[Contribution from the Department of Chemistry, Duquesne University]

p-Nitro *p*-Acylphenyl Sulfides and Related Compounds

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The investigation of acylation reactions of *p*-nitrophenyl phenyl sulfide (I) was continued. I can be acetylated by acetic anhydride in the presence of boron trifluoride. The acylation procedure employing a carboxylic acid and trifluoroacetic anhydride was improved by the addition of boron trifluoride (II). A number of derivatives of *p*-(4-nitrophenylmercapto)-acetophenone are described.

In a previous publication on this subject[1] there was described the preparation of two *p*-nitrophenyl *p'*-acylphenyl sulfides by means of the reaction of alkyl cadmiums[2] with *p*-(4-nitrophenylmercapto)-benzoyl chloride. Also, it was stated that the application of the conventional Friedel–Crafts procedure with *p*-nitrophenyl phenyl sulfide (I) gave negative results. The re-examination of the Friedel–Crafts procedure with I under more vigorous conditions showed that a small yield of the desired ketone could be obtained, but, at the same time, most of the unreacted starting material I was apparently destroyed.

In view of the poor results with the conventional Friedel–Crafts reaction, and because of the inconveniences involved in the use of the Cason procedure, the search was continued for other acylation methods applicable to I.

The use of acetic anhydride in the presence of II gave either of two products depending on the reaction temperature. At ice-bath temperatures the exclusive product was the desired *p*-(4-nitrophenylmercapto)-acetophenone,[1] while at room temperature the corresponding acetoacetyl derivative of I was obtained together with unreacted I. Acetoacetylation of aromatic compounds under similar conditions has been observed previously.[3] The structure of the acetoacetyl derivative of I was proven by oxidation to the known *p*-(4-nitrophenylsulfonyl)-benzoic acid[1] and by the formation of a pyrazole with hydrazine.

Since the use of the acid anhydride–boron trifluoride method is not convenient when acylations with higher aliphatic acids are desired, there was next investigated the acylation procedure employing a carboxylic acid in the presence of trifluoroacetic anhydride.[4] This procedure failed to give an acetylation of I, but it was found that the additional use of II gave satisfactory yields of *p*-(4-nitrophenylmercapto)-acetophenone. Also, excellent yields of *p*-(4-nitrophenylmercapto)-benzophenone were obtained when a mixture of I, benzoic acid, trifluoroacetic anhydride, and II was allowed to react.

p-(4-Nitrophenylmercapto)-acetophenone was subjected to a series of oxidation and reduction reactions summarized below. The main purpose of these reactions was the preparation of the 1-phenethyl alcohols containing the amino–sulfide or the amino–sulfone functions.

The failure to obtain a satisfactory Friedel–Crafts acylation of I is of interest in view of the successful acylations of *p*-nitrophenyl phenyl ether[5] and the parent compound, namely, phenyl sulfide.[6] Our inability to recover I from the unsuccessful acylations raised the suspicion that the starting material was being cleaved and this suspicion was confirmed when *p*-nitrochlorobenzene was isolated. The comparison of the behavior of I with that of the two above mentioned compounds which can be acylated under Friedel–Crafts conditions indicates that the cleavage of I is caused by the presence of both the nitro and sulfide functions. The smaller resonance interaction of sulfur in phenyl sulfide (as compared to the resonance interaction of oxygen in phenyl ether) is evident from the behavior of these compounds in sulfuric acid,[7] and as a consequence of this difference one would expect the sulfur atom in I to complex more readily with a Lewis acid such as aluminum chloride than the oxygen atom of *p*-nitrophenyl phenyl ether. The resulting complex can then be visualized to undergo nucleophilic attack by chloride ion to give *p*-chloronitrobenzene in a manner similar to other known cleavage reactions of sulfides.[8]

The acylation procedure employing a carboxylic acid and trifluoroacetic anhydride[9] is known to involve the formation of a mixed anhydride, according to the equation

$$\mathrm{R{-}CO_2H + (CF_3CO)_2O \longrightarrow R{-}CO{-}O{-}CO{-}CF_3 + CF_3{-}CO_2H}$$

The mixed anhydride then either dissociates to give trifluoroacetate and an acylonium ion (whereupon the latter attacks the electron-rich site of an aromatic molecule), or, more probably, the aromatic molecule by virtue of its nucleophilic character attacks the mixed anhydride with simultaneous displacement of the trifluoroacetate ion. The latter viewpoint explains why this acylation procedure has been successful, so far, only with highly nucleophilic aromatic systems (alkyl aryl ethers, dialkylbenzenes, thiophene, furan)[9] and failed when applied to benzene or toluene.[10]

In order to increase the electrophilic reactivity of the mixed anhydride (obtained from trifluoroacetic anhydride and a carboxylic or a sulfonic acid), it was found in this Laboratory[11,12] that the

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[1] H. H. Szmant and G. Levitt, This Journal, **76**, 5459 (1954).

[2] J. Cason, *Chem. Revs.*, **40**, 15 (1947).

[3] C. R. Hauser, *et al.*, This Journal, **75**, 4109, 5030 (1953).

[4] E. J. Burton, M. Stacey, J. C. Tatlow and R. Worrall, *J. Chem. Soc.*, 2006 (1954).

[5] A. W. Rakston and C. W. Christenson, U.S. Patent 2,033,540, *C.A.*, **30**, 3123 (1936).

[6] H. H. Szmant and F. Palopoli, This Journal, **72**, 1757 (1950).

[7] H. H. Szmant and G A Brost, *ibid.*, **73**, 4175 (1951).

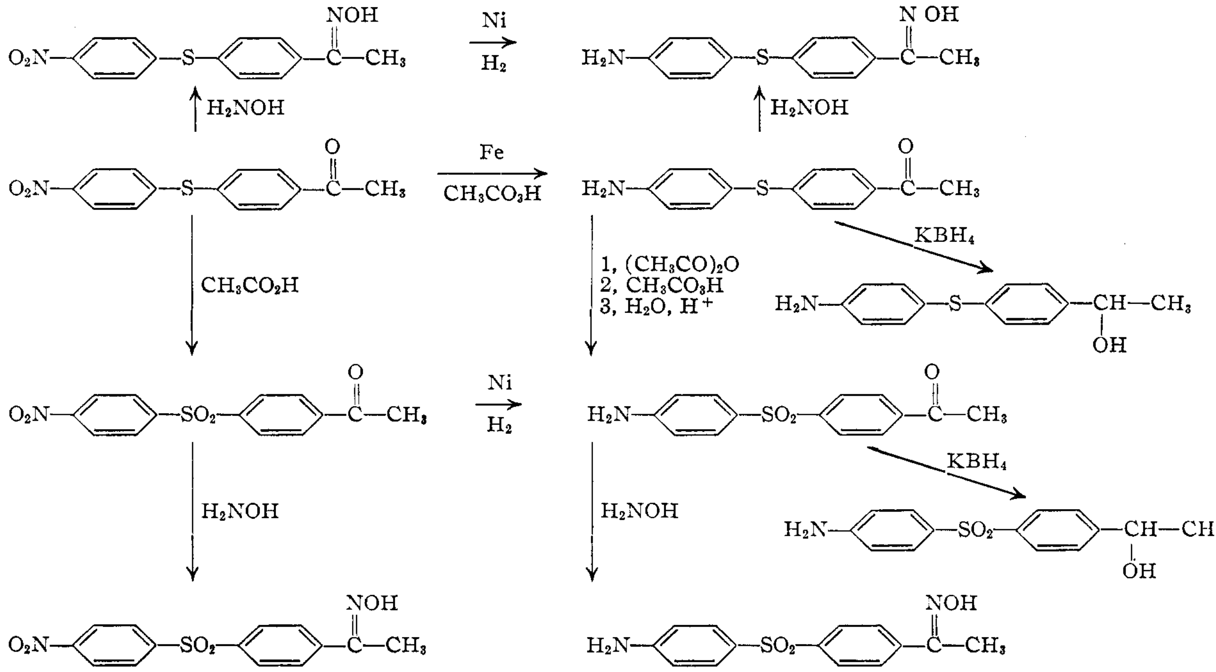
[8] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 43 (1951).

[9] J. M. Tedder, *ibid.*, **55**, 787 (1955).

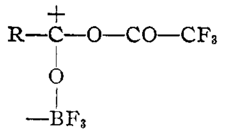
[10] Only trace yields of *p*-methylacetophenone are reported[9] in the acylation of toluene.

[11] H. H. Szmant and G. Suld, This Journal, **78**, 3400 (1956).

[12] H. H. Szmant and C. Harmuth, manuscript in preparation.



addition of II was rather effective. Thus II was shown to promote acylation reactions of the mixed anhydride in situations where the reaction failed in its absence. The catalytic effect of boron trifluoride can be interpreted by postulating the formation of a complex in which the electrophilic character of the potential acyl group is greatly increased.


$$R-\overset{+}{C}(-O-BF_3)-O-CO-CF_3$$

Experimental[13]

p-**Nitrophenyl phenyl sulfide**[14a] was prepared according to the method of Shirley[14b] from *p*-chloronitrobenzene in 90% yield.

Friedel–Crafts Reactions of I.—(A) *p*-**(4-Nitrophenylmercapto)-acetophenone.**[1]—Acetyl chloride, 16 g., and 46 g. of I were added to 200 ml. of carbon disulfide. The mixture was cooled in an ice-bath and 78 g. of aluminum chloride was added slowly with stirring. The reaction mixture was then heated to reflux for 24 hr. It was then poured into a mixture of ice and dilute hydrochloric acid to hydrolyze the complex aluminum compounds formed in the reaction. A tarry mixture obtained was separated. The distillation of the carbon disulfide layer gave a residue which was recrystallized from ethanol and gave the desired ketone. The tarry mixture from the hydrolysis was dissolved in ethanol and upon separation and recrystallization, more of the ketone was obtained; m.p. 117–119°; yield 1.5 g. (7%). The starting sulfide was not recovered.

A portion of the tarry mixture (*ca.* 5 g.) from an experiment such as the one described above was distilled under high vacuum, and there was isolated 0.2 g. of *p*-nitrochlorobenzene, m.p. and mixed m.p. 82–83°.

(B) *p*-**(4-Nitrophenylmercapto)-laurophenone.**—A mixture of 35 g. of I and 50 g. of lauroyl chloride in 200 ml. of carbon disulfide was cooled in an ice-bath. Aluminum chloride, 55 g., was added slowly with stirring. The reaction mixture was allowed to come to room temperature and to stand for 55 hr. It was then poured into a mixture of dilute hydrochloric acid and ice to hydrolyze the complex aluminum compounds formed in the reaction. Finally, the resulting acid mixture was steam distilled. The tarry residue could not be crystallized; it was vacuum distilled to give 30.5 g. of lauric acid. Upon successive recrystallizations of the distillation residue from ethanol, the desired ketone, m.p. 81–82°, was obtained in a yield of 4% (2 g.).

Anal. Calcd. for $C_{24}H_{31}O_3NS$: C, 69.7; H, 7.52. Found: C, 69.5; H, 7.77.

The starting sulfide was not recovered.

(C) *p*-**(4-Nitrophenylsulfonyl)-stearophenone.**—A mixture of 40.3 g. of I and 48.2 g. of stearoyl chloride in 300 ml. of carbon disulfide was cooled in an ice-bath. Aluminum chloride, 75 g., was added slowly with stirring. The reaction mixture was allowed to come to room temperature and to stand for 6 days. It was then poured into a mixture of dilute hydrochloric acid and ice to hydrolyze the complex aluminum compounds formed in the reaction. The carbon disulfide layer was separated and distilled. The sulfide could not be isolated from the residue in a pure state and thus it was oxidized with peracetic acid to yield the (slightly impure) sulfone in a yield of approximately 1 g., recrystallized from ethanol, m.p. 108–109°. No starting sulfide was recovered.

Anal. Calcd. for $C_{30}H_{43}O_5NS$: C, 68.1; H, 8.13. Found: C, 67.6; H, 8.57.

p-**(4-Nitrophenylmercapto)-acetophenone.**[1]—(A). A mixture of 0.2 mole of I and 0.4 mole of acetic anhydride was treated at 0° with II, and after 6 hr. the mixture was hydrolyzed. Upon working up of the reaction mixture there was isolated 12 g. (0.044 mole) of the desired ketone, m.p. 117–118°, and 28.3 g. (0.122 mole) of unreacted I.

(B).—Acetic acid, 12 g., was added to 42 g. of trifluoroacetic anhydride at 0°. The mixture was allowed to stand to form the mixed anhydride and 46.2 g. of I was then added. II (bubbled through 95% sulfuric acid) was passed into the mixture for 1.5 hr. after which time some of the reaction mixture solidified. Water was added and the precipitated solid was filtered and recrystallized from ethanol, m.p. 117–118°; yield 87% (21.5 g.), calculated on recovered starting sulfide (24.7 g.).

p-**(4-Nitrophenylmercapto)-benzoylacetone.**—Commercial II was bubbled through 95% sulfuric acid and then passed into a mixture of 46.2 g. of I and 55.8 g. of acetic anhydride stirred at room temperature. After a 2 hr. passage of II (nearly saturated) the mixture partially solidified. Water was then added and the precipitated solid was filtered and recrystallized from ethanol. The ketone, m.p. 139–140°,

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(13) Microanalyses by Drs. Strauss and Weiler, Oxford, England. Melting points are uncorrected.

(14) (a) H. H. Hodgson and R. Smith, *J. Chem. Soc.*, 1634 (1937); (b) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 222.

was obtained in a yield of 99% (26 g.) calculated on recovered starting sulfide (27 g.).

Anal. Calcd. for $C_{16}H_{13}O_4NS$: C, 60.97; H, 4.15; N, 4.44. Found: C, 60.60; H, 3.98; N, 4.12.

The Oxidation of *p*-(4-Nitrophenylmercapto)-benzoylacetone.—In an attempt to oxidize *p*-(4-nitrophenylmercapto)-benzoylacetone to the corresponding sulfone using peracetic acid, the desired sulfone was not isolated and instead the diketone was degraded to the known *p*-(4-nitrophenylsulfonyl)-benzoic acid,[1] m.p. 304.5–305.5°.

***p*-(4-Nitrophenylmercapto)-benzoylacetone 2,4-dinitrophenylhydrazone** was prepared in the usual manner and was recrystallized from ethanol; m.p. 166–167°.

Anal. Calcd. for $C_{22}H_{16}O_6N_5S$: N, 14.1. Found: N, 14.0.

2-(*p*-Nitrophenylmercaptophenyl)-4-methylpyrazolone was prepared by heating the diketone with hydrazine and was recrystallized from ethanol, m.p. 186–187°.

Anal. Calcd. for $C_{22}H_{16}O_2N_3S$: C, 61.5; H, 4.48; N, 13.4. Found: C, 61.3; H, 4.20; N, 13.3.

***p*-(4-Nitrophenylmercapto)-benzophenone.**—Benzoic acid, 24.4 g., was added to 42 g. of trifluoroacetic anhydride at room temperature and was allowed to stand until the mixture became homogeneous; I, 46.2 g., was then added and II (bubbled through 95% sulfuric acid) was passed into the reaction mixture until saturated. The mixture was stirred for 5 hr. After hydrolysis, the precipitated solid was filtered and recrystallized from ethanol. The ketone, m.p. 142–143°, was obtained in a 96.5% yield (45 g.) calculated on recovered starting sulfide (14 g.).

Anal. Calcd. for $C_{19}H_{13}O_3NS$: C, 68.1; H, 3.88. Found: C, 68.0; H, 4.08.

In the absence of II only unreacted I could be isolated.

***p*-(4-Nitrophenylmercapto)-benzophenone 2,4-dinitrophenylhydrazone** was prepared in the usual manner and was recrystallized from acetic acid, m.p. 237.5–238.5°.

Anal. Calcd. for $C_{25}H_{17}O_6N_5S$: N, 13.59. Found: N, 13.40.

***p*-(4-Nitrophenylmercapto)-acetophenone oxime**[1] was prepared in the usual manner and was recrystallized from ethanol–water; m.p. 165–166°.

***p*-(4-Aminophenylmercapto)-acetophenone.**—*p*-(4-Nitrophenylmercapto)-acetophenone, 5 g., was heated with 10 10 g. of iron powder in 200 ml. of glacial acetic acid. After refluxing for 3 hr., the mixture was cooled and filtered. The acetic acid portion was diluted with water and filtered. The desired amine was recrystallized from ethanol–water; m.p. 158–159°; yield 3.5 g. (80%).

Anal. Calcd. for $C_{14}H_{13}ONS$: C, 69.2; H, 5.35. Found: C, 69.0; H, 5.2.

***p*-(4-Aminophenylmercapto)-acetophenone oxime** was prepared in the usual manner and was recrystallized from ethanol–water, m.p. 169–169.5°.

Anal. Calcd. for $C_{14}H_{14}ON_2S$: C, 65.1; H, 5.43; N, 10.8. Found: C, 64.85; H, 5.15; N, 10.8.

From another preparation the product on crystallization from methanol gave m.p. 192–193° (geometrical isomer?) but gave also a satisfactory analysis.

Found: C, 64.7; H, 5.53.

***p*-(4-Aminophenylmercapto)-phenyl-1-ethanol.**—The corresponding ketone, 3.5 g., was dissolved in ethanol and potassium borohydride (0.225 g. in 1.5 cc. of water) was added. The mixture was allowed to react at room temperature for 3 hr. with stirring. Sodium hydroxide, 10 ml. of a 10% solution, was added and the mixture was heated slightly in order to destroy the borate complexes. The solution was then diluted with water and the precipitated solid was filtered and recrystallized from benzene; m.p. 150.5–151.5°; yield 3 g. (86%).

Anal. Calcd. for $C_{14}H_{15}ONS$: N, 5.71. Found: N, 5.75.

***p*-(4-Diacetylaminophenylmercapto)-acetophenone.**—The corresponding amino compound was acetylated with excess acetic anhydride in acetic acid. After being refluxed for 3 hr., the reaction mixture was poured into water and filtered. The precipitated solid was recrystallized from ethanol; m.p. 119–120°.

Anal. Calcd. for $C_{18}H_{17}O_3NS$: C, 66.06; H, 5.23; N, 4.4. Found: C, 65.70; H, 5.13; N, 4.70.

Hydrolysis of this compound gave *p*-(4-aminophenylmercapto)-acetophenone.

***p*-(4-Acetylaminophenylmercapto)-acetophenone.**—The corresponding amine was acetylated with an equimolar amount of acetic anhydride in acetic acid. After being refluxed for 3 hr., the reaction mixture was poured into water. The precipitated solid was filtered and recrystallized from ethanol; m.p. 156–156.5°.

Anal. Calcd. for $C_{16}H_{15}O_2NS$: C, 67.4; H, 5.27; N, 4.9. Found: C, 67.2; H, 4.96; N, 4.65.

***p*-(4-Acetylaminophenylsulfonyl)-acetophenone.**—The corresponding sulfide was oxidized with peracetic acid in acetic acid for 5 minutes and then poured into water. The precipitated solid was filtered and recrystallized from ethanol; m.p. 198–199°.

Anal. Calcd. for $C_{16}H_{15}O_4NS$: C, 60.6; H, 4.39; N, 4.4. Found: C, 60.3; H, 4.65; N, 4.3.

Hydrolysis of *p*-(4-Acetylaminophenylsulfonyl)-acetophenone.—The sulfonyl compound was hydrolyzed in a mixture of dilute hydrochloric acid and ethanol. After being refluxed for 2 hr., the reaction mixture was poured into water. The precipitated solid was filtered and recrystallized from ethanol–water to yield the known *p*-(4-aminophenylsulfonyl)-acetophenone, m.p. 180–181°.

***p*-(4-Nitrophenylsulfonyl)-acetophenone**[1] was prepared from the corresponding sulfide by oxidation with peracetic acid in acetic acid. The sulfone was recrystallized from methanol; m.p. 180–181°.

***p*-(4-Nitrophenylsulfonyl)-acetophenone oxime** was prepared in the usual manner and was recrystallized from ethanol; m.p. 223–224°.

Anal. Calcd. for $C_{14}H_{12}O_5N_2S$: C, 52.5; H, 3.75. Found: C, 52.3; H, 3.88.

***p*-(4-Aminophenylsulfonyl)-acetophenone.**—The corresponding nitro sulfone in acetic acid was hydrogenated at 60 p.s.i. in the presence of Raney nickel. After the solution was filtered, the acetic acid portion was diluted with water and filtered. The precipitated solid was recrystallized from ethanol–water; m.p. 179–180°.

***p*-(4-Aminophenylsulfonyl)-acetophenone oxime** was prepared in the usual manner and was recrystallized from ethanol; m.p. 188.5–189°.

Anal. Calcd. for $C_{14}H_{14}O_3NS$: C, 58.0; H, 4.85; N, 9.67. Found: C, 57.72; H, 4.5; N, 10.1.

***p*-(4-Aminophenylsulfonyl)-phenyl-1-ethanol.**—The corresponding ketone, 2 g., was dissolved in ethanol and potassium borohydride (0.109 g. in 1.0 cc. of water) was added. The mixture was allowed to react at room temperature for 3 hr. and 10 ml. of a 10% solution of sodium hydroxide was added. The solution was then heated slightly in order to break any borate complexes formed. After the solution was poured into water, the precipitated solid was filtered and recrystallized from benzene, m.p. 141–141.5°; yield 1.8 g. (90%).

Anal. Calcd. for $C_{14}H_{15}O_3NS$: C, 60.7; H, 5.42; N, 5.06. Found: C, 60.9; H, 5.43; N, 5.38.

4,4′-Di-(*p*-acetophenylmercapto)-azoxybenzene.—*p*-(4-Nitrophenylmercapto)-acetophenone, 5 g., was dissolved in ethanol and hydrogenated at 60 p.s.i. in the presence of Raney nickel and the solution was filtered. A yellow crystalline solid precipitated (approximately 1.5 g.) and was identified as 4,4′-di-(*p*-acetylphenylmercapto)-azoxybenzene, m.p. 186–187.5°.

Anal. Calcd. for $C_{28}H_{22}O_3N_2S_2$: C, 67.44; H, 4.45; N, 5.6. Found: C, 67.32; H, 4.12; N, 5.8.

The bis-2,4-dinitrophenylhydrazone was prepared in the usual manner and was recrystallized from nitrobenzene; m.p. 294–296° dec.

Anal. Calcd. for $C_{40}H_{30}N_{10}S_2$: N, 15.7. Found: N, 15.7.

Reduction of the azoxy compound with iron and acetic acid yielded the known *p*-(4-aminophenylmercapto)-acetophenone, m.p. 158–159°.

The alcoholic solution from the hydrogenation after filtration of the azoxy compound was poured into water. The precipitated amino compound was filtered and recrystallized from ethanol–water; m.p. 158–159°, yield 1 g. (22%).

4,4′-Di-(*p*-acetylphenylmercapto)-azo- and Azobenzene Dioxime.—An alcoholic solution of 5 g. of *p*-(4-nitrophenylmercapto)-acetophenone oxime was hydrogenated at 60 p.s.i. in the presence of Raney nickel. After the solution was filtered, a yellow crystalline solid precipitated (approximately 1.5 g.) which was identified as 4,4'-di-(*p*-acetylphenylmercapto)-azoxybenzene dioxime, m.p. 222–223°.

Anal. Calcd. for $C_{28}H_{24}O_3N_4S_2$: C, 63.7; H, 4.54; N, 10.5. Found: C, 63.04; H, 4.46; N, 9.7.

An attempt to hydrolyze the compound to the corresponding diketone failed due to its insolubility in a mixture of acetic and hydrochloric acids.

The alcoholic solution from the hydrogenation after filtration of the azoxy compound was poured into water. The precipitated solid was filtered and recrystallized to yield the desired amino oxime, m.p. 169–169.5°; yield 1.5 g. (33.5%).

In another hydrogenation experiment using 3 g. of oxime in the presence of ammonia, there was again isolated the desired amino oxime, m.p. 169–169.5°; yield 1.5 g. (33.5%). In addition to this compound there was also obtained approximately 1.5 g. of an orange material, m.p. 246–247°. The analysis of this compound agrees closely with that expected for 4,4'-di-(*p*-acetylphenylmercapto)-azobenzene dioxime.

Anal. Calcd. for $C_{28}H_{26}O_2N_4S_2$: C, 65.74; H, 4.68; N, 10.9; S, 12.5. Found: C, 65.87; H, 5.00; N, 10.3; S, 12.12.

It was shown that short hydrogenation of the above azoxy compound, m.p. 223–224°, in alcoholic ammonia gave the azo compound, m.p. 246–247°.

This compound, unlike the azoxy compounds described above, showed a peculiar color change in the presence of strong acids. A solution of the material in concentrated hydrochloric acid gave an intense violet color which disappeared upon dilution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF VANDERBILT UNIVERSITY]

Grignard Reagents of Sulfones. IV. Reactions with Nitriles, Esters and an Isocyanate[1]

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Addition of *p*-tolylsulfonylmethylmagnesium bromide (I) to benzonitrile and to trimethylacetonitrile resulted, after hydrolysis, in the corresponding ketones, but addition to acetonitrile led to variable and generally much less satisfactory results. The course of reaction between the Grignard reagent I and methyl benzoate was delineated, α-(*p*-tolylsulfonyl)-acetophenone being formed in good yield. A similar reaction occurred with ethyl acetate. Ethyl chloroformate reacted as an acyl halide and gave diethyl *p*-tolylsulfonylmalonate. Phenyl isocyanate yielded *p*-tolylsulfonylmalonanilide with compound I, in contrast to its reaction with α-(*p*-tolylsulfonyl)-ethylmagnesium bromide, with which it gave α-(*p*-tolylsulfonyl)-propionanilide. Factors which determine the nature of the foregoing reactions are discussed.

Grignard reagents of sulfones, exemplified by *p*-tolylsulfonylmethylmagnesium bromide (I), undergo a variety of reactions in a manner which is generally rather typical of Grignard reagents as a class.[2] The characteristics of the reactions between a Grignard reagent of a sulfone and nitriles, esters and phenyl isocyanate are considered in the present paper.

Since the reactivity of Grignard reagents with benzophenone decreases with increasing electronegativity of the organic moiety,[3] compounds such as the reagent I should have a lower order of capability in such addition reactions than most Grignard reagents. Although no such diminution of activity was conspicuous in a reaction with benzaldehyde (in comparison with phenylmagnesium bromide),[4] it may well have failed to appear because of the high degree of reactivity and lack of selectivity of benzaldehyde. Nitriles, on the other hand, possess one of the least reactive of the common functional groups toward phenylmagnesium bromide,[5] and the nature of their reactions with Grignard reagents of sulfones therefore merited exploration.

A gum resulted when benzonitrile was added to the white solid reagent I, which had been prepared as shown by the equation. Heating at 70° and hydrolysis with aqueous ammonium chloride then resulted in 2-imino-2-phenylethyl *p*-tolyl sulfone (III) in 82% yield. One may reasonably conclude that the gum which appeared at the outset was a complex of the reagent I and the nitrile which rearranged[6] to the actual addition product fairly rapidly only upon being heated, because when the heating period was omitted the product was quite impure and was obtained in only 40% yield. The reaction of Grignard reagents such as I with nitriles is therefore less facile than with carbonyl compounds, which react readily at room temperature[4] and may indeed give less satisfactory results with heating.[7] Hydrolysis of the imine III resulted in the ketone IV in 95% yield, thus both confirming the structure of III and demonstrating a practical conversion of a nitrile to a ketosulfone.

Acetonitrile was next studied, as representing the class of lower aliphatic nitriles reasonably well. No extensive attempts were made to isolate an intermediate imine. Instead, the product was hydrolyzed directly to *p*-tolylsulfonylacetone (V), which was isolated in 46% yield. When attempts to improve this yield actually eventuated in much poorer ones, an effort was made to repeat the original experiment. This effort failed, however, and the ketone V was obtained in only 11% yield. Although no explanation for the original relatively

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(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society at Birmingham, Ala., Oct. 21–23, 1954. Abstracted from a portion of the Ph.D. thesis of J. W. McF., June, 1953, and from the M.A. thesis of J. E. L., June, 1956.

(2) For leading references, see paper III of this series, L. Field, THIS JOURNAL, **78**, 92 (1956).

(3) M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

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(5) C. E. Entemann, Jr., and J. R. Johnson, *ibid.*, **55**, 2900 (1933).

(6) C. G. Swain, *ibid.*, **69**, 2306 (1947).

(7) L. Field, *ibid.*, **74**, 3919 (1952).