# The Reaction of Benzil with Methylsulfinyl Carbanion. The Phenoxide Ion Generation of Methylsulfinyl Carbanion in Low Concentration

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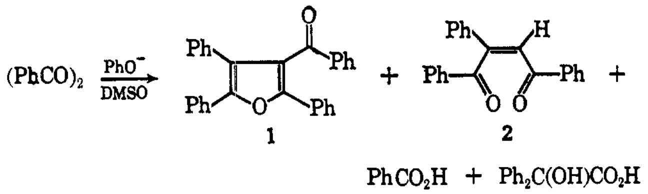
Phenoxide ion is shown to effect a reaction between benzil and dimethyl sulfoxide to yield 3-benzoyl-2,4,5-triphenylfuran (1), *cis*-$\alpha,\beta$-dibenzoylstyrene (2), benzoic acid, and benzilic acid. A method for the generation of methylsulfinyl carbanion in very low concentration is presented. The structure proof of previously unreported 1 is described.

While certain alkoxide ions are reported to transform benzil to the corresponding benzilic ester,[1] phenoxide ion, due to its low reactivity, has been shown to be incapable of effecting the transformation in aqueous ethanol[2] and benzene.[1] In view of the many recent reports[3] of enhanced anion reactivity in polar aprotic solvents such as dimethyl sulfoxide (DMSO), it was felt that a new attempt to cause phenoxide ion to react with benzil was in order. This report describes the results obtained from the attempted reaction plus the characterization and structure determination of the reaction products.

No reaction was observed between benzil and phenoxide ion in DMSO at room temperature. On heating the solution to 100° for 48 hr, reaction occurred and the products isolated were 3-benzoyl-2,4,5-triphenylfuran (1), *cis*-$\alpha,\beta$-dibenzoylstyrene (2), benzoic acid, and benzilic acid.



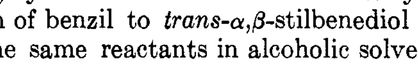
The possibility of some phenyl benzilate formation with subsequent hydrolysis to benzilic acid by water, an assumed by-product in the reaction(s) leading to 1 and 2, cannot be ruled out. The benzilic acid probably arises, however, from the reaction of benzil with this water by phenoxide ion catalysis.

Whereas details of the reaction mechanism are as yet incomplete, certain observations can be made at this time. It is believed, for example, that the reactive nucleophile in the system is methylsulfinyl carbanion (3) which is generated by proton exchange between solvent and the weakly basic phenoxide ion (eq 1). The conclusion is supported by the fact that, when methylsulfinyl carbanion is generated in the usual manner[4] and then added to a stirred solution of benzil in DMSO, the same reaction products are obtained. However, the latter reaction is less satisfactory owing to lower yields of isolable products and greater yields of oils and tars. This reaction also establishes that benzilic acid formation is not limited to phenyl benzilate hydrolysis in the original reaction. To demonstrate the necessity of phenoxide ion in effecting the transformation, benzil was heated in DMSO at 100° for 48 hr, and only starting material was recovered.

$$\mathrm{PhO^- + CH_3S(O)CH_3 \rightleftharpoons PhOH + \underset{3}{CH_3S(O)CH_2{:}^-}} \qquad (1)$$

The observation that the reaction using phenoxide ion is essentially complete only after heating at 100° for two days indicates that the concentration of methylsulfinyl carbanion in the reaction is very low. This conclusion is supported by the fact that the reaction between benzil and prepared methylsulfinyl carbanion occurs rapidly at 20° and is noticeably exothermic. Phenoxide ion will possibly find general applicability as a reagent for generating methylsulfinyl carbanion in reactions where a low concentration of this nucleophile is necessary or desirable. However, such applications will necessarily be limited to situations where phenoxide ion competes ineffectively with the anion as a nucleophile and where higher temperatures are permissable.

Russell and coworkers have investigated extensively the reduction of the various types of diketones by anions in DMSO-*t*-butyl alcohol solution and have detected the formation of the corresponding semidiones (5) in appreciable concentrations.[5] Benzil (4, R = R′ = Ph) is reported to form the corresponding semidione when treated with benzoin in basic solution.[5a,6] Whether this reduction is occurring in the reaction under investigation or to what extent is not known.



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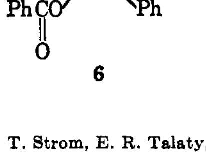
Another unusual cleavage reaction of benzil in DMSO was recently observed in this laboratory.[7] In this instance, cyanide ion was shown to catalyze the isomerization of benzil to *trans*-$\alpha,\beta$-stilbenediol dibenzoate (6); the same reactants in alcoholic solvent are



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[1] W. von E. Doering and R. S. Urban, *J. Amer. Chem. Soc.*, **78**, 5938 (1956).

[2] F. H. Westheimer, *ibid.*, **58**, 2209 (1936).

[3] D. Martin, A. Weise, and H.-J. Niclas, *Angew. Chem., Intern. Ed. Engl.*, **6**, 318 (1967); A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[4] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

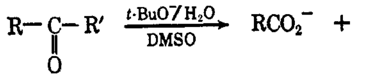
[5] (a) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *ibid.*, **88**, 1998 (1966); (b) E. T. Strom, G. A. Russell, and J. H. Schoeb, *ibid.*, **88**, 2004 (1966), and references to earlier reports cited therein.

[6] J. L. Ihrig and R. G. Caldwell, *ibid.*, **78**, 2097 (1956).

[7] J. C. Trisler and J. L. Frye, *J. Org. Chem.*, **30**, 306 (1965).

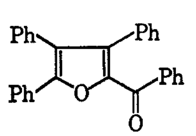
reported to yield benzaldehyde and the corresponding benzoate ester.[8]

A general method for cleaving nonenolizable ketones is reported to occur under mild conditions in aprotic solvents containing *t*-butoxide ion and water.[9]



$$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[\text{DMSO}]{t\text{-BuO}^-/H_2O} RCO_2^- + R'H$$

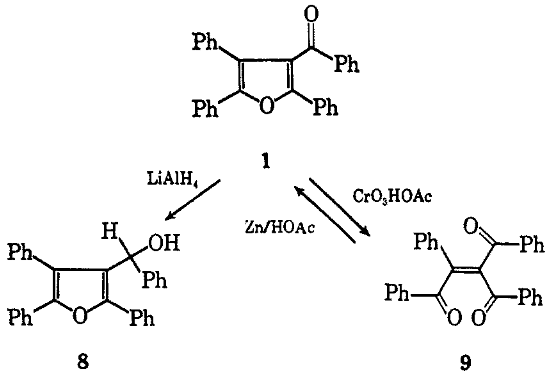
While 2-benzoyl-3,4,5-triphenylfuran (7) is known,[10]



**7**

its isomer, **1**, is previously unreported. Compound **1** was characterized according to Scheme I.

SCHEME I



Functional group assignment was made in each case from the infrared spectrum. Data from nmr spectra confirmed the single carbonyl character of **1** in that: (a) the integrated proton ratio revealed deshielding of only two *ortho* hydrogens by the carbonyl anisotropic effect[11] and (b) only two hydrogens were gained in the reduction of **1** to 3-(α-hydroxybenzyl)-2,4,5-triphenylfuran (**8**) Oxidation of **1** to 2-benzoyl-1,3,4-triphenyl-2-butene-1,4-dione (**9**) is characteristic of 2,5-diphenylfurans.[12] Also, the reduction of **9** to **1** is characteristic of 2-butene-1,4-diones.[13]

Finally, **1** was prepared by independent synthesis from ω-desylacetophenone (**10**) according to Scheme II.

Although enolate ions are more susceptible to O-acylation than to C-acylation, where enolate ion is present in excess and time is allowed for product equilibration, the stable anion of the C-acylated product will predominate.[14] In the above reaction this stable anion can only be **13**. When the anions of ω-desylacetophenone (**11** and **12**) were reacted with benzoyl chloride in 1,2-dimethoxyethane, using a reactant ratio of 2:1, respectively, 2-benzoyl-1,3,4-triphenylbutane-1,4-dione (**14**) was isolated in 58% yield. It is interesting to note that acylation of 1,4-diketones, *via* the enolate ions, leads to intermediate products that should be subject to facile intramolecular isomerization in addition to regular intermolecular isomerization.[14] For example, O-benzoylation of **11**, the more stable enolate ion,[15] should give **15**, the isomerization of which is easily illustrated (Scheme III).

On heating **14** with hydrochloric acid in ethanol, **1** was obtained in near quantitative yield. The reaction is characteristic of enolizable 1,4-diketones.[16]

Attempts to prepare **13** by treating the anion of dibenzoylmethane with desyl chloride in DMSO at elevated temperatures were unsuccessful presumably owing to the inertness of the anion. In each case dibenzoylmethane was recovered.

Other reaction products are well known. Mixture melting points and infrared spectra were used for characterization in each case.

## Experimental Section[17]

**Starting Materials.**—Benzil, mp 94–95°, was obtained commerically and was used without further purification. Sodium phenoxide, prepared by the method of Kornblum and Lurie,[18] was dried overnight at 110° (1 mm) prior to use. ω-Desylacetophenone was prepared by the method of Smith.[19] Dimethyl sulfoxide was dried over molecular sieve (4A) and distilled from calcium hydride (1 mm).[4] Other materials were of reagent grade and were used without further purification.

**Benzil and Phenoxide Ion in Dimethyl Sulfoxide.**—Benzil (2.10 g, 0.01 mol) and sodium phenoxide (1.16 g, 0.01 mol) were added to 135 ml of anhydrous dimethyl sulfoxide and heated in a closed system, under an atmosphere of nitrogen, at 100° for 48 hr. The dark brown reaction mixture was poured onto cracked ice, acidified, and extracted with ether. The ethereal solution was extracted with sodium bicarbonate solution followed by a 5% solution of sodium hydroxide. The ether layer was washed with water, dried over calcium chloride, and evaporated. The solid residue, on trituration with ethanol, afforded 0.32 g of 3-benzoyl-2,4,5-triphenylfuran (**1**), mp 170–173°. Recrystallization from ethanol resulted in pale yellow crystals (very light and fluffy), mp 175–176°. The infrared spectrum showed a band at 6.05 μ (carbonyl) and a characteristic absorption at 11.15 μ which was used for the qualitative identification of **1** in reaction mixtures. The nmr spectrum exhibited multiplets at δ 7.5–7.8 and 6.9–7.4 in a ratio of 2:18.

*Anal.* Calcd for $C_{29}H_{20}O_2$: C, 87.00; H, 5.00; mol wt, 400. Found: C, 86.94; H, 5.11; mol wt, 385.

The mother liquor from the ethanol trituration was evaporated, dissolved in 10 ml of benzene, and placed on a column containing 70 g of alumina (Alcoa, F-20). The column was developed with 600 ml of petroleum ether (bp 30–60°). Elution with petroleum ether–ethyl ether (90:10) resulted in an additional 0.13 g of **1** followed by 0.10 g of an oil which, on recrystallization from ethanol, yielded benzil, mp 93–94°. An unidentified oil, 0.18 g, was eluted with petroleum ether–ethyl ether (80:20 and 70:30). Elution with petroleum ether–ethyl ether (50:50) resulted in the isolation of 0.24 g of *cis*-α,β-dibenzoylstyrene (**2**), mp 128–129° (from ethanol), lit.[20] mp 129°. Mixture melting point and infrared spectra were used for identification.

*Anal.* Calcd for $C_{22}H_{16}O_2$: C, 84.62; H, 5.13. Found: C, 84.56; H, 5.30.

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[8] H. Kwart and M. Baevsky, *J. Amer. Chem. Soc.*, **80**, 580 (1958).

[9] P. G. Gassman, J. T. Lumb, and F. V. Zalar, *ibid.*, **89**, 946 (1967).

[10] P. Yates and G. H. Stout, *ibid.*, **76**, 5110 (1954).

[11] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 123.

[12] C.-K. Dien and R. E. Lutz, *J. Org. Chem.*, **22**, 1355 (1957).

[13] R. C. Elderfield and T. N. Dodd, Jr., in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p 131, and references cited therein.

[14] H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

[15] The phenyl group has been shown to exert a stabilizing influence in determining the direction of enolization.[14]

[16] Reference 13, p 127.

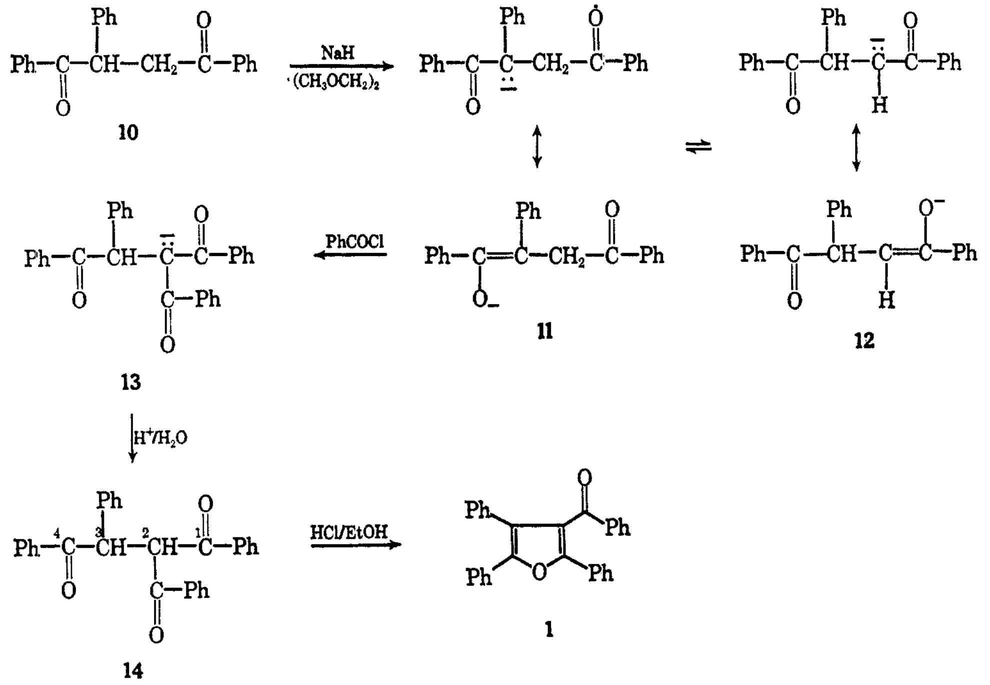
[17] Melting points are uncorrected. Elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined using the Nujol mull technique. The nmr spectra were determined in deuterated chloroform at 100 Mc using tetramethylsilane as an internal standard.

[18] N. Kornblum and A. P. Lurie, *J. Amer. Chem. Soc.*, **81**, 2705 (1959).

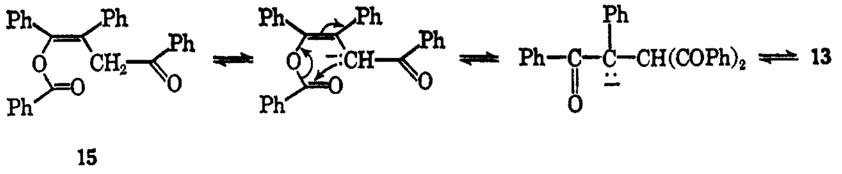
[19] A. Smith, *J. Chem. Soc.*, **57**, 643 (1890).

[20] F. R. Japp and F. Klingeman, *ibid.*, **57**, 673 (1890).

SCHEME II



SCHEME III



Finally, elution of the column with methanol produced a trace of red-brown oil that was not further characterized.

The sodium bicarbonate extract of the reaction mixture was acidified and extracted with ether. The ether layer was washed with water, dried with calcium chloride, and evaporated. Sublimation of the residue yeilded 0.39 g of benzoic acid, mp 119–121°, and a residue (0.30 g) of benzilic acid, mp 145–147° (from hexane–chloroform). Mixture melting point with an authentic sample in each case showed no depression.

From a reaction between phenoxide ion and benzil in DMSO at 90° for 24 hr, very low yields of products were obtained while large quantities of starting material were recovered.

From an experiment in which a solution of benzil in DMSO was heated for 48 hr at 100° in the absence of phenoxide ion, starting material was recovered in quantitative yield.

**Benzil and Methylsulfinyl Carbanion in Dimethyl Sulfoxide.**—Methylsulfinyl carbanion was generated by treating 0.45 g (0.01 mol) of sodium hydride, 56% by weight in mineral oil, with 60 ml of anhydrous dimethyl sulfoxide using the method of Corey and Chaykovsky.[4] The resulting solution was transferred, under nitrogen, to a dropping funnel *via* a connecting tube and added dropwise to a stirred solution of benzil (2.10 g, 0.01 mol) in 50 ml of dimethyl sulfoxide. The temperature was maintained at 20° throughout the addition (30 min). After stirring for an additional 1 hr, the solution was added to cracked ice, acidified, and extracted with ether. The ether layer was extracted with sodium bicarbonate solution and with 5% sodium hydroxide solution, washed with water, dried over calcium chloride, and evaporated. The oily residue failed to produce a solid on trituration with ethanol. The residue was then dissolved in 10 ml of benzene and placed on a column containing 80 g of alumina (Alcoa, F-20). The column was developed with 600 ml of petroleum ether (bp 30–60°). Elution with petroleum ether–ethyl ether (90:10) yielded 0.14 g of 3-benzoyl-2,4,5-triphenylfuran (1), mp 175–176° (from ethanol). Mixture melting point and infrared spectra showed the compound to be identical with the corresponding compound in the previous reaction. Elution with petroleum ether–ethyl ether (80:20 and 70:30) resulted in 0.16 g of an unidentified oil. Elution with petroleum ether ethyl ether (50:50) resulted in the isolation of 0.24 g of *cis-α,β* dibenzoylstyrene (2), mp 128–129° (from ethanol); the sample was identical (mixture melting point and infrared spectra) with the corresponding material in the previous reaction. Elution with methanol produced 0.35 g of an unidentified red oil.

The sodium bicarbonate extract of the reaction mixture was acidified and extracted with ether. The ether layer was washed with water, dried over calcium chloride, and evaporated. The solid residue, on sublimation, yielded 0.34 g of benzoic acid, mp 119–121° (from water) and 0.52 g of benzilic acid, mp 145–147° (from hexane–chloroform). A mixture melting point with an authentic sample in each case showed no depression.

**3-(α-Hydroxybenzyl)-2,4,5-triphenylfuran** (8).—A solution of 1 (0.26 g, 0.00066 mol) in 50 ml of ether was added dropwise to 0.25 g (0.006 mol) of lithium aluminum hydride in 150 ml of ether under an atmosphere of dry nitrogen. The reaction mixture was refluxed for 6 hr. Excess lithium aluminum hydride was destroyed with an ethereal solution of ethanol. Aqueous acid was added and the layers were separated. The ether layer was washed with water, dried over magnesium sulfate, and evaporated to yield 0.26 g (100%) of 8, mp 131–132° (from petroleum ether, bp 30–60°). The infrared spectrum showed weak hydroxyl absorption at 2.85 μ. The nmr spectrum revealed a 20 H multiplet at δ 6.8–7.8 (aromatic), a 1 H singlet at 5.94 (hydroxyl), and a 1 H singlet at 1.96 (methinyl).

*Anal.* Calcd for $C_{29}H_{22}O_2$: C, 86.57; H, 5.47. Found: C, 87.10; H, 5.67.

**2-Benzoyl-1,3,4-triphenyl-2-butene-1,4-dione** (9).—A solution of 1 (1.26 g, 0.0032 mol) and 0.63 g (0.0063 mol) of chromium trioxide in 200 ml of glacial acetic acid was heated at 80° for 40 min. The reaction mixture was added to ice and extracted with ether. The ether layer was washed with water and extracted with 5% sodium hydroxide solution until the extracts were alkaline. The ethereal solution was then washed with water, dried over calcium chloride, and evaporated. The pale yellow residue was triturated with hexane to yield 1.01 g (84% yield) of 9, mp 130–131° (from ethyl ether). The infrared spectrum showed absorption at 6.05 $\mu$ (carbonyl) and the nmr spectrum exhibited only aromatic proton absorption, a 6 H multiplet at $\delta$ 7.8–8.1 and a 14 H muliplet at 7.0–7.5.

*Anal.* Calcd for $C_{29}H_{20}O_3$: C, 83.65; H, 4.81; mol wt, 416. Found: C, 83.39; H, 4.81; mol wt, 420, 415.

**Reduction of 2-Benzoyl-1,3,5-triphenyl-2-butene-1,4-dione (9).**—A sample of 9 (0.43 g, 0.001 mol) and 0.41 g (0.006 mol) of zinc powder were refluxed in 50 ml of glacial acetic acid for 1 hr. The reaction mixture was added to water and extracted with ether. Acetic acid was removed by extraction with 5% sodium hydroxide solution until the extracts were alkaline. The ethereal solution was washed with water, dried over calcium chloride, and evaporated to yield a residue (0.34 g, 85% yield), mp 168–172°. On recrystallization from ethanol, pale yellow crystals (mp 175–176°) were obtained that were identified as 1 from mixture melting point and spectral data.

**2-Benzoyl-1,3,4-triphenylbutane-1,4-dione (14).**—Sodium hydride (1.2 g, 0.028 mol), 56% by weight in mineral oil, was washed three times with small quantities of petroleum to remove the mineral oil, and added, under nitrogen, to a flask containing 150 ml of anhydrous 1,2-dimethoxyethane. $\omega$-Desylacetophenone[19] (8.0 g, 0.026 mol) was added and the system was heated at 55° until the evolution of hydrogen gas had ceased (45 min). Vigorous evolution of gas occurred only near the end of the reaction. Benzoyl chloride, 1.75 g (0.01 mol), in 25 ml of 1,2-dimethoxyethane, was added dropwise to the dark-red solution. The reaction mixture was heated for 30 min and poured onto cracked ice. After acidification, the reaction mixture was extracted with ether. The ether solution was extracted with 5% sodium hydroxide solution until the extracts produced no more solid on acidification. The alkaline extracts were combined, acidified, and extracted with ether. The ethereal solution was washed with water, dried over calcium chloride, and evaporated to yield 3.07 g (58% yield) of 14, mp 164.5–165° (from ethyl ether). The infrared spectrum showed carbonyl absorption at 5.95 and 6.05 $\mu$. The nmr spectrum revealed 1 H (methinyl) doublets centered at $\delta$ 6.33 and 5.73 ($J \cong 5.1$ cps) and a 20 H (aromatic) multiplet at 6.8–8.0.

*Anal.* Calcd for $C_{29}H_{22}O_3$: C, 83.25; H, 5.26. Found: C, 83.22; H, 5.21.

The ether solution remaining after alkaline extraction was washed with water, dried over calcium chloride, and evaporated. Recrystallization of the residue gave 3.95 g (99% recovery) of $\omega$-desylacetophenone, mp 124–126° (lit.[19] mp 126°).

**Dehydration of 2-Benzoyl-1,3,4-triphenylbutane-1,4-dione (14).**—A sample of 14 (1.0 g, 0.0024 mol) and 6.0 ml of concentrated hydrochloric acid were refluxed in 200 ml of ethanol for 2.5 hr. After evaporation of solvent, the residue was triturated with ethanol to yield 0.83 g (87% yield) of pale yellow solid, mp 175–176° (from ethanol). On admixture with 1, no depression was observed in the melting point. The infrared spectra of the two samples were identical.

**Registry No.**—1, 15440-99-0; 2, 13249-75-7; 3, 13810-16-7; 4 (R = R′ = Ph), 134-81-6; 8, 15441-02-8; 9, 15441-03-9; 14, 15441-04-0; phenoxide ion, 3229-70-7.

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# Directive Effects in the Chlorination of Benzyl Chloromethyl Sulfides[1]

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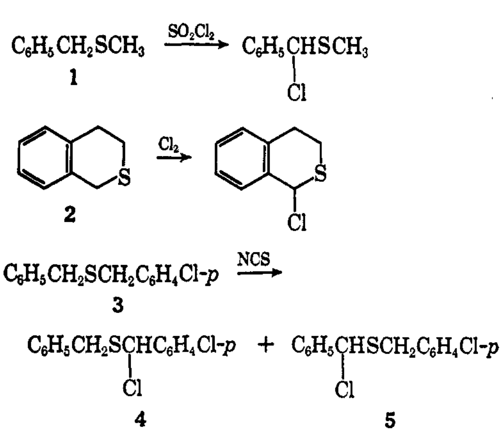
A series of benzyl chloromethyl sulfides has been prepared and treated sequentially with sulfuryl chloride and *m*-chloroperbenzoic acid. Separation and analysis of the resulting chloro sulfone mixtures have established the much greater directing influence of a chlorine atom when compared with a substituted phenyl group, except when the aromatic ring carries a *p*-nitro substituent.

When a sulfide possessing at least one hydrogen at an $\alpha$-carbon atom is treated with 1 equiv of chlorine,[4] sulfuryl chloride,[5,6] or N-chlorosuccinimide (NCS)[1,7] in an inert solvent, $\alpha$-chloro sulfides are produced. Addition of larger amounts of chlorinating agent generally results in more extensive halogenation.[6a,8] A major portion of the interest associated with this reaction derives from the unresolved nature of the detailed mechanism involved in the $\alpha$-chlorination process.[5,6,9]

Only a limited number of isolated reports have appeared concerning directive effects in the chlorination of sulfides. Thus, chlorination of benzyl alkyl sulfides such as 1[10] and 2[11] has been shown to lead only to $\alpha$-chlorobenzyl sulfides. Chlorinated isomers 4 and 5 are formed in the ratio of 1.6:1 when benzyl *p*-chlorobenzyl sulfide (3) is treated with an equimolar quantity of N-chlorosuccinimide in carbon tetrachloride solu-



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(2) Alfred P. Sloan Foundation Research Fellow, 1965–1967.

(3) Undergraduate research participant, 1965–1966.

(4) H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949), and pertinent references cited therein.

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(8) (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964); (b) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967); (c) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967); (d) L. S. Wittenbrook, unpublished observations.

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