Products of the Base-catalyzed Reaction of Benzophenone with Dimethyl Sulfoxide[1]

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Several recent studies have demonstrated that the basic properties of alkoxide ions are greatly enhanced in strongly polar nonhydroxylic solvents such as dimethyl sulfoxide.[2] Accordingly, it seemed plausible to investigate the base-catalyzed homogeneous hydrogenation of benzophenone[3] in this medium, to see if the reaction could be realized under milder conditions than are required in *t*-butyl alcohol (180°, 2000 lbs./in.^{2} hydrogen pressure). Initial experiments showed a fairly rapid disappearance of benzophenone, even at 80°, but with no consumption of hydrogen or production of benzhydrol. Further study showed that hydrogen was indeed not involved in the process, and heating benzophenone in dimethyl sulfoxide under nitrogen in the presence of either potassium *t*-butoxide or dimethyl sulfoxide anion (from dimethyl sulfoxide and sodium hydride) led to a variety of hydrocarbon products including 1,1-diphenylethylene, diphenylmethane, and 1,1-diphenylcyclopropane.[4] Yields of some typical experiments, determined by gas–liquid chromatographic analysis (g.l.c.) are shown in Table I. Several nonhydrocarbon products were also detected and are discussed below.

TABLE I

BASE-CATALYZED REACTIONS OF BENZOPHENONE AND DIMETHYL SULFOXIDE

(Equimolecular quantities of base and ketone at 70–80°)

		Yield (%)		
Time	Base	Ph_2CH_2	$Ph_2CH{=}CH_2$	Ph_2
10 min.	BuOK	1.5	6.8	trace
12 hr.[a]	BuOK	10	3.6	trace
2 min.	NaH	. . .	32.5	8.8
4.5 hr.	NaH	1.4	10.1	trace
14 hr.	NaH	4.8	17.3	. . .

[a] Base added slowly over first 10 hr.

Our results reflect the striking complexity of base-catalyzed reactions in dimethyl sulfoxide, and we proposed that our products can be rationalized by the following reaction scheme:

$$CH_3SOCH_3 + C_4H_9O^- \rightleftharpoons C_4H_9OH + CH_3SOCH_2^- \quad (1)$$

$$CH_3SOCH_2^- + Ph_2CO \rightleftharpoons CH_3SOCH_2CPh_2O^- \quad (2)$$

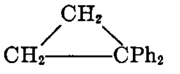
$$CH_3SOCH_2CPh_2O^- \longrightarrow CH_3SO_2^- + CH_2{=}CPh_2 \quad (3)$$

$$CH_3SOCH_2^- + CH_2{=}CPh_2 \rightleftharpoons CH_3SOCH_2CH_2\bar{C}Ph_2^- \quad (4)$$

$$CH_3SOCH_2CH_2\bar{C}Ph_2 \longrightarrow CH_3SO\bar{C}HCH_2CHPh_2 \quad (5)$$

$$CH_3SO\bar{C}HCH_2CHPh_2 \longrightarrow CH_3SOCH{=}CH_2 + \bar{C}HPh_2 \longrightarrow CH_2PH_2 \quad (6)$$

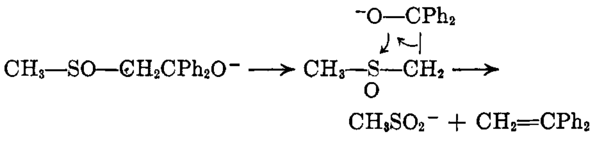
$$CH_3SOCH_2CH_2\bar{C}CPh_2 \longrightarrow CH_3SO^- +$$



(7)

Reaction 1 is expected, since the sulfoxide is a weak base, and 2 has recently been reported by Corey and Chaykovsky[5] and also by Russell.[6] However, we find that the equilibrium indicated is measurable and strongly temperature dependent. Thus, while quenching a reaction mixture of benzophenone and the dimethyl sulfoxide anion at 25° gives an 80% yield of 2-methylsulfinyl-1,1-diphenylethanol, $CH_3SOCH_2Ph_2OH$, quenching at 65° (or treating the alcohol with a mole of NaH at that temperature and quenching) gives 80% benzophenone.

Step 3 appears analogous to the Wittig reaction, and should probably be formulated as occurring *via* a cyclic transition state



$$CH_3{-}SO{-}CH_2CPh_2O^- \longrightarrow CH_3{-}\underset{O}{S}{-}CH_2 \ (\text{with } ^-O{-}CPh_2) \longrightarrow CH_3SO_2^- + CH_2{=}CPh_2$$

(8)

Sequence (4,5,6) amounts to carbanion addition to diphenylethylene, a prototropic shift, and a reverse Michael addition. Reaction 7 is essentially an internal S_N2 displacement analogous to those involved in several other cyclopropane ring syntheses. It requires the expulsion of a rather unusual anion, which presumably disproportionates or is otherwise consumed.

In addition to hydrocarbon products, the reaction scheme proposed also predicts the formation of several less volatile sulfur containing molecules. We have recovered a mixture of water soluble sulfur containing salts from our reaction mixtures, and g.l.c. analysis shows additional peaks of longer retention time from which sulfur containing products have been isolated, but have not been definitely identified.

Since 1,1-diphenylethylene is postulated as an intermediate in the formation of diphenylmethane and 1,1-diphenylcyclopropane, we have also examined its reaction with dimethyl sulfoxide anion. On heating the two together for fifteen hours in dimethyl sulfoxide at 80° the diphenylethylene is entirely consumed and diphenylmethane (17%) and 1,1-diphenylcyclopropane (6%) are both produced, consistent with our scheme. However, the major reaction product isolated on quenching and distillation is another hydrocarbon, 3,3-diphenylpropene. This interesting reaction, which appears to be general for a number of olefins, will be the subject of a subsequent communication.

Experimental

Equilibrium Addition of Dimethyl Sulfoxide to Benzophenone.—One mole of sodium hydride was dissolved in 400 ml. of freshly distilled dry dimethyl sulfoxide with warming. The mixture was cooled to 25°, an equivalent of benzophenone added in small portions, and the mixture allowed to stand for 30 min. On quenching with ice–water an 80% yield of 1,1-diphenyl-2-methylsulfinylethanol was isolated, m.p. after recrystallization from benzene, 150–150.5°.[5] When a similar experiment was carried out at 65°, 80% benzophenone was recovered and identified by mixed melting point and infrared spectra. Addition of the addi-

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[1] Support of this work by a grant from the National Science Foundation and a fellowship to L.B. by American Cyanamid Co. is gratefully appreciated.

[2] *Cf.* for example A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961).

[3] C. Walling and L. Bollyky, *ibid.*, **83**, 2968 (1961).

[4] While this work was in progress we learned of a similar finding by Professor E. J. Corey. Our studies are published simultaneously by mutual agreement.

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

[6] G. A. Russell, E. G. Janzen, H. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962).

tion product to dimethyl sulfoxide to which an equivalent of sodium hydride had been added, followed by heating at 65° for 24 hr. and quenching with water at that temperature also gave benzophenone, 80%.

Reaction of Benzophenone and Dimethyl Sulfoxide.—Equivalent quantities of potassium *t*-butoxide (or sodium hydride) and benzophenone were added to dimethyl sulfoxide in a dry box to give an approximately 0.5 *M* solution which was stirred under nitrogen at 70–80°. The reaction mixture (or an aliquot) was cooled and poured into water, and the resulting mixture extracted with carbon disulfide or methylene chloride, the extract dried, and solvent removed. The residue was examined by g.l.c., either directly or after a preliminary vacuum distillation, using an Aerograph Model A 350 instrument and silicone column programmed at 160–240°, 6°/min. with biphenyl as an internal standard. Products were identified as follows.

Diphenylmethane, 1,1-Diphenylethylene.—Products obtained by collection of g.l.c. peaks had retention times, infrared spectra and n.m.r. spectra identical with authentic samples.

1,1-Diphenylcyclopropane.—The product obtained by collection of the appropriate g.l.c. peak showed an infrared spectrum consistent with the indicated structure, and a two-peak n.m.r. spectra, $\tau = 2.95$ (aromatic) and $\tau = 8.76$ (methylene) relative areas 5:2.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.73%; H, 7.36%. Found: C, 92.46%; H, 7.36%.

Reaction of 1,1-Diphenylethylene with Dimethyl Sulfoxide.—The reaction was carried out in the same manner as those involving benzophenone. After heating for 18 hr. at 80°, the mixture was quenched with water, extracted, the solvent removed, and the residue vacuum distilled. G.l.c. analysis showed diphenylmethane (17%) and 1,1-diphenylcyclopropane (6%), identified as above, together with another major peak (77%) of longer retention time. This was collected and identified as 3,3-diphenylpropene, on the basis of infrared, ultraviolet, and n.m.r. spectra and analysis. Infrared and ultraviolet spectra were those expected for two phenyl groups and an unconjugated $—CH{=}CH_2$. The n.m.r. spectra showed three peaks (relative areas 10:1:3, respectively), 3.06, (singlet, aromatic H); 3.9 (broad multiplet $—CH{=}$); and 5.26 (unsymetric multiplet $Ph_2CH—$ plus $=CH_2$).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.73%, H, 7.36%. Found: C, 92.97%, H, 7.31%.

Synthesis and Absorption Spectra of 5-(Substituted) Amino-1,2,3-thiadiazoles[1]

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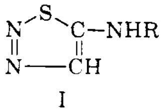
A series of 5-(substituted) amino-1,2,3-thiadiazoles (I) have been prepared by the reaction of diazomethane with organic isothiocyanates, first discovered by Pechmann[4,5] and later examined by Sheehan.[6] Its extension to diazo derivatives other than diazomethane has not been studied. A further limitation of the reaction is the inertness of diazomethane to methyl isothiocyanate. This paper reports on the synthesis of eight new compounds of type I (Table I) as well as the successful condensation of phenyldiazomethane with phenyl isothiocyanate to form 4-phenyl-5-anilino-1,2,3-thiadiazole (II). The infrared and ultraviolet absorption spectral data for these compounds have also been studied. (See p. 258 for Tables I, II, and III.)



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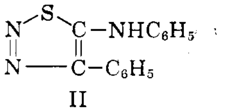

II

The ultraviolet absorption data (Table II) in I clearly show that the thiadiazole ring is aromatic in nature. Comparison of the spectra of I with those of 5-(substituted phenyl)amino-1,2,3,4-thiatriazoles[7] indicates that the thiadiazole ring is less electronegative than the thiatriazole ring. This is understandable since in the later heterocycle a nitrogen atom replaces a carbon of the thiadiazole system. It has been similarly found that the tetrazole ring is more electronegative than the triazole ring.[8]

The major characteristic infrared frequencies of the 5-(substituted phenyl)amino-1,2,3-thiadiazoles are listed in Table III with the appropriate assignments. The assignments were made following the recent review on the infrared spectra of heterocyclic systems by Katritsky.[9] It is not possible to assign frequencies to the N=N and C=C of the thiadiazole ring since it is a conjugate system.

Experimental[10]

The mode of synthesis is essentially that described by Sheehan.[5] The results are summarized in Table I. With two exceptions, noted in Table I, the product precipitates on refrigeration over periods from 1 to 3 days. Where precipitation of product did not occur the ether was removed and the residue recrystallized or precipitated by means of another solvent. The typical procedure is illustrated for one of the new compounds and for II.

5-Benzylamino-1,2,3-thiadiazole (I. R = $C_6H_5CH_2$).—To a solution of 15 g. (0.10 mole) of benzyl isothiocyanate was added 0.2 mole of a cold etheral solution of diazomethane.[11] The solution was refrigerated overnight and the ether evaporated to dryness. Yellow needles weighing 1.4 g. (7.3%) were obtained. The analytical sample was recrystallized from absolute ethanol yielding white needles, m.p. 93–95°.

5-(*p*-Nitrophenylamino)-1,2,3-thiadizole (I. R = 4-$O_2NC_6H_5$).—A tan powder results on the reaction of *p*-nitrophenyl isothiocyanate and diazomethane in cold ether. Many attempts were made in numerous solvents to obtain an analytically pure specimen. The evidence shows it to be the least stable type I and that it is obtained in its highest state of purity on initial precipitation from the reaction mixture.

4-Phenyl-5-anilino-1,2,3-thiadiazole (II).—To a solution of phenyl isothiocyanate (0.008 mole, 1.1 g.) in 10 ml. of dry ether was added 40 ml. (0.008 mole) of phenyldiazomethane in ether[12] and the mixture allowed to refrigerate overnight. The ether was removed by evaporation and the liquid residue was boiled in 50 ml. of dry ethanol. On cooling a yellow powder is precipitated (in some trials a portion of the ethanol must be removed before precipitation can be induced), yielding 1.1 g. (53%) which melted to a viscous liquid at 80–83°.

Anal. Calcd. for $C_{14}H_{11}N_3S$: N, 16.72; S, 12.67. Found N, 16.48; S, 13.18.

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(1) The authors gratefully acknowledge the support of these studies by the U. S. Army Research Office.

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(10) Analyses were done by Drs. G. W. Weiler and F. B. Strauss, Oxford, England. Melting points (Fisher block) are uncorrected. The infrared spectra were obtained with the Perkin-Elmer 21-C infrared spectrophotometer with sodium chloride optics. The ultraviolet spectra were obtained in purified dioxane (0.05 mg./ml.) on a Beckman DU spectrophotometer. The wave lengths throughout are expressed in millimicrons and the intensities of absorption in terms of the logarithm of the molar extinction coefficients.

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