formed. The latter was filtered and dried (2.38 g., 88%) then recrystallized from 95% ethanol as yellow needles, m.p. 194–196° (lit.,[12] m.p. 192–193°). It was shown to be identical to that prepared from A above by admixture melting point and comparison of infrared spectra.

C. **From 9-(1-Pyridinium)fluorenylide.**—Treatment of 1-(9-fluorenyl)pyridinium bromide with nitrosobenzene as described previously[2] gave yellow needles, m.p. 192–193°, identical to that prepared from A and B above.

Warming the nitrone (IVa) in ethanolic sulfuric acid for 1 hr. led to a disappearance of the yellow color. Quenching with water followed by extraction of the neutral and basic fragments with ether led to the recovery of the oily β-phenylhydroxylamine, λ_{max} 2.91 and 3.05 μ, and fluorenone, which crystallized from hexane as yellow needles, m.p. 81–83°, identical to an authentic sample.

A solution of 0.54 g. of the nitrone (IVa) and 0.34 g. of diethyl fumarate in 15 ml. of benzene was heated under reflux for 24 hr. Removal of the solvent followed by trituration with 95% ethanol gave 0.10 g. of unchanged nitrone, m.p. 194–196°. Dilution of the filtrate with water afforded 0.42 g. (58%) of crude 2-phenyl-3,3-diphenylene-4,5-dicarbethoxyisoxazolidine, m.p. 74–80°. Recrystallization from 80% ethanol gave colorless microcrystals, m.p. 76–78°, λ_{max} 5.65, 5.75, 13.25, 13.64, and 14.55μ.

Photolysis of the Nitrone (IVa).—A solution of 0.27 g. of the nitrone in 25 ml. of acetonitrile was irradiated in a quartz tube for 3 hr. using a Hanovia quartz lamp. No color change could be observed. Evaporation of the solvent and crystallization of the tan residue from 95% ethanol afforded unchanged nitrone, m.p. 193–194.5°.

Oxidation of Fluorenone Anil.—Ten milliliters of a solution of peracetic acid in methylene chloride prepared according to Emmons[5] directions, was added to a cold stirred solution of 1.25 g. of fluorenone anil[4,13] in 10 ml. of methylene chloride. After standing overnight at room temperature the solution was washed with water and dilute ammonia then dried. Removal of the solvent *in vacuo* left a brown solid which, upon trituration, afforded yellow crystals (0.90 g., 68%), m.p. 182–187°, which crystallized from 95% ethanol as fine yellow needles, m.p. 191–193°, identical to an authentic sample of the nitrone (IVa).

N-Phenylbenzophenone Ketoxime. A. From Diphenyldiazomethane.—To a red solution of 1.0 g. of diphenyldiazomethane[14] in 25 ml. of dry ether was added 0.55 g. of nitrosobenzene. Heat and nitrogen were evolved immediately and the nitrosobenzene slowly dissolved as a colorless precipitate began to form. After 15 min. the precipitate (0.96 g., 68%) was removed by filtration and dried. It crystallized from 60% ethanol as colorless fine plates, m.p. 223–225°, λ_{max} 6.10, 6.27, 6.65, 7.45, 12.79, and 14.50 μ; λ_{max}^{EtOH} 230 mμ (log ε 4.2) and 310 mμ (4.0).

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.56; H, 5.49; N, 5.35.

B. **From Dimethylsulfonium(diphenyl)methylide.**—Treating a slurry of dimethylbenzhydrylsulfonium bromide. in tetrahydrofuran with butyllithium resulted in a deep red solution of the sulfur ylid. Reaction of this solution with nitrosobenzene followed by quenching with water and extracting with ether gave the crude nitrone, m.p. 210–220°. Crystallization from 60% ethanol afforded colorless plates, m.p. 223–226°, identical to that prepared in A above.

Warming a solution of the nitrone (0.54 g.) in 20 ml. of 95% ethanol containing 6 ml. of 50% sulfuric acid for 1 hr. led to dissolution of the solid. The colorless solution was quenched with water then the neutral and basic components were separated and removed by ether extraction. The basic fraction (an oil) was identified as β-phenylhydroxylamine by its infrared spectrum. The neutral fraction was identified as benzophenone by its infrared spectrum and by conversion to its hydrazone, m.p. 97–100°, identical to an authentic sample.

N-Phenyl(2-nitro)fluorenone Ketoxime (IVb).—To a purple solution of 0.96 g. of dimethylsulfonium(2-nitro)fluorenylide (Ib) in 30 ml. of methylene chloride was added 0.30 g. of nitrosobenzene. The solution was heated under reflux for 1 hr. during which time the color changed to yellow. Evaporation of the solvent and trituration of the residue afforded 0.60 g. (76%) of crude nitrone (IVb), m.p. 217–220°. Crystallization from benzene afforded fine light orange needles, m.p. 224–225°, λ_{max} 6.60, 7.50, 13.00, 13.20, 13.75, and 14.43 μ.

(13) G. Reddelien, *Chem. Ber.*, **43**, 2479 (1910).

(14) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

Some New Reactions of Methylsulfinyl and Methylsulfonyl Carbanion[1]

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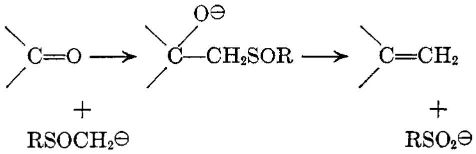
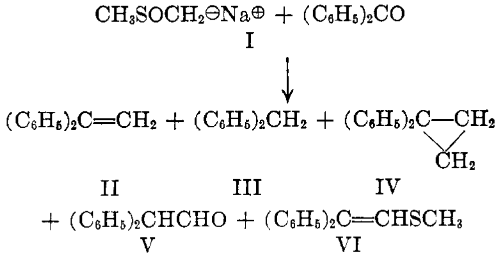
Recently we have described the generation and properties of the methylsulfinyl carbanion (I) and some applications of this extremely useful reagent in synthesis. In this and subsequent work, for example, solutions of the anion in dimethyl sulfoxide have been employed as the key feature of a very convenient and effective modification of the Wittig olefin synthesis.[2,3] It occurred to us that the reactivity of the methylsulfinyl carbanion and the extraordinary properties of dimethyl sulfoxide as a solvent might allow a Wittig type of olefin synthesis directly from the sulfinyl carbanion and certain carbonyl compounds:



(1)

Consequently an investigation was initiated of the reaction of such carbanions with benzophenone under conditions which are more drastic than those required to form the simple carbonyl addition product. The case of benzophenone seemed especially favorable since the carbonyl addition reaction is known to proceed in good yield[2] and is obviously not complicated by competing reactions such as enolate formation.[4]

In fact, the reaction of methylsulfinyl carbanion with benzophenone at 75–100° did afford distillable hydrocarbon products; a satisfactory conversion was obtained by rapid heating of the reactants from room temperature to 100° and maintenance at the higher temperature for several hours. Under these conditions a volatile product was obtained containing the hydro-



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(1) This work was supported by a grant (RG-6966) from the National Institutes of Health.

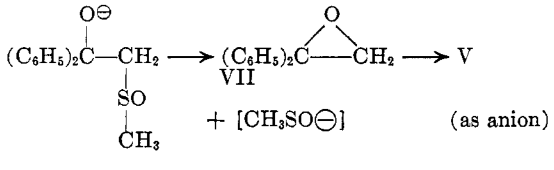
(2) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(3) A solution of the methylsulfinyl carbanion in dimethyl sulfoxide is prepared by heating sodium hydride with excess dry sulfoxide under nitrogen at 75° and then standardized by aqueous titration of an aliquot with standard acid. An equivalent amount of this anion is then added to a solution of the phosphonium salt in dry dimethyl sulfoxide (under nitrogen). After a few minutes the carbonyl compound is added with stirring and the reaction is allowed to proceed at room temperature for thirty minutes (or longer with hindered carbonyl compounds). Dilution with water, extraction, and appropriate isolation procedures then afford the Wittig product in very satisfactory yields (often much superior to those obtained under the customary conditions in ether or tetrahydrofuran).

(4) During this investigation we learned of similar studies in the laboratory of Prof. C. Walling, Columbia University. Our results are published simultaneously through mutual agreement.

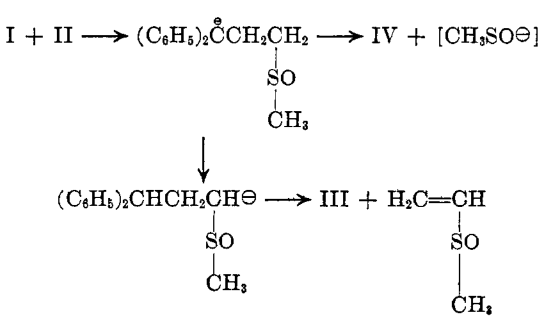
carbons 1,1-diphenylethylene, diphenylmethane, and 1,1-diphenylcyclopropane and, in addition, diphenylacetaldehyde and 1,1-diphenyl-2-methylthioethylene (VI). The nondistillable products were not investigated. The reaction of the carbanion I with 1,1-diphenylethylene under the same conditions was studied next and it was found that both diphenylmethane and 1,1-diphenylcyclopropane resulted.

It is evident that the process of olefin formation described by equation 1 does occur and also that other reaction pathways are available to the intermediate β-oxysulfoxide anion and to the olefinic product as well. The formation of diphenylacetaldehyde (V) probably occurs by base-catalyzed rearrangement of 1,1-diphenylethylene oxide (VII):



$$(C_6H_5)_2\overset{O^{\ominus}}{C}-\underset{\underset{CH_3}{SO}}{CH_2} \longrightarrow \underset{VII}{(C_6H_5)_2C\overset{O}{—}CH_2} \longrightarrow V \quad + [CH_3SO^{\ominus}] \quad \text{(as anion)}$$

The epoxide V may also be a precursor of the olefin II although this seems less likely than the pathway given by equation 1. It is possible that the cyclopropane IV and diphenylmethane result from the sequence:



$$I + II \longrightarrow (C_6H_5)_2\overset{\ominus}{C}CH_2\underset{\underset{CH_3}{SO}}{CH_2} \longrightarrow IV + [CH_3SO^{\ominus}]$$

$$\downarrow$$

$$(C_6H_5)_2CHCH_2\underset{\underset{CH_3}{SO}}{CH^{\ominus}} \longrightarrow III + H_2C{=}\underset{\underset{CH_3}{SO}}{CH}$$

Finally we have observed that the reaction of methylsulfonyl carbanion ($CH_3SO_2CH_2^-$) with benzophenone in dimethyl sulfoxide under similar conditions also gave the hydrocarbons II, III, and IV and diphenylacetaldehyde.

These new reactions, though not of obvious synthetic utility at the moment, raise a number of questions which warrant additional attention and which might lead to serviceable preparative procedures.

Experimental

Reaction of Methylsulfinyl Carbanion with Benzophenone.—A solution of methylsulfinyl carbanion was prepared by heating with stirring a mixture of 0.055 mole of powdered sodium hydride and 50 ml. of dry dimethyl sulfoxide (distilled from calcium hydride, b.p. 64°/4 mm.) under nitrogen at 75°, until the evolution of hydrogen ceased (about 40 min.). The pale yellow solution was cooled to about 15° in a water bath and a solution of 9.1 g. (0.05 mole) of benzophenone in 20 ml. of dimethyl sulfoxide was added by hypodermic syringe over a 3-min. period. After stirring for 5 min., the reaction mixture was placed in an oil bath, the temperature was rapidly raised to 100°, and stirring was continued at this temperature for 2 hr., during which time a deep red color developed. The cooled mixture was poured into 200 ml. of cold water, extracted with ether, and the extracts washed three times with water, dried over anhydrous sodium sulfate, and evaporated to yield 7.9 g. of an orange oil. Distillation of the oil under reduced pressure through a short-path Vigreux column yielded a first fraction of 4.5 g. of colorless liquid, b.p. 75–115°/0.2 mm., and a second fraction of 0.5 g. of pale yellow oil, b.p. 115–140°/0.2 mm. A dark red resinous material remained in the distilling flask.

Vapor phase chromatographic (v.p.c.) analysis of the first fraction on an F and M Model 300 gas chromatograph, using a 6-ft. column of 20% silicone rubber on Chromosorb, temperature 225°, input pressure 20 p.s.i., flow rate 34 ml. helium/min., showed the presence of four components, which were identified as being diphenylmethane, 1,1-diphenylethylene, 1,1-diphenylcyclopropane, and diphenylacetaldehyde. Retention times were 9 min. 10 sec., 11 min. 31 sec., 14 min. 30 sec., and 17 min. 46 sec., respectively, and the percentages were 30, 47, 3, and 20%, respectively. Identification was accomplished by collecting a sample of each compound from the v.p.c. column and comparing the infrared spectrum with that of an authentic sample. The infrared spectrum of authentic 1,1-diphenylcyclopropane was kindly provided by Dr. H. Simmons, Du Pont Co. The v.p.c. retention time of each authentic sample was also matched with the corresponding one in the mixture. The 2,4-dinitrophenylhydrazone (m.p. 152–153°) of the diphenylacetaldehyde from the mixture had an undepressed melting point when mixed with the same derivative from authentic diphenylacetaldehyde.

The following n.m.r. data (Varian A-60) were obtained for these products (τ values at 60 mc.). Diphenylacetaldehyde: (carbon tetrachloride) doublet centered at 0.02 τ (J 2.7 c.p.s.), 1 proton; singlet at 2.65 τ, 10 protons; doublet centered at 5.33 τ (J 2.7 c.p.s.), 1 proton. Diphenylethylene: (neat) multiplet at 2.75 τ center, 10 protons; singlet at 4.57 τ, 2 protons. Diphenylmethane: (neat) singlet at 2.86 τ, 10 protons; singlet at 6.22 τ, 2 protons. 1,1-Diphenylcyclopropane: (carbon tetrachloride) singlet at 2.87 τ, 10 protons; singlet at 8.78 τ, 2 protons.

The second distillate fraction was filtered through 20 g. of Merck alumina, using pentane as eluent, in order to remove the coloring matter and a trace of diphenylacetaldehyde. V.p.c. analysis of the colorless oil thus obtained, under the above conditions, showed a single component with retention time 37 min. 46 sec. A sample collected from the v.p.c. column crystallized when scratched with a glass rod. Recrystallization from 95% ethanol gave colorless needles, m.p. 72.5–73.5°. The structure assigned to the solid was 1,1-diphenyl-2-methylthioethylene on the basis of its n.m.r. spectrum and analysis. The n.m.r. spectrum had a methyl singlet at 7.7 τ, an olefinic proton singlet at 3.5 τ and sharp phenyl peaks at 2.63 and 2.75 τ. The proton integral ratio was 3:1:10, respectively.

Anal. Calcd. for $C_{15}H_{14}S$[5]: C, 79.61; H, 6.23; S, 14.17. Found: C, 79.46; H, 6.23; S, 14.22.

Reaction of Methylsulfonyl Carbanion with Benzophenone.—A solution of methylsulfonyl carbanion was prepared by heating with stirring a mixture of 0.055 mole of sodium hydride, 5.64 g. (0.06 mole) of dimethyl sulfone and 50 ml. of dry dimethyl sulfoxide under nitrogen, at 75°, until hydrogen evolution ceased (30 min.). The same procedure as described above was repeated, using 9.1 g. (0.05 mole) of benzophenone, etc. Evaporation of the ether gave 8.1 g. of orange oil. Upon distillation, distillate boiling over the range 70–112°/0.15 mm. was collected to yield 4.4 g. of colorless liquid. V.p.c. analysis under the same conditions as above showed that the liquid consisted of three major components which were identified as diphenylmethane (38%), 1,1-diphenylethylene (46%), and diphenylacetaldehyde (15%). A small amount of 1,1-diphenylcyclopropane (less than 1%) was also present.

Reaction of Methylsulfinyl Carbanion with 1,1-Diphenylethylene.—A solution of methylsulfinyl carbanion was prepared under nitrogen as described from 0.044 mole of sodium hydride and 50 ml. of dry dimethyl sulfoxide. Diphenylethylene (7.2 g., 0.04 mole) was added neat to the stirred solution at room temperature to produce a deep red color. The procedure described above was again repeated to yield, after evaporation of the ether, 9.4 g. of red oil. Upon distillation, distillate boiling over the range 60–95°/0.15 mm. was collected to yield 2.8 g. of pale yellow liquid. A dark red resinous material remained in the distilling flask. The distillate was filtered through 20 g. of Merck alumina, using pentane as eluent, to remove the small amount of coloring matter. The recovery of colorless liquid was almost quantitative. V.p.c. analysis of the liquid under the same conditions as above showed the presence of two components, identified as diphenylmethane (64%) and 1,1-diphenylcyclopropane (36%). Samples of each were collected and their infrared and n.m.r. spectra were found to be identical to those of authentic samples.

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(5) By C. Daesslé, Montreal.