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Cleavage Reactions of Trityl Sulfides

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The cleavage reactions of trityl phenyl sufide (I) and trityl benyl sulfide (II) with iodobenzene dichoride (III), iodobenzene diacetate (IV), and *N*-bromosuccinimide are reported. The stability of I towards nucleophilic reagents (sodium ethoxide and phenylmagnesium bromide) is demonstrated.

In 1926, R. Knoll[1] reported the preparation of trityl phenyl sulfoxide, by the chromium trioxide oxidation of the sulfide, a reaction which could not be substantiated by Gregg and his co-workers.[2]

Since iodobenzene diacetate (IV) showed mild oxidizing properties toward sulfides to give sulfoxides,[3] an attempt was made to study the behavior of this compound toward phenyl trityl sulfide (I). However, no sulfoxide or sulfone could be isolated from the reaction of I or II with either IV or iodobenzene dichloride (III), but instead cleavage of the sulfides occurred to give triphenylcarbinol or triphenylmethyl chloride in good yield.

The sulfur portion from the cleavage was identified by oxidation and by reaction with mercaptan. In the reaction of II with III, the sulfur portion presumably α-phenylmethanesulfenyl chloride, reacted with benzyl mercaptan to give with the evolution of hydrogen chloride a 47% yield of dibenzyl disulfide. Oxidation of the reaction mixture with peracetic acid gave a mixture of triphenylmethyl chloride and α-phenylmethanesulfonyl chloride from which after repeated recrystallization a small amount of each of the pure compounds could be isolated.

In the reaction of I and III, the sulfur portion, presumably benzenesulfenyl chloride, reacted with phenyl mercaptan yielding with hydrogen chloride evolution diphenyl disulfide (82%).

Phenyl trityl sulfide contains a group that contributes a large steric effect and which on cleavage is stabilized by resonance. Such cleavage of these sulfides could occur through (a) a cation mechanism, (b) an anion mechanism, or (c) a free radical mechanism.

The cleavage of trityl sulfides in acidic media has been reported by several workers.[4,5]

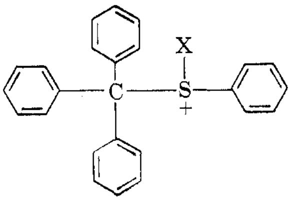
Tarbell and Harnish[5] claim that phenyl trityl sulfide is converted by alcoholic iodine at room temperature to triphenylcarbinol, diphenyl disulfide, and ethyl trityl ether. There is also a report in the literature where cleavage occurs in nonacidic medium in the oxidation with ruthenium tetroxide.[6]

To determine whether such cleavage could occur by attack of base, phenyl trityl sulfide was refluxed with an ethanolic solution of sodium ethoxide but only unchanged starting material was recovered. Reaction of phenylmagnesium bromide with phenyl trityl sulfide afforded a similar result.

It has been known that reactions of *N*-bromosuccinimide in carbon tetrachloride catalyzed by benzoyl peroxide follow a free radical mechanism.[7] For this reason a carbon tetrachloride solution of phenyl trityl sulfide was treated with an equimolar quantity of *N*-bromosuccinimide mixed with a catalytic amount of benzoyl peroxide as free radical initiator. *N*-Tritylsuccinimide and diphenyl disulfide were obtained as products.

With the above considerations in view, it could be said that the cleavage reaction of the trityl sulfides with either III or IV could follow a reaction mechanism of type (a) or (c).

However, it is suggested that the reaction with either III or *N*-bromosuccinimide occurs through the formation of intermediate V, which rapidly decomposes to the triphenylmethyl cation and phenyl sulfenyl halide.



V

It should be noted that cleavage occurs in the case of benzyl trityl sulfide, in spite of the fact that this sulfide has two hydrogens on one of the *alpha* carbon atoms.

EXPERIMENTAL[8]

Iodobenzene dichloride (III) was prepared by the method of Lucas and Kennedy.[9] Iodobenzene diacetate (IV) m.p.

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[1] R. Knoll, *J. prakt. Chem.*, **113**, 40 (1926).

[2] D. C. Gregg, K. Hazelton, and T. P. McKeon, *J. Org. Chem.*, **18**, 36 (1953).

[3] H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956).

[4] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).

[5] D. S. Tarbell and D. P. Harnish, *J. Am. Chem. Soc.*, **74**, 1862 (1952).

[6] C. Djerrassi and R. R. Engle, *J. Am. Chem. Soc.*, **75**, 3838 (1953).

[7] Jack Hine, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1956, pp. 429–430.

157°, was prepared according to the method employed by Pausacker.[10]

Phenyltrityl sulfide (I) was prepared by the method of Finzi and Bellavita[11], m.p. 106–107°, lit.[11] m.p. 106°.

Benzyl trityl sulfide (II). To a solution of triphenylcarbinol (52.1 g., 0.2 mole) in 400 ml. of glacial acetic acid was added with constant shaking 24.8 g. (0.2 mole) of benzyl mercaptan and 20 ml. of concd. sulfuric acid. After the mixture was allowed to stand for 2 hr., it was poured into 500 g. of crushed ice. The solid that separated was filtered, washed with cold water and crystallized from petroleum ether (b.p. 30–60°) yielding needles, m.p. 82–83° (43.2 g.). Concentration of the mother liquor gave an additional 15.8 g. Total yield 80%.

Anal. Calcd. for $C_{26}H_{22}S$: C, 85.20; H, 6.05; S, 8.75. Found: C, 84.93; H, 6.04; S, 9.16.

Reaction of III *with phenyl trityl sulfide* (I). To a solution of 17.6 g. (0.05 mole) of I in 200 ml. of dry carbon tetrachloride or in dry chloroform were added 13.8 g. (0.05 mole) of III. There was no evolution of hydrogen chloride gas. The mixture was allowed to stand overnight. The solvent was removed under reduced pressure, 6.5 g. of trityl chloride separated and the supernatant liquid distilled under vacuum to give 15.0 g. of liquid. The residue in the pot solidified; crystallization from petroleum ether gave an additional 6.2 g. of trityl chloride m.p. 111–113°, lit. 113°.[12] Mixed melting point with authentic material showed no depression.

Total yield of trityl chloride was 91%. Two and two-tenths grams of the liquid distillate when treated with 1.0 g. of phenyl mercaptan reacted vigorously with the evolution of hydrogen chloride to give 1.3 g. (82%) of diphenyl disulfide m.p. 60–61°, from ethanol.

Reaction of III *with benzyl trityl sulfide* (II). To a solution of 18.3 g. (0.05 mole) of II in 200 ml. of dry carbon tetrachloride or chloroform were added 13.8 g. (0.05 mole) of III in small quantities with constant shaking. There was no apparent evolution of hydrogen chloride gas. The mixture was allowed to stand overnight.

One third of the mixture was treated with 15 ml. of 40% peracetic acid and the heterogeneous mixture was stirred overnight. The carbon tetrachloride layer was separated from the peracetic acid, the carbon tetrachloride evaporated, and the residue washed with petroleum ether to give 2.5 g. of triphenylcarbinol, m.p. 160–161°, lit. 162°. An additional 0.5 g. of triphenylcarbinol was obtained from peracetic acid layer, giving a total 69% yield of triphenylcarbinol. From the petroleum ether washings was obtained 0.3 g. (6.4%) of triphenylmethyl chloride, m.p. 111–113°, lit.[12] m.p. 113° and 0.2 g. (6.3%) of α-phenylmethanesulfonyl chloride, m.p. 92–93°.[13] Infrared spectrum was identical with the spectrum of an authentic compound. The solvent was distilled under reduced pressure from the second third of the original mixture and the residue carefully washed with petroleum ether. The remaining solid, m.p. 111–113°, represented a 95% yield of trityl chloride. The petroleum ether washings were treated with 2.0 g. of benzyl mercaptan and set aside for 3 hr. Evaporation of the petroleum ether and iodobenzene under vacuum left a solid which was crystallized from ethanol to give 1.4 g. (47.6%) of dibenzyl sulfide m.p. 71–72°, lit.[14] m.p.. 69–70°.

Reaction of iodobenzene diacetate (IV) *with* I. To a solution of 3.5 g. (0.01 mole) of phenyl trityl sulfide in 100 ml. of glacial acetic acid in an Erlenmeyer flask was added IV (3.2 g., 0.01 mole) with constant swirling. The mixture was allowed to stand for 24 hr. after which it was poured into a beaker containing some crushed ice. The solid that separated was filtered, washed with cold water, and recrystallized from alcohol to yield 1.95 g. (74.9%) of triphenylcarbinol, m.p. 159–160°.[15] Mixed melting point with an authentic sample gave no depression.

Reaction of IV *with* II. A solution of 3.7 g. (0.01 mole) of II in 50 ml. of dry benzene and 3.2 g. (0.01 mole of IV was allowed to stand at room temperature for 24 hr. After concentration of the reaction mixture there was obtained triphenylcarbinol (2.1 g.) which upon recrystallization from ligroin gave no depression in melting point with an authentic sample, m.p. 160°.[15] Further concentration of the mother liquor yielded a dark brown viscous liquid from which no crystals were obtained even on prolonged cooling. No attempt was made to isolate the sulfur fraction of the sulfide; yield of triphenylcarbinol, 81%.

Reaction of N-bromosuccinimide with I. A mixture of 35.2 g. (0.1 mole) of I, 17.8 g. (0.1 mole) of *N*-bromosuccinimide and 2.4 g. of benzoyl peroxide in 150 ml. of dry carbon tetrachloride were refluxed for about 6 hr. in a water bath. The mixture was washed with a 5% solution of sodium hydroxide in order to remove the bromine and benzoic acid that was formed during the reaction. The solvent was distilled and the solid residue thus obtained was stirred well with petroleum ether and filtered. From the filtrate was obtained 7.3 g. (67%) of diphenyl disulfide. The residue (33.2 g., 97%) was recrystallized from a mixture of acetone and ligroin to give shining plates of *N*-tritylsuccinimide, m.p. 203–204°.

Anal. Calcd. for $C_{23}H_{19}NO_2$: C, 80.90; H, 5.61; N, 4.10. Found: C, 80.76; H, 5.62; N, 4.10.

In a separate run using chloroform as solvent, an aliquot quantity of the reaction mixture was taken and titrated with standard sodium thiosulfate iodometrically; the bromine titrated quantitatively. Also a 48% yield of diphenyl disulfide was obtained without washing the reaction mixture with sodium hydroxide.

Reaction of phenyl trityl sulfide with ethoxide. Phenyl trityl sulfide (17.6 g., 0.05 mole) was refluxed for 3 hr. with a solution of sodium ethoxide prepared from 5 g. of sodium and an excess of absolute ethanol. Upon cooling 14.5 g. of solid crystallized, m.p. 105–106° after one recrystallization from ethanol. This gave no depression in melting point with a sample of the starting material. An additional 1.6 g. was obtained on evaporating the ethanol, washing with water, and extracting with ether.

Reaction of phenyl trityl sulfide with phenylmagnesium bromide. To phenyl Grignard, prepared from 2.4 g. of magnesium and 15.7 g. of bromobenzene in ethyl ether, was added a solution of 17.0 g. (0.05 mole) of phenyl trityl sulfide in about 100 ml. of dry benzene. After 12 hr. of stirring, the mixture was hydrolyzed with a saturated solution of ammonium chloride; the organic layer was separated and the aqueous layer was extracted several times with benzene. From the combined benzene extracts 15.3 g. of the unchanged phenyl trityl sulfide were recovered.

Hydrolysis of the reaction mixture with dilute acid solution gives cleavage products, due the reaction of the acid with phenyl trityl sulfide.

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[8] All microanalyses were carried out by Elek Microanalytical Laboratories, Los Angeles, Calif., or Dr. Alfred Bernhardt, Mikroanalytisches Laboratorium, Mulheim, Germany. Melting points reported are uncorrected.

[9] H. J. Lucas and R. R. Kennedy, *Org. Syntheses*, **Coll. Vol. III**, 432 (1955).

[10] K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

[11] C. Finzi and V. Bellavita, *Gazz. chim. ital.*, **62**, 699–709 (1932).

[12] W. E. Bachmann, *Org. Syn.*, **23**, 100 (1943).

[13] L. V. Pechmann, *Ber.*, **6**, 534 (1873).

[14] E. Fromm and P. Schenoldt, *Ber.*, **40**, 2870 (1907).

[15] Shriner and Fuson, *Identification of Organic Compounds*, Third Edition, John Wiley & Sons, New York, p. 282.