared by treating cyclohexene oxide with concentrated hydrochloric acid followed by esterifying

(20) Melting and boiling points are uncorrected. Melting points, unless otherwise indicated, were taken in an air-bath melting point apparatus similar to that described by A. May, *Anal. Chem.*, **21**, 1427 (1949). Infrared curves were obtained using a Baird double beam recording instrument with sodium chloride optics.

(21) R. L. Frank and P. V. Smith, THIS JOURNAL, **68**, 2103 (1946).

(22) R. W. Bost, J. O. Turner and M. W. Conn, *ibid.*, **55**, 4956 (1933).

(23) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

(24) The method of oxidation is a modification of the method of S. F. Birch, W. J. Oldham and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

(25) B. A. Ellis, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 18.

(26) L. Schmerling, THIS JOURNAL, **68**, 195 (1946).

(27) J. D. Roberts, L. Urbanek and R. Armstrong, *ibid.*, **71**, 3049 (1949).

(28) C. Willgerodt and P. Mohr, *J. prakt. Chem.*, [2] **34**, 123 (1886).

(29) J. M. Sprague and T. B. Johnson, THIS JOURNAL, **59**, 2439 (1937).

(30) We are indebted to Mr. Leroy Miller for checking these results.

(31) P. D. Bartlett, THIS JOURNAL, **57**, 224 (1935).

(32) H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

(33) S. Winstein, *ibid.*, **70**, 816 (1948).

with acetic anhydride according to the directions of Winstein.[33]

Acknowledgment.—R. K. M. is obliged to the National Science Foundation for the assistance provided with a predoctoral fellowship. The coöperation of Mr. Leroy Miller in phases of this work is also recognized with gratitude.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

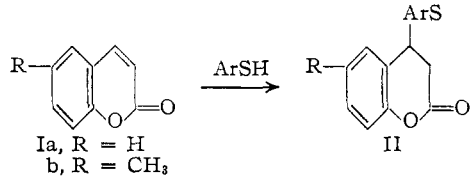
Reactions with Mercaptans. III.[1] Action of Aromatic Thiols on Coumarins, 4-Styrylcoumarins and 2-Styrylchromones

BY AHMED MUSTAFA, MOHAMED KAMEL, MOHAMED ALY ALLAM, ABDEL HAMID EL-SAYED HARHASH AND ALAA ELDIN ABDEL AZIZ HASSAN

RECEIVED MARCH 26, 1956

Coumarin and 6-methylcoumarin add aromatic thiols to give the 4-arylmercapto-3,4-dihydrocoumarins (II). Thioncoumarin is stable toward the action of aromatic thiols under parallel conditions. The treatment of 4-styrylcoumarins (III and V) with aromatic thiols results in the formation of the thiol adducts, believed to have structures like IVa or IVb, and VIa and VIb, respectively; they are readily oxidized to the corresponding sulfones. Whereas 2-methylchromone is stable toward the action of aromatic thiols, 2-styrylchromones (VIII), which may be regarded as vinylogs of chalcones, add the thiols to yield thiol adducts, believed to have a structure like IX. IX (R = $C_6H_4OCH_3$-*p*, Ar = $C_6H_4CH_3$-*p*) reacts with hydrazine hydrate to give the pyrazole derivative (XIa or XIb), and not the hydrazone derivative; similarly, it reacts with hydroxylamine hydrochloride in presence of pyridine to yield the corresponding isoxazole derivative (XIIIa or XIIIb).

In conjunction with a study of the pharmacological action of sulfur-containing compounds against Bilharziasis,[1,2] 4-arylmercapto-3,4-dihydrocoumarin (II,R = H) and 4-arylmercapto-6-methyl 3,4-dihydro-coumarin (II,R = CH_3) were prepared through the addition of aromatic thiols to coumarin (Ia) and 6-methylcoumarin (Ib), respectively.



Ia, R = H
b, R = CH_3

II

Although the addition of organic sulfur compounds to coumarin and its derivatives has not been investigated extensively, addition products have been obtained from coumarin and potassium cyanide,[3] and/or sodium bisulfite.[4] Similarly, coumarin adds cyanoacetamide, malonic ester and ethyl phenylacetate[5,6] to give substituted dihydrocoumarin derivatives. The unsaturated system in the pyrone ring functions as a dienophile in the Diels–Alder synthesis.[7]

The aromatic thiols employed in this investigation generally react with Ia and/or Ib in the presence or absence of piperidine[8] to give the corresponding addition product II in 75–95% yield. All the sulfides (*cf.* Table I) were sharp melting crystalline compounds.

The pure sulfides were stable under the normal conditions, but were decomposed into the original components by refluxing with 4% alcoholic potassium hydroxide solution. The regenerated thiol was readily characterized by the formation of a yellow lead salt with lead acetate. The adducts are almost insoluble in cold aqueous sodium hydroxide, and give no color reactions with alcoholic ferric chloride solution.

Coumarins in their reactions may behave as unsaturated lactones,[9] and in view of the well established mechanism for the conjugate addition of thiols to α,β-unsaturated compounds, *e.g.*, α,β-unsaturated ketones,[10] 1-cyanocyclohexene,[11] α,β-unsaturated esters[12] and allylacrylonitriles,[13] we have assigned structure II to the sulfides, particularly since the reactions were not carried out under the influence of peroxides.[14]

In agreement with the finding of Dey and Row[15] that alkyl groups inhibit the addition reaction of 4-methylcoumarin with sodium bisulfite, we have found that under the given experimental conditions, 4-methylcoumarin is stable toward the action of *p*-thiocresol in the presence or absence of piperidine. However, in contrast to the observation of Seshardi and Venkateswarlu[16] that the methyl group in the 6-position markedly slows down the addition of cyanoacetamide to 6-methylcoumarin (Ib), the latter reacts readily with aromatic thiols in a similar manner to Ia.

Whereas, Ia readily adds aromatic thiols, thioncoumarin is recovered almost unchanged when allowed to react with thiols in the presence or ab-

(1) A. Mustafa, A. H. E. Harhash and M. Kamel, THIS JOURNAL, **77**, 3860 (1955).

(2) N. O. Nolan, H. W. Bond and E. R. Mann, *Am. J. Trop. Med. and Hyg.*, **2** [4], 716 (1953).

(3) J. Bredt and J. Kallen, *Ann.*, **293**, 366 (1896).

(4) F. D. Dodge, THIS JOURNAL, **52**, 1724 (1930).

(5) T. R. Seshardi, *J. Chem. Soc.*, 166 (1928).

(6) R. Connor and Wm. R. McClelland, *J. Org. Chem.*, **3**, 570 (1939).

(7) R. Adams, W. D. McPhee, R. B. Carlin and Z. W. Wicks, THIS JOURNAL, **65**, 356 (1943); R. Adams and R. B. Carlin, *ibid.*, **65**, 360 (1943).

(8) R. M. Ross, *ibid.*, **71**, 3158 (1949).

(9) R. C. Elderfield, ed., "Heterocyclic Compounds," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 197.

(10) T. Posner, *Ber.*, **35**, 809 1902); B. H. Nicolet, THIS JOURNAL, **53**, 3066 (1931).

(11) R. M. Ross and F. W. Raths, *ibid.*, **73**, 129 (1951).

(12) B. H. Nicolet, *ibid.*, **57**, 1098 (1935).

(13) R. M. Ross, H. L. Bushey and R. J. Rolih, *ibid.*, **73**, 540 (1951).

(14) S. O. Jones and E. E. Reid, *ibid.*, **60**, 2452 (1938); M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry & Industry*, 752 (1938).

(15) B. B. Dey and K. K. Row, *J. Chem. Soc.*, **125**, 554 (1924).

(16) T. R. Seshardi and V. Venkateswarlu, *Proc. Indian Acad. Sci.* **15A**, 424 (1942).