absorptions at −24.1 ppm, tris(diethylamino)phosphine oxide, and −57.7 ppm, III. The integrated proton nmr spectrum showed these materials to be present in the ratio 2:3.

Reaction of *p*-Bromoanisole and Lithium Diethylamide in the Presence of Tris(dimethylamino)phosphine Oxide. Lithium diethylamide, 0.064 mole, was prepared as a suspension in 150 ml of benzene and 48 ml of hexane. Tris(dimethylamino)phosphine oxide (5.83 g, 0.0325 mole) was added with stirring and this was followed by the slow addition of 6.09 g (0.0325 mole) of *p*-bromoanisole. After 16 hr the mixture was concentrated and treated with 30 ml of water and 100 ml of ether. The aqueous phase was extracted with 80 ml more of ether. Concentration of the ether gave 9.29 g of liquid which was examined by glpc. Tris(dimethylamino)phosphine oxide and two other components, presumably *p*- and *m*-methoxy-N,N-diethylanilines, were present. Quantitative glpc indicated 2.27 g of oxide. The aqueous layer was concentrated and extracted with 75 ml of methylene chloride. Concentration afforded 6.48 g of impure tris(dimethylamino)phosphine oxide: 54% by glpc; 60% by nmr. The total recovery of oxide was *ca.* 100%.

A Sulfone α-Elimination Rearrangement and a Related Diazoethane Decomposition

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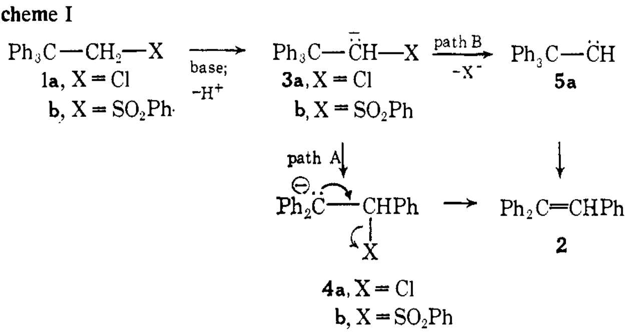
Abstract: The reaction of 2,2,2-triphenylethyl phenyl sulfone with phenyllithium and phenylsodium was found to give triphenylethylene. In the similar reaction of 2-anisyl-2,2-diphenylethyl phenyl sulfone, the statistically corrected anisyl migratory aptitude for this reaction was found to be 0.86. This contrasts with the 1.9 value found for the thermal rearrangement of 2-anisyl-2,2-diphenyldiazoethane in hydrocarbon solvents. The nature of the rearranging divalent species is considered.

The research described here concerns a novel α-elimination reaction of 2,2,2-triarylethyl phenyl sulfones and a parallel study of the reactions of an analogous diazo compound. Interest in the α-elimination reactions of sulfones was prompted by our finding[1] of the α-elimination rearrangement of 1-chloro-2,2,2-triphenylethane (**1a**) by treatment with amylsodium to give triphenylethylene (**2**). For this reaction two extreme mechanisms may be considered. In path A (note Scheme I), after proton removal by base, the carbanion **3a** rearranges, followed by loss of chloride to give the olefin. In path B, the same carbanion loses chloride to yield a carbene (**5a**), which then rearranges to afford the ethylene **2**. In between these extreme possibilities, mechanistic gradations are possible.

Scheme I



It seemed possible that 2,2,2-triphenylethyl phenyl sulfone (**1b**) would also produce triphenylethylene by α-elimination with base. The decomposition of 2,2,2-triphenyldiazoethane[2] (**6**) was of interest because of its relationship to the base-induced α-elimination reaction under consideration. Hellerman[2] found that this diazoethane (**6**) lost nitrogen under a variety of conditions, both thermal and acidic, to give triphenylethylene.

$$\underset{\mathbf{6}}{Ph_3C{-}\overset{-}{C}H{-}\overset{+}{N}{\equiv}N} \xrightarrow[-N_2]{\Delta} \underset{\mathbf{2}}{Ph_2C{=}CHPh}$$

Synthesis of Starting Materials. For the study of the sulfone α-elimination, both 2,2,2-triphenylethyl phenyl sulfone (**1b**) and a *p*-methoxy-substituted analog were needed. 2-Anisyl-2,2-diphenylethyl phenyl sulfone (**1c**) was selected for the latter. Both compounds were prepared by the oxidation of the corresponding sulfides (**9b** and **9c**) with peracetic acid. The sulfides, in turn, were obtained from the reaction of α-chlorothioanisole[3] with triphenylmethylsodium (**8b**) and anisyldiphenylmethylsodium (**8c**), respectively. These organosodium derivatives were conveniently prepared from the corresponding triarylchloromethanes by treatment with a 0.75% (liquid) sodium amalgam using high-speed stirring.[4] The synthetic scheme is outlined in Scheme II.

The synthesis of 2-anisyl-2,2-diphenyldiazoethane (**6c**) started with anisyldiphenylacetonitrile[5] (**10**). This was reduced with lithium aluminum hydride to give a 54% yield of the previously unknown 2-anisyl-2,2-diphenylethylamine (**11**), mp 92.0–93.5°. The latter was treated with ethyl chloroformate and triethylamine to afford ethyl N-(2-anisyl-2,2-diphenylethyl)carbamate (**12**), mp 74.5–76.0°, in 70% yield. Nitrosation of **12** with sodium nitrite in acetic anhydride–acetic acid using

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(1) H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957).

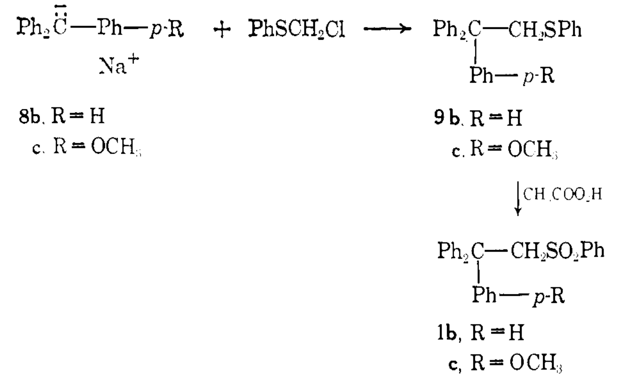
(2) L. Hellerman and R. L. Garner, *ibid.*, **57**, 139 (1935).

(3) F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955).

(4) See H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963), for the general method.

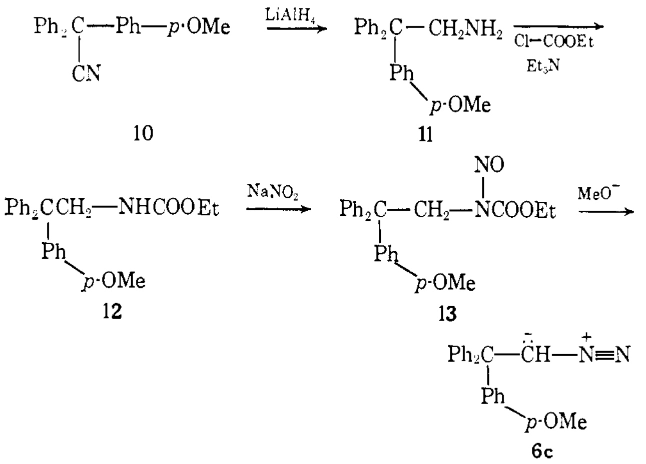
(5) I. Lifschitz and G. Girbes, *Ber.*, **61**, 1463 (1928).

Scheme II

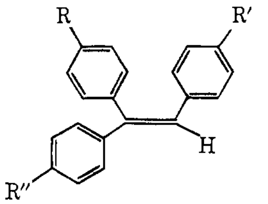


the general procedure of White[6] led to ethyl N-nitroso-N-(2-anisyl-2,2-diphenylethyl)carbamate (**13**). Treatment of the nitrosocarbamate **13** with sodium methoxide in ether–methanol led to the desired 2-anisyl-2,2-diphenyldiazoethane (**6c**). This synthetic sequence is given in Scheme III.

Scheme III



Synthesis of Anisyldiphenylethylenes and Analysis of Mixtures. In order to be able to evaluate the migratory aptitude of the anisyl group relative to phenyl in reactions of 2-anisyl-2,2-diphenylethyl phenyl sulfone (**1c**) and 2-anisyl-2,2-diphenyldiazoethane (**6c**), mixtures of the three possible anisyldiphenylethylenes needed to be analyzed.



2a, R = H; R' = OMe; R'' = H
b, R = H; R' = H; R'' = OMe
c, R = OMe; R' = H; R'' = H

The general method of Hauser[7] was used for the preparation of 1,1-diphenyl-2-(4-methoxyphenyl)ethylene. The other two isomers, *cis*- and *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene (**2b** and **2c**, respectively), were known.[8]

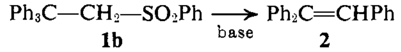
Mixtures of the three isomers were conveniently analyzed by integration of the methoxyl proton peaks in the nmr spectrum. Results of the analysis of three synthetic mixtures are given in Table I. The analysis of *cis*- plus *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene (**2b** and **2c**) relative to 1,1-diphenyl-2-(4-methoxyphenyl)ethylene (**2a**) proved more accurate than analysis of the *cis* and *trans* isomers themselves due to smaller nmr differences between the latter.

Table I. Nmr Analyses of Known Mixtures of the Anisyldiphenylethylenes

	Comp, %					
	Actual			Found[a]		
Mixture	2b	2c	2a	2b	2c	2a
1	9.1	35.8	55.1	13.1	32.9	54.0
2	29.0	34.7	36.3	28.1	33.8	38.1
3	38.6	0	61.4	39.3	0	60.7

[a] Probable uncertainty ±2% units.

α-Elimination of 2,2,2-Triphenylethyl Phenyl Sulfone. Treatment of 2,2,2-triphenylethyl phenyl sulfone with phenyllithium or phenylsodium[9] yielded triphenylethylene (**2**). The conversions fell in the range of 15–90% depending on reaction conditions; the results are summarized in Table II.



$$\underset{\mathbf{1b}}{Ph_3C{-}CH_2{-}SO_2Ph} \xrightarrow[\text{base}]{} \underset{\mathbf{2}}{Ph_2C{=}CHPh}$$

Table II. Products of the Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenyllithium and Phenylsodium

Base, equiv	Solvent	Temp, °C	Time, hr	Recovered 1b, %	Product 2, %
PhLi, 5.0	Ether	Reflux	18	78[a]	22[a]
PhLi, 1.2	Xylene	Reflux	24	43[a]	57[a]
PhLi, 2.0	Benzene	Reflux	6	65[a]	35[a]
PhLi, 2.0	THF	Reflux	4	65	24
PhLi, 3.0	THF	Reflux	4	45	32
PhLi, 1.1	THF	Reflux	4	63[a]	37[a]
PhLi, 1.1	THF	24	4	49	54
PhNa, 8.0	Benzene–THF	48	4	20[a]	80[a]
PhNa, 1.2	Benzene–THF	48	4	24	74
PhNa, 1.2	Benzene	48	4	27	68

[a] Percentages are normalized to 100%; total weight 105–114% of theory due to solvent.

When 2,2,2-triphenylethyl phenyl sulfone (**1b**) was treated with 2.0 equiv of 4-*t*-butylphenyllithium in tetrahydrofuran at room temperature for 1 hr, 73% of sulfone **1b** and 28% of triphenylethylene (**2**) were found. However no *t*-butylphenyl-containing products were obtained, confirming that the role of phenyllithium was only that of a base. This also provides evidence for the intramolecularity of the reaction.

After heating alone for 24 hr at xylene reflux temperature, 2,2,2-triphenylethyl phenyl sulfone (**1b**) could be recovered in 100% yield, showing that the α-elimination required base and was not thermal. Weaker bases than those listed in Table I were not effective. Thus sodamide in liquid ammonia–THF, sodium *t*-butoxide

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(6) E. H. White, *J. Am. Chem. Soc.*, 77, 6008 (1955).

(7) P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, 81, 2096 (1959).

(8) D. Y. Curtin, E. E. Harris, and E. K. Meislich, *ibid.*, 74, 2901 (1952).

(9) Note H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, 80, 3060 (1958).

Table III. Reaction of 2-Anisyl-2,2-diphenylethyl Phenyl Sulfone with Phenyllithium and Phenylsodium

Base	Time, hr	Recovered reactant **1c**,[a] %	Total ethylenes,[a] %	Ethylene distribution[b] **2b**	**2c**	**2a**	Anisyl migr apt[c]
PhLi	4	89	12	35	35	30	0.85 ± 0.08
PhLi	4	86	18	31	36	32	0.96 ± 0.09
PhNa	4	83	18	33	37	30	0.86 ± 0.08
PhNa	8	33	65	34	38	28	0.77 ± 0.07

[a] Absolute percentages. [b] Per cent of ethylenic product. [c] Statistically corrected.

Table IV. Product Distribution in the Rearrangement of 2-Anisyl-2,2-diphenyldiazoethane

Solvent	Temp, °C	Reagent[a]	Time, hr	Ethylene distribution,[b] % **2b**	**2c**	**2a**	Anisyl migr apt[c]
CCl_4	24	Cu	3.0	32	32	37	1.16 ± 0.11
CCl_4	24	Cu	5.0	31	31	39	1.26 ± 0.11
CCl_4	24	Cu	4.0	29	32	39	1.27 ± 0.11
Benzene	24	TsOH, 0.01 *M*	0.5	35	29	36	1.10 ± 0.10
Benzene	24	TsOH, 0.001 *M*	0.5	36	31	33	0.99 ± 0.10
Benzene	80	None	6.0	24	26	50	2.02 ± 0.17
Benzene	80	None	4.0	22	25	53	2.30 ± 0.18
Xylene	138	None	0.5	26	27	47	1.76 ± 0.15
Xylene	138	None	0.5	27	27	47	1.79 ± 0.15
Xylene	80	None	2.0	24	27	49	1.91 ± 0.16
Xylene	80	None	2.0	25	28	47	1.80 ± 0.15
THF	65	None	8.0	28	30	42	1.47 ± 0.12
THF	65	None	10.0	28	28	44	1.59 ± 0.13
THF	65	LiCl	20.0	20	21	59	2.91 ± 0.26
THF	65	LiCl	8.0	21	22	57	2.61 ± 0.23
THF	65	LiCl	8.0	22	23	54	2.39 ± 0.20
THF	65	$LiClO_4$	0.5	27	29	45	1.63 ± 0.14
THF	65	$LiClO_4$	1.5	27	28	45	1.68 ± 0.14
Benzene	80	DIB[d]	4.0	22	23	55	2.44 ± 0.21
Benzene	80	DIB[d]	4.0	24	23	53	2.23 ± 0.19

[a] 0.11 *M* LiCl and $LiClO_4$ used, 0.5 *M* DIB used. [b] Total ethylene yield nearly quantitative except in DIB runs. [c] Statistically corrected. [d] Diazabicyclooctane.

in *t*-butyl alcohol–dimethyl sulfoxide, and the dimethyl sulfoxide conjugate base in dimethyl sulfoxide[10] led to no reaction.

α-Elimination of 2-Anisyl-2,2-diphenylethyl Phenyl Sulfone. In order to cast light on the mechanism of the rearrangement reaction, the analog bearing one anisyl and two phenyl groups was studied. It was felt that the migratory aptitude of anisyl *vs.* phenyl would indicate the electronic requirements of the sulfone bearing carbon atom during rearrangement.

Treatment of 2-anisyl-2,2-diphenylethyl phenyl sulfone (**1c**) either with 1.2 equiv of phenyllithium in tetrahydrofuran at room temperature for 4 hr or with 1.2 equiv of phenylsodium in benzene at 48° for 4 hr (or 8 hr) produced mixtures of the isomeric anisyldiphenylethylenes. After chromatographic separation of reactant, the anisyldiphenylethylene fraction was analyzed by nmr as described above. These runs are summarized in Table III. It is noted that the product distribution is the same within experimental error for the various runs. The statistically corrected anisyl migratory aptitude is 0.87 ± 0.09.

Some control runs were carried out to make certain that the olefinic isomers were not equilibrating during reaction. Thus, it was found that 1,1-diphenyl-2-(4-methoxyphenyl)ethylene (**2a**) produced no isomeric anisyldiphenylethylenes when treated with excess phenylsodium.

2-Anisyl-2,2-diphenyldiazoethane Studies. It was felt to be of interest to attempt to generate the 2-anisyl-2,2-diphenylethylcarbene (**5b**) in order to observe its behavior, since this type of species (note Scheme I) is a potential intermediate in the sulfone α-elimination. Also, it seemed of general value to investigate the behavior of 2-anisyl-2,2-diphenyldiazoethane (**6c**) under varying conditions to see if the migratory aptitude would prove susceptible to change in the reaction conditions.

Conditions used were decomposition with copper in carbon tetrachloride, with *p*-toluenesulfonic acid in benzene, with lithium chloride in THF, with lithium perchlorate in THF, with 1,4-diazabicyclo[2.2.2]octane in benzene, and by thermal decomposition in benzene, xylene, and THF. These various reaction conditions led to the anisyldiphenylethylene isomers as the only observed products with essentially all of the material accounted for. The anisyl migratory aptitude varied from 1.05 in the case of reaction with *p*-toluenesulfonic acid in benzene to 2.63 for the decomposition with lithium chloride in THF. The results are gathered in Table IV.

Discussion and Conclusions

The purpose of the triaryldiazoethane studies was to provide background information on the behavior of a carbene species in order that the migratory aptitudes might be compared with the selectivity found in the sulfone α-elimination reaction. It seems wise to consider the triaryldiazoethane rearrangements first and then to proceed to consideration of the sulfone reaction.

Inspection of Table IV reveals that under all conditions the diazo compound **6c** rearranged with an excess of anisyl migration over statistical. The one possible exception to this statement is the *p*-toluenesulfonic acid catalyzed reaction where protonation seems likely to be

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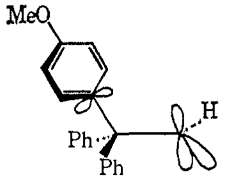
(10) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

the first step with subsequent loss of molecular nitrogen from the β,β,β-triarylethyldiazonium species thus generated. The nearly statistical product distribution seems likely to arise from generation of the triarylethyl cation and rearrangement with minimal selectivity.

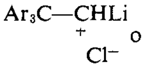
Carbene behavior seems most likely to be defined by the thermal runs in benzene, xylene, and THF. Here anisyl held competititive advantages of 2.15, 1.80, and 1.53, respectively. This fits a picture in which the anisyl group migrates with bonding to an electron-deficient orbital, as in **14**.[11,12]



14

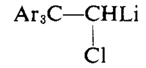
The lower selectivity observed in THF compared to the hydrocarbon solvents could be due to interaction of the solvent unshared pairs with the vacant p orbital. The failure of the tertiary amine, diazabicyclooctane, to exhibit a similar effect could derive merely from the lower concentration.[13]

The enhanced selectivity in the lithium chloride[14] runs probably derives from a carbenoid species in which lithium is bonded to carbon[15] (*i.e.*, **15**).



$$\mathrm{Ar_3C{-}\overset{+}{C}HLi\ \ Cl^-}$$

or



$$\mathrm{Ar_3C{-}CH(Cl)Li}$$

15a **15b**

Comparing now these carbene and carbenoid rearrangements with the results of the sulfone α-elimination, we note (Table III), in contrast, that in the α-elimination reactions anisyl migrates less readily than phenyl. Not only is it clear that the migratory behavior is different in the α-elimination reaction from that characteristic of a carbene, but also the disinclination of anisyl to migrate is suggestive of aryl migrating to an electron-rich center. Hence, of the two possibilities delineated in Scheme I, path A is the more reasonable.[16] As in the case of the carbanion rearrangement of *p*-tolyl[12] where *p*-methyl inhibits rearrangement, one would expect *p*-methoxyl to slow down aryl migration to an electron-rich center as required in this mechanism.

Experimental Section[17]

Preparation of 2,2,2-Triphenylethyl Phenyl Sulfide. A 1-l., round-bottomed flask was fitted with a condenser with a capillary outlet, a high-speed stirrer with nitrogen inlet, and a pressure-equalizing addition funnel. To 120 ml (1.6 kg, 8 moles) of mercury in the flask under nitrogen was added 12.0 g (0.52 g-atom) of cut sodium piece by piece. A solution of 72.4 g (0.260 mole) of triphenylchloromethane in 500 ml of dry ether was added to the amalgam. After 16 min of high-speed stirring, a red color suddenly appeared. Stirring was continued 1.5 hr. The mixture was then cooled to below −50° with a Dry Ice–acetone bath. To the mixture was added 39.6 g (0.250 mole) of α-chlorothioanisole.[3] Stirring was resumed for 8 hr during which time the temperature of the mixture was allowed to rise gradually to above 30°.

Water (*ca.* 200 ml) was then added to the mixture; the mixture was exhaustively ether extracted, and the extracts were washed with water, dried over calcium chloride, and concentrated *in vacuo* to yield 90 g of crude product. Recrystallization from ligroin (bp 90–100°) yielded 40 g (44%) of 2,2,2-triphenylethyl phenyl sulfide, mp 117–120°.

Anal. Calcd for $C_{26}H_{22}S$: C, 85.20; H, 6.05. Found: C, 85.22, 85.31; H, 6.25, 6.34.

Preparation of 2,2,2-Triphenylethyl Phenyl Sulfone. In 550 ml of glacial acetic acid was dissolved 11.00 g (0.0300 mole) of 2,2,2-triphenylethyl phenyl sulfide. The solution was heated to 45° and 19.8 ml (24 g, 0.12 mole) of 40% peracetic acid was added over 11 min. The solution was stirred at 40–45° for 5 hr. Water was added and the mixture benzene extracted. The extracts were washed, in turn, with water, saturated sodium hydroxide solution, saturated sodium thiosulfate solution, and water and then dried over sodium sulfate. The solution was concentrated *in vacuo* to leave 11.09 g (93%) of 2,2,2-triphenylethyl phenyl sulfone, mp 176–179°. Recrystallization from chloroform–ligroin (bp 90–100°) yielded 7.69 g, mp 177–180°.

Anal. Calcd for $C_{26}H_{22}O_2S$: C, 78.36; H, 5.56. Found: C, 77.96; H, 5.79.

Phenyllithium was prepared and the concentration of the phenyllithium solution was determined immediately before use by the method of Gilman.[18]

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenyllithium in Ether at Reflux. A 500-ml flask was fitted with stirrer, pressure-equalizing dropping funnel, nitrogen inlet, and condenser with capillary outlet. The flask was flushed with nitrogen during the reaction. Into the nitrogen-filled flask was put 15.1 ml (0.0125 mole) of 0.87 *N* ethereal phenyllithium solution. A solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 300 ml of dry ether was added with stirring. The reaction mixture turned yellow immediately. After 0.5 hr the reaction mixture was heated to reflux. Heating and stirring were continued for 18 hr.

To the reaction mixture was added 100 ml of saturated aqueous ammonium chloride. The water phase was ether extracted. The combined ether solutions were extracted with saturated sodium hydroxide solution, washed with water, and dried over sodium sulfate. Concentration left 922 mg of neutral material which was chromatographed on a 4.5 × 90 cm silica gel column slurry packed in hexane. Fractions (500 ml) were eluted as follows: 1–3, hexane; 4–5, 1% benzene in hexane; 6–7, 2% benzene in hexane; 8–9, 5% benzene in hexane; 10–11, 10% benzene in hexane; 12–13, 25% benzene in hexane; 14–15, 50% benzene in hexane; 16–17, benzene; 18–19, 1% chloroform in benzene; 20–21, 2% chloroform in benzene; 22–23, 5% chloroform in benzene; 24–25, 10% chloroform in benzene; 26–27, 25% chloroform in benzene; 28–29, 50% chloroform in benzene; 30–32, chloroform; 33–34, 1% methanol in chloroform; 35–36, 2% methanol in chloroform; 37–38, 5% methanol in chloroform; 39–40, 10% methanol in chloroform; and 41, 25% methanol in chloroform. Fractions 15 and 16 contained 159 mg (25%) which after seeding and recrystallization from hexane gave 23 mg of triphenylethylene, mp 68.5–70.5°. Fraction 40 contained 918 mg (92%) which after recrystallization from chloroform–ligroin (bp 90–100°) afforded 510 mg of unreacted sulfone, mp 177–180°. The infrared spectrum of fractions 15 and 16 agreed with that of triphenylethylene and the

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(11) While it may be the triplet species which is of lower energy, it seems likely that intersystem crossing to the singlet is sufficiently rapid to allow this to be available for rearrangement. Migration to a vacant p orbital of the singlet carbene should be preferred over migration to an odd electron containing orbital[12] of the triplet and the energy required to obtain the singlet may be more than regained. Also, we note that in approaching product the odd electron spins must eventually pair and considerable energy is to be gained.

(12) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

(13) The low selectivity in the copper-catalyzed runs no doubt derives from a copper-bonded carbene being involved with selectivity different from that of a free carbene.

(14) The lithium perchlorate run is anomalous. While one might attempt to conclude the necessity of chloride from the lack of efficacy of lithium perchlorate, the lithium perchlorate run seemed to proceed unusually rapidly and some oxidative mode of catalysis not involving the carbene may be proceeding.

(15) (a) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, 31, 2759 (1966); G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964), and related papers; (b) W. T. Miller, Jr., and D. M. Whalen, *ibid.*, **86**, 2089 (1964); (c) G. Kobrich, K. Flory, and W. Drischel, *Angew. Chem.*, **76**, 536 (1964).

(16) The extreme two-step mechanism need not be obtained. The experimental results require only that departure of sulfinate be slower than aryl migration.

(17) All melting points were taken on a hot stage calibrated with compounds of known melting point.

(18) H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 286 (1954).

spectrum of fraction 40 agreed with that of 2,2,2-triphenylethyl phenyl sulfone.

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenyllithium in Xylene at Reflux. Using the equipment described above for the similar reaction in ether, 9.5 ml (6.0 mmoles) of 0.63 *N* ethereal phenyllithium solution was added to a solution of 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 300 ml of sodium-dried xylene. The solution immediately became dark yellow; it was heated at xylene reflux for 24 hr.

The same work-up as above yielded 1.769 g of material which was subjected to chromatography on a 4.5 × 85 cm silica gel column slurry packed in hexane. Fractions (500 ml) were eluted: 1, hexane; 2–3, 10% benzene in hexane; 4–5, 50% benzene in hexane; 6–7, benzene; 8–9, 25% chloroform in benzene; 10–11, chloroform; 12–13, 2% methanol in chloroform; 14–15, 10% methanol in chloroform; 16–17, 50% methanol in chloroform; and 18–19, methanol. Fractions 6 and 7 contained 843 mg (65%) of oil and fractions 17 and 18 contained 990 mg (49%) of crystalline material, which was recrystallized to afford 495 mg of recovered reactant sulfone, mp 178–181°. Recrystallization of fractions 6 and 7 yielded 273 mg, mp 68.5–70.5°. The infrared spectrum of the latter was identical with that of triphenylethylene and the elemental analysis was checked.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.77, 93.81; H, 6.04, 6.11.

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenyllithium in Benzene at Reflux. The general procedure was as above. To 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone dissolved in 300 ml of benzene was added 12.00 ml (6.0 mmoles) of 0.50 *N* ethereal phenyllithium solution. After 5 min a color test[19] for excess phenyllithium was negative and 3.0 ml (1.5 mmoles) of phenyllithium solution was added. Fourteen minutes after the start of the reaction the color test was repeated. It was negative and 5.0 ml (2.5 mmoles) of phenyllithium solution was added. A color test 21 min after the start of the reaction was positive. Total phenyllithium used was 0.0100 mole. Heating was started and the mixture was heated and stirred at benzene reflux for 6 hr.

Work-up as before yielded 2.150 g of material. Chromatography exactly as in the benzene run above yielded fractions 6–9 which contained 0.521 g (40%), mp 60–70°, and fractions 18 and 19 which contained 1.477 g (79%), mp 160–180°. Recrystallization yielded 218 mg of triphenylethylene, mp 67–69°, and 780 mg of recovered sulfone, mp 177–180°.

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenyllithium in Tetrahydrofuran at Reflux. Using the general procedure above, phenyllithium solution was added to a solution of 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 300 ml of tetrahydrofuran dried by distillation from lithium aluminum hydride. At the start 20.0 ml (7.8 mmoles) of 0.39 *N* phenyllithium solution was used. The reaction mixture became bright red and darkened with stirring. After 5 min a color test for organometallics was positive and heating at reflux was begun. After 20 min a second color test was negative and 5.0 ml (2.0 mmoles) of phenyllithium solution was added. Another 5.0 ml of phenyllithium was added 15 min later following another negative Gilman test. The total amount of phenyllithium used was 0.0117 mole. At 50 and 80 min from the start color tests were positive, but at 2.3 hr the test was negative. Stirring and heating were stopped after 4 hr at reflux.

Work-up as before yielded 2.328 g of neutral material which was chromatographed on a 4.5 × 85 cm silica gel column slurry packed in hexane. Fractions (500 ml) were eluted: 1, hexane; 2–3, 1% benzene in hexane; 4–5, 2% benzene in hexane; 6–7, 5% benzene in hexane; 8–9, 10% benzene in hexane; 10–11, 25% benzene in hexane; 12–13, 50% benzene in hexane; 14–15, benzene; 16–17, 1% chloroform in benzene; 18–19, 2% chloroform in benzene; 20–21, 5% chloroform in benzene; 22–23, 10% chloroform in benzene; 24–25, 25% chloroform in benzene; 26–27, 50% chloroform in benzene; 28–29, chloroform; 30–31, 1% methanol in chloroform; 32–33, 2% methanol in chloroform; 34–35, 5% methanol in chloroform; 36–37, 10% methanol in chloroform; 38–39, 25% methanol in chloroform; 40–41, 50% methanol in chloroform; 42–43, methanol; 44–45, 1% water in methanol; and 46–47, 2% water in methanol. Fractions 12–16 contained 230 mg (18%), which was recrystallized to yield 152 mg of triphenylethylene, mp 68–70°. Fractions 38–46 contained 1.678 g. After recrystallization from chloroform–ligroin (bp 90–100°), fraction 39 still melted over a 40° range and all material from fractions 38–46 was combined and rechromatographed on a 4.5 × 85 cm alumina column slurry packed in hexane. Fractions (500 ml) were eluted: 1, hexane; 2–3, 10% benzene in hexane; 4–5, benzene; 6–7, 5% chloroform in benzene; 8–9, 25% chloroform in benzene; 10–11, chloroform; 12–13, 1% methanol in chloroform; 14–15, 2% methanol in chloroform; 16–17, 5% methanol in chloroform; 18–19, 10% methanol in chloroform; 20–21, 25% methanol in chloroform; and 22, 50% methanol in chloroform. Fractions 13–15 contained 632 mg (31%) of reactant sulfone, mp 175–180°. Fraction 16 contained 68 mg and fraction 17, 521 mg (33%), mp 165–190°. Recrystallization from chloroform–ligroin (bp 90–100°) of fraction 17 gave 199 mg of a new sulfone, mp 199–201°. The infrared spectrum ($CHCl_3$) shows strong absorption characteristic of sulfones at 7.63 and 8.66 μ: ultraviolet spectrum, λ_{max} (95% ethanol) 263 mμ (ϵ 1182), 269 (1367), 276 (1189), inflection 257 (779); nmr ($CDCl_3$), τ 2.7 (m, 14.3 H), 5.74 (s, 2.0 H).

Anal. Calcd for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03; S, 10.01; mol wt, 320. Found: C, 75.24, 75.06; H, 5.06, 4.95; S, 10.23; mol wt (vapor pressure osmometer, $CHCl_3$), 311.

In a second run, 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone was treated with 8.7 ml (0.0100 mole) of 1.14 *N* phenyllithium solution. A Gilman color test made 1.1 hr after reflux had started was negative.

Work-up yielded 1.878 g of neutral material which was chromatographed on a 4.5 × 85 cm alumina column slurry packed in hexane. Fractions (500 ml) were eluted as follows: 1, hexane; 2–3, 5% benzene in hexane; 4–5, 25% benzene in hexane; 6–7, benzene; 8–9, 5% chloroform in benzene; 10–11, 25% chloroform in benzene; 12–13, chloroform; 14–17, 1% methanol in chloroform; 18–19, 2% methanol in chloroform; and 20–21, 5% methanol in chloroform. Fractions 5–8 contained 311 mg (24%), mp 52–68°, which yielded 198 mg of triphenylethylene, mp 67–69°, after recrystallization. Fraction 12 contained 60 mg, mp 163–174°; fraction 13, 204 mg, mp 174.5–177.5°; fraction 14, 447 mg, mp 176.5–179.0°; fraction 15, 315 mg, mp 172–175°; fraction 16, 168 mg, mp 172–175°; fraction 17, 65 mg; fraction 18, 148 mg; and fraction 19, 55 mg. A single recrystallization of each fraction from 12 to 15 gave uniform melting points at 178–180° corresponding to reactant sulfone, but recrystallization of fraction 16 lowered and widened the melting range. Fractions 16–19 were combined and rechromatographed on a 2 × 85 cm alumina column slurry packed in benzene. Fractions (125 ml) were eluted as follows: 1, benzene; 2–5, 50% chloroform in benzene; 6–9, chloroform; 10–11, 1% methanol in chloroform; and 12–13, 2% methanol in chloroform. Fractions 6–8 contained 177 mg of reactant sulfone, a total of 65% including material from the first column, and had mp 176–179° after recrystallization. Fractions 9 and 10 afforded 99 mg (6%) of the new sulfone, mp 197–200° after recrystallization.

In a third run 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone was treated with 19.5 ml (0.0150 mole) of 0.77 *N* phenyllithium solution. A Gilman test carried out 1 hr after the beginning of reflux was weak or negative.

Work-up yielded 2.0 g of very oily material which was chromatographed on a 4.5 × 85 cm alumina column slurry packed in hexane. Fractions (500 ml) were eluted as follows: 1, hexane; 2–3, 10% benzene in hexane; 4–5, benzene; 6–7, 10% chloroform in benzene; 8–11, chloroform; 12–15, 1% methanol in chloroform; and 16–18, 2% methanol in chloroform. Fractions 4–7 contained 403 mg (32%), mp 50–60°, which was recrystallized to yield 258 mg of triphenylethylene, mp 67–69°. Fractions 11–14 contained 899 mg, which after recrystallization gave 807 mg of reactant sulfone, mp 175–178°. Fraction 15 contained 94 mg, which was recrystallized to yield 51 mg of the new sulfone, mp 199–202°. Identity of compounds was confirmed by infrared spectroscopy.

In a fourth run, 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone was treated with 9.2 ml (5.5 mmoles) of 0.60 *N* phenyllithium solution. A Gilman test made 0.5 hr after the beginning of reflux was negative.

Work-up yielded 1.812 g of material which was chromatographed on a 4.5 × 85 cm alumina column. Fractions (500 ml) were eluted as follows: 1, hexane; 2–3, 5% benzene in hexane; 4–5, 25% benzene in hexane; 6–7, benzene; 8–9, 5% chloroform in benzene; 10–11, 25% chloroform in benzene; 12–15, chloroform; 16–19, 1% methanol in chloroform; 20–21, 2% methanol in chloroform; and 22, 5% methanol in chloroform. Fractions 6–8 contained 531 mg (41%), mp 50–67°, which after recrystallization gave 346 mg of triphenylethylene, mp 68–70°. Fractions 18–22 contained 1.381 g (69%) and recrystallization of each fraction of this gave 930

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(19) H. Gilman in "Organic Chemistry," Vol. 1, H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1938, p 413.

mg of recovered reactant sulfone, mp 177–180°. Combination of fractions 21 and 22 and rechromatography gave no evidence of any sulfone other than the starting material.

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenyllithium in Tetrahydrofuran at Room Temperature. Using the general procedure above, a solution of 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 300 ml of tetrahydrofuran was treated with 6.6 ml (5.5 mmoles) of 0.83 *N* phenyllithium solution with stirring for 4 hr at room temperature.

The usual work-up yielded 1.704 g of material which was chromatographed on a 4.5 × 85 cm alumina column. Fractions (500 ml) were eluted: 1, hexane; 2–3, 5% benzene in hexane; 4–5, 25% benzene in hexane; 6–7, benzene; 8–9, 10% chloroform in benzene; 10–15, chloroform; 16–19, 1% methanol in chloroform; and 20–21, 2% methanol in chloroform. Fractions 6–9 contained 690 mg (54%), mp 63–69°, which was recrystallized to yield 349 mg of triphenylethylene, mp 68.0–69.5°. Fractions 18–20 contained 964 mg (48%) which gave 663 mg of reactant sulfone, mp 175–178° after recrystallization.

Preparation of 4-*t*-Butylbromobenzene. A 500-ml, round-bottomed flask was equipped with stirrer, condenser, and addition funnel. In this was placed 5.59 g (0.100 g-atom) of iron filings and 155 ml (134 g, 1.00 mole) of *t*-butylbenzene. Over a period of 3.2 hr 59 ml (134 g, 1.15 moles) of bromine was added dropwise with stirring. Slight heating was used at the beginning to start the reaction. Stirring was continued for 3.8 hr after addition of bromine was finished. By this time evolution of hydrogen bromide had stopped.

The mixture was washed with 10% sodium carbonate solution, then dried over sodium sulfate. The mixture was fractionally distilled twice to yield 133.8 g (63%) of 4-*t*-butylbromobenzene; bp 115–116° (25 mm); $n^{25}{}_{D}$ 1.5317 (lit.[20] bp 104–106° (14 mm)).

Preparation of 4-*t*-Butylphenyllithium. The procedure was the same as for the preparation of phenyllithium[18] above except that 133.8 g (0.628 mole) of 4-*t*-butylbromobenzene and 9.16 g (1.32 moles) of lithium wire were used.

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with 4-*t*-Butylphenyllithium. Using the general procedure given above for reactions with phenyllithium, a solution of 1.993 g (5.00 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 300 ml of dry tetrahydrofuran was treated with 13.7 ml (0.0100 mole) of 0.73 *N* 4-*t*-butylphenyllithium solution for 1 hr with stirring at room temperature. Color tests for organometallics made after 5, 15, and 25 min were all positive.

The usual work-up yielded 2.189 g of material which was chromatographed on a 4.5 × 85 cm alumina column. Fractions (500 ml) were eluted as follows: 1, hexane; 2–3, 5% benzene in hexane; 4–5, 10% benzene in hexane; 6–7, 25% benzene in hexane; 8–9, 50% benzene in hexane; 10–11, benzene; 12–13, 10% chloroform in benzene; 14–17, chloroform; 18–21, 1% methanol in chloroform; and 22–24, 2% methanol in chloroform. Fractions 3–5 contained 88 mg which was recrystallized to give 26 mg; mp 125–128° (lit.[20] 128–129° for 4,4′-di-*t*-butylbiphenyl); ultraviolet, λ_{min} (95% ethanol) 226.5 mμ (ϵ 5010) and λ_{max} 257 mμ (23,400) (lit.[21] λ_{min} 227 mμ (ϵ 6310) and λ_{max} 256 mμ (27,290) for 4,4′-dimethylbiphenyl).

Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.86; H, 9.78.

Fractions 7–10 contained 365 mg (28%), mp 62–68°, which was recrystallized to yield 105 mg of triphenylethylene, mp 68.0–69.5°. Fractions 18–23 contained 1.461 g (73%), mp 175–179°, which was recrystallized separately to yield 1.153 g of recovered sulfone, mp 177–179°. Identity of products was confirmed by infrared spectroscopy.

Reaction of 2,2,2-Triphenylethyl Phenyl Sulfone with Phenylsodium. A 300-ml Morton flask was fitted with a high-speed stirrer with nitrogen inlet and an adapter with addition funnel and condenser with capillary outlet. A dispersion was formed by stirring 0.92 g (0.040 mole) of sodium and 5 mg of stearic acid in 15 ml of *n*-octane at reflux. After cooling the dispersion to 45–50°, 2.25 g (0.020 mole) of chlorobenzene in 15 ml of dry benzene was added over a period of 1 hr. After stirring for an additional 1.5 hr a solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 35 ml of benzene was added. Stirring was continued for 2 hr after which 100 ml of dry tetrahydrofuran was added and the mixture stirred 2 hr more, still at 45–50°; 100 ml of saturated ammonium chloride solution was added.

The same work-up as used for the corresponding reaction with phenyllithium above yielded 1.005 g of material which was chromatographed on a 3 × 90 cm alumina column slurry packed in hexane. Fractions (250 ml) were eluted: 1–2, hexane; 3–4, 5% benzene in hexane; 5–6, 10% benzene in hexane; 7–8, 25% benzene in hexane; 9–16, benzene; 17–20, chloroform; 21–24, 1% methanol in chloroform; and 25–30, 2% methanol in chloroform. Fractions 7–12 contained 583 mg (90%) which gave 351 mg of triphenylethylene, mp 68–70° after recrystallization. Fractions 27 and 28 contained 227 mg (23%) which was recrystallized to yield 138 mg of reactant sulfone, mp 176–179°. Identities of products were confirmed by infrared spectroscopy.

In a second run the dispersion was made using 0.14 g (6 mmoles) of sodium, 5 mg of stearic acid, and 15 ml of *n*-octane. During a 13-min period 0.32 g (3.0 mmoles) of chlorobenzene in 5 ml of dry benzene was added. After stirring for 1 hr, 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone dissolved in 25 ml of benzene was added. After 2 hr, 120 ml of dry tetrahydrofuran was added and stirring was continued for an additional 2 hr.

Work-up as before yielded 0.787 g of material which was chromatographed on a 3 × 90 cm alumina column. Fractions (250 ml) were eluted as follows: 1–2, hexane; 3–4, 5% benzene in hexane; 5–6, 10% benzene in hexane; 7–8, 25% benzene in hexane; 9–14, 50% benzene in hexane; 15–16, benzene; 17–18, chloroform; 19–20, 1% methanol in chloroform; 21–24, 2% methanol in chloroform; and 25–27, 5% methanol in chloroform. Fractions 8–12 contained 473 mg (74%), mp 40–60°, which was recrystallized to yield 127 mg of triphenylethylene, mp 68.5–70.0°. Fractions 25 and 26 contained 236 mg (24%), mp 100–170°, which yielded 143 mg of recovered sulfone, mp 175–178° after recrystallization. Infrared spectroscopy was used to confirm the identity of the products.

In a third run the same procedure was used except that no tetrahydrofuran was added. A dispersion was made from 0.14 g (6 g-atoms) of sodium, 5 mg of stearic acid, and 15 ml of *n*-octane. A solution of 0.34 g (3.0 mmoles) of chlorobenzene in 5 ml of dry benzene was added over an 11-min period. After 1-hr stirring, 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone was added dissolved in 45 ml of dried benzene. The mixture was stirred an additional 4 hr.

The work-up yielded 0.795 g of material which was chromatographed on a 3 × 90 cm alumina column. Fractions (250 ml) were eluted as follows: 1–2, hexane; 3–4, 5% benzene in hexane; 5–12, 25% benzene in hexane; 13–14, benzene; 15–18, chloroform; 19–22, 1% methanol in chloroform; 23–26, 2% methanol in chloroform; and 25, 5% methanol in chloroform. Fractions 8–11 contained 435 mg (68%), mp 50–70°, which was recrystallized to yield 297 mg of triphenylethylene, mp 68.5–70.0°. Fractions 24–26 contained 268 mg (27%), mp 130–180°, which was recrystallized to give 185 mg of reactant sulfone, mp 175–178°. The identities of the products were confirmed by infrared spectroscopy.

Thermal Stability of 2,2,2-Triphenylethyl Phenyl Sulfone. Using the same equipment as for the reaction with phenyllithium, a solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 250 ml of dry xylene was heated at reflux under nitrogen with stirring for 24 hr. The usual work-up yielded 0.995 g (100%) of unchanged reactant as white crystals, mp 177–180°.

Stability of 2,2,2-Triphenylethyl Phenyl Sulfone in the Presence of Potassium *t*-Butoxide. A 500-ml, round-bottomed flask was fitted with a condenser with capillary outlet, nitrogen inlet, addition funnel, and magnetic stirrer. In the flask was placed 25 ml (20 g, 0.27 mole) of dry *t*-butyl alcohol and in the addition funnel a solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 125 ml of dimethyl sulfoxide. After 0.12 g (3 mmoles) of potassium had been dissolved in the *t*-butyl alcohol under nitrogen, the sulfone solution was added causing a slight orange color. The mixture was stirred for 2 hr at room temperature before adding 100 ml of saturated aqueous ammonium chloride solution. Work-up as in other reactions of 2,2,2-triphenylethyl phenyl sulfone above yielded 0.981 g (98%) of unchanged reactant sulfone, mp 176–179°.

In a second run a solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 100 ml of dimethyl sulfoxide was added to a solution of 0.78 g (0.020 g-atom) of potassium dissolved in 100 ml (79 g, 1.1 moles) of *t*-butyl alcohol. The mixture was stirred at 60° for 4.5 hr. Work-up yielded 0.982 g (99%), mp 176–179°, again indicating no reaction.

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(20) A. E. Tchitchibabin, S. Elgasine, and V. Lengold, *Bull. Soc. Chim. Belges*, 43, 238 (1928).

(21) R. A. Freidel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum No. 165.

Stability of 2,2,2-Triphenylethyl Phenyl Sulfone in the Presence of Sodium Methylsulfinyl Carbanion. The procedure was similar to that used in the reactions attempted with potassium *t*-butoxide above. A solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 100 ml of dimethyl sulfoxide was added to a solution[10] made by stirring 0.50 g (0.020 mole) of sodium hydride (52% mineral oil dispersion) in 100 ml (110 g, 1.4 moles) of dimethyl sulfoxide for 1 hr at 65–70° under nitrogen. The mixture was stirred for 3.5 hr at 65–70° and worked up in the same manner as for similar reactions above. The yield was 0.958 g (96%) of unchanged sulfone, mp 176–179°.

In a second run a solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 125 ml of dry tetrahydrofuran was added to a solution made from 0.50 g (0.020 mole) of sodium hydride and 25 ml (27 g, 0.35 mole) of dimethyl sulfoxide. After 4 hr of stirring at reflux, work-up yielded 1.042 g, mp 160–176°. An infrared spectrum of this material showed it to be essentially unchanged sulfone and gave no evidence of triphenylethylene.

Stability of 2,2,2-Triphenylethyl Phenyl Sulfone in the Presence of Sodamide. A 500-ml, round-bottomed flask was fitted with a stirrer, Dry Ice condenser with capillary outlet, and inlets for nitrogen and ammonia. In the flask was condensed 50 ml (40 g, 2 moles) of ammonia. To this under nitrogen was added 0.46 g (0.020 g-atom) of cut sodium and *ca.* 5 mg of ferric nitrate. After 7 hr of stirring the blue color had faded to the gray of sodamide. The ammonia inlet was replaced by an addition funnel and a solution of 0.996 g (2.50 mmoles) of 2,2,2-triphenylethyl phenyl sulfone in 150 ml of dry tetrahydrofuran was added. The mixture turned light green. The Dry Ice condenser was replaced by a water condenser and the mixture was allowed to warm gradually. Finally it was heated at reflux for 3 hr. Work-up as above yielded 0.974 g (98%) of unchanged reactant, mp 170–177°. An infrared spectrum showed no evidence of triphenylethylene.

Preparation of 2-Anisyl-2,2-diphenylethyl Phenyl Sulfide. The procedure was the same as for 2,2,2-triphenylethyl phenyl sulfide above. The amalgam was made with 50 ml (0.34 kg, 3.4 moles) of mercury and 4.62 g (0.200 g-atom) of sodium. Into the mixture was washed 30.9 g (0.100 mole) of anisyldiphenylchloromethane with 200 ml of dry ether. The red color formed in 17 min and stirring was continued 1.2 hr more before cooling. After addition of 15.9 g (0.100 mole) of phenyl chloromethyl sulfide,[3] stirring was continued for 6.7 hr. There was obtained 39 g of sticky solid which could not be crystallized. Chromatography of this material on a silica gel column 8 × 80 cm slurry packed in 10% ether in hexane and elution with the same solvent yielded 26 g (65%) of 2-anisyl-2,2-diphenylethyl phenyl sulfide, which remained noncrystalline.

Preparation of 2-Anisyl-2,2-diphenylethyl Phenyl Sulfone. The procedure used above for 2,2,2-triphenylethyl phenyl sulfone was followed. Addition over 20 min of 57 ml (0.35 mole) of 40% peracetic acid to the solution of 23.3 g (0.59 mole) of 2-anisyl-2,2-diphenylethyl phenyl sulfide in 1.1 l. of glacial acetic acid and stirring at 40–45° for 6 hr yielded 26.1 g of material. Two recrystallizations from ether yielded 9.4 g (37%) of 2-anisyl-2,2-diphenylethyl phenyl sulfone, mp 116–119°.

Anal. Calcd for $C_{27}H_{24}O_3S$: C, 75.67; H, 5.65. Found: C, 75.39; H, 5.66.

Preparation of 1,1-Diphenyl-2-(4-methoxyphenyl)ethylene. The method of Hauser[7] was used. In a 1-l., round-bottomed flask fitted with stirrer, Dry Ice condenser, and gas inlet and cooled in a Dry Ice–acetone bath was condensed 200 ml of ammonia. A crystal (*ca.* 5 mg) of ferric nitrate and 2.3 g (0.100 g-atom) of cut sodium were added and the gas inlet was replaced by an addition funnel. After 45 min the solution had turned gray and 16.8 ml (16.8 g, 0.100 mole) of diphenylmethane was added in 200 ml of dry ether. Then 12.1 ml (13.6 g, 0.100 mole) of anisaldehyde, treated with sodium carbonate and distilled, bp 149° (44 mm), in 200 ml of ether was added. The Dry Ice condenser was replaced by a water-cooled condenser. The ammonia was allowed to evaporate and 225 ml of 10% ammonium chloride solution was added. The ether phase was decanted, washed with 20% sulfuric acid and saturated sodium chloride solution, and dried over sodium sulfate. Evaporation of the ether left 28 g of crude material which was distilled from 2.0 g (0.017 mole) of sodium bisulfate. The yield was 17 g of crystalline material, bp about 170° (0.02 mm). Recrystallization from methanol left 13 g (45%) of 1,1-diphenyl-2-(4-methoxyphenyl)ethylene, mp 83.5–85.5°.

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.02; H, 6.36.

Preparation of *cis*- and *trans*-1,2-Diphenyl-1-(4-methoxyphenyl)ethylene. In a 500-ml, round-bottomed flask fitted with stirrer, addition funnel, and reflux condenser was placed 2.92 g (0.120 g-atom) of magnesium. To this was added 5 ml of dry ether and 3 ml of benzyl chloride. After the reaction had started, another 5 ml of ether was added followed over an 8-min period by a solution of 11 ml of benzyl chloride in 50 ml of ether, making a total of 13.8 ml (15.2 g, 0.120 mole). The mixture was heated at reflux for 45 min. After cooling, a solution of 21.2 g (0.100 mole) of 4-methoxybenzophenone in 50 ml of ether was added. After heating for 2 hr the mixture was poured onto 100 g of ice in 100 ml of 20% sulfuric acid. The mixture was shaken and the aqueous phase discarded. The ether phase was washed with 10% sulfuric acid and saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the ether yielded 31 g of material which was distilled from 2.0 g (0.017 mole) of sodium bisulfite. The final product was 25 g (87%) of yellow oil, bp about 190° (0.03 mm).

On a 4.5 × 85 cm alumina column slurry packed in hexane was placed 5.03 g of crude *cis–trans* mixture. Eluted with 10% benzene–hexane (500-ml fractions) were fractions 4, 0.13 g; 5, 0.03 g; 6, 0.06 g; 7, 0.02 g; 9, 0.04 g; 10, 0.24 g; 11, 0.41 g; 12, 0.52 g; 13, 0.42 g; 14, 0.40 g; 15, 0.33 g; 16, 0.28 g; 17, 0.30 g; 18, 0.31 g; 19, 0.26 g; 20, 0.22 g; 21, 0.17 g; 22, 0.12 g; 23, 0.08 g; 24, 0.06 g; 25, 0.04 g; 26, 0.03 g; and 27, 0.02 g. Fractions 4–7 were crystalline and 10–14 eventually crystallized. Combination of fractions 9–14 and recrystallization from methanol yielded 1.01 g of *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene, mp 90–92° (lit.[8] mp 90–91° for the *trans* isomer). In several additional chromatograms, some with exclusion of light to prevent any *cis–trans* photoisomerization, *cis* olefin was obtained invariably as an oil.

Analysis of Anisyldiphenylethylenes by Nmr. Since all attempts to separate physically *cis*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene, *trans*-1,2-diphenyl-2-(4-methoxyphenyl)ethylene, and 1,1-diphenyl-2-(4-methoxyphenyl)ethylene were unsuccessful, mixtures of these olefins were analyzed by means of nmr spectra in carbon tetrachloride (tetramethylsilane reference), using the areas of the methoxyl proton peaks. Besides the aromatic and vinyl absorption between τ 2.6 and 3.6, each of the isomers had a sharp separated methoxyl singlet. The 1,1-diphenyl-2-(4-methoxyphenyl)ethylene absorbs at 6.43. The *cis*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene absorbs 0.063 lower at 6.37 and the *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene another 0.024 lower at 6.34. Enlarged spectra of the area containing these three peaks were made on the 50-cycle sweep. At least three integrations were made sweeping upfield and the same number sweeping downfield. The integrations were measured and averaged to give the percentage of each component in the olefin mixture. Three test mixtures were run which were made up of weighed amounts of pure crystalline 1,1-diphenyl-2-(4-methoxyphenyl)ethylene and *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and chromatographically purified *cis*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene which an nmr spectrum showed to be free of any detectable amount of the *trans* isomer. Amounts of *cis*- and *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 1,1-diphenyl-2-(4-methoxyphenyl)ethylene, respectively, are as follows: 1, 5.6 mg, 9.1%; 22.0 mg, 35.8%; 33.9 mg, 55.1%; 2, 17.9 mg, 29.0%; 21.4 mg, 34.7%; 22.4 mg, 36.3%; 3, 24.1 mg, 38.6%; 0; 38.4 mg, 61.4%. Found by nmr integration: 1, 13.1, 32.9, and 54.0%; 2, 28.1, 33.8, and 38.1%; 3, 39.3, 0, and 60.7%.

Reaction of 2-Anisyl-2,2-diphenylethyl Phenyl Sulfone with Phenyllithium. Using the general procedure given above for the reaction of 2,2,2-triphenylethyl phenyl sulfone with phenyllithium, a solution of 1.071 g (2.50 mmoles) of 2-anisyl-2,2-diphenylethyl phenyl sulfone in 150 ml of dry tetrahydrofuran was treated with 4.2 ml (3.0 mmoles) of 0.72 *N* phenyllithium solution with stirring for 4 hr at room temperature.

Work-up as before yielded 1.089 g of material which was chromatographed on a 3 × 90 cm alumina column slurry packed in hexane. Fractions (250 ml) were eluted as follows: 1–2, hexane; 3–6, 10% benzene in hexane; 7–14, 50% benzene in hexane; 15–16, benzene; 17–20, chloroform; 21–24, 1% methanol in chloroform; 25–28, 2% methanol in chloroform; and 29–30, 5% methanol in chloroform. Fractions 8–13 contained 89 mg (12%) of anisyldiphenylethylenes. Fractions 22–26 afforded 960 mg (89%) of recovered sulfone. The identities of the products were checked by infrared spectroscopy. Nmr analysis of combined fractions 8–13 showed 29.8% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene and 34.7% *cis*- and 35.5% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene present.

In a second run 1.071 g (2.50 mmoles) of 2-anisyl-2,2-diphenylethyl phenyl sulfone was treated with 4.6 ml (3.0 mmoles) of 0.66

N phenyllithium solution. Work-up gave 1.074 g of material which was chromatographed exactly as in the first run above. Fractions 8–13 contained 128 mg (18%) of ethylenes and fractions 23–26 contained 925 mg (81%) of recovered sulfone. The identities of the products were confirmed by infrared spectroscopy. Nmr analysis of combined fractions 8–13 showed the presence of 32.4% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene and 31.2% *cis*- and 36.4% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene.

Reaction of 2-Anisyl-2,2-diphenylethyl Phenyl Sulfone with Phenylsodium. The procedure was the same as that used for the reaction of 2,2,2-triphenylethyl phenyl sulfone with phenylsodium above. The dispersion was made with 0.14 g (6.0 g-atoms) of sodium, 5 mg of stearic acid, and 15 ml of *n*-octane. A solution of 0.34 g (3.0 mmoles) of chlorobenzene in 5 ml of dry benzene was added over 15 min at 45–50°. Stirring at this temperature was continued for 1 hr before addition of a solution of 1.071 g (2.50 mmoles) of 2-anisyl-2,2-diphenylethyl phenyl sulfone in 45 ml of dry benzene and was continued for 4 hr afterward.

Work-up yielded 1.033 g of material which was chromatographed on alumina exactly as in the corresponding reaction with phenyllithium. Fractions 9–12 contained 133 mg (18%) of olefins and fractions 23–27 contained 895 mg (83%) of recovered sulfone. The identities of these materials were checked by infrared spectroscopy. Nmr analysis of combined fractions 9–12 showed the presence of 30.2% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene and 32.9% *cis*- and 36.9% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene.

In a second run the dispersion was made from 0.14 g (6.0 g-atoms) of sodium and 5 mg of stearic acid in 15 ml of *n*-octane. The solution of 0.34 g (3.0 mmoles) of chlorobenzene in 5 ml of dry benzene was added over an 18-min period and the reaction was allowed to continue for 8 hr after the addition of 1.071 g (2.50 mmoles) of 2-anisyl-2,2-diphenylethyl phenyl sulfone. Work-up yielded 0.862 g of material which was chromatographed exactly as above. Fractions 9–12 contained 463 mg (65%) of ethylenes and fractions 24–27 contained 349 mg (33%) of recovered sulfone. The product identities were checked by infrared spectroscopy. Nmr analysis of combined fractions 9–12 showed that there was present 27.9% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene and 33.8% *cis*- and 38.3% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene.

Stability of 1,1-Diphenyl-2-(4-methoxyphenyl)ethylene in the Presence of Phenylsodium. The same general procedure was used as for the reaction of 2-anisyl-2,2-diphenylethyl phenyl sulfone with phenylsodium above. A solution of 0.34 g (3.0 mmoles) of chlorobenzene in 5 ml of dry benzene was added over 17 min to a dispersion of 0.14 g (6.0 g-atoms) of sodium and 5 mg of stearic acid in 15 ml of *n*-octane. After stirring for 1 hr at 45–50°, a solution of 143 mg (0.50 mmole) of 1,1-diphenyl-2-(4-methoxyphenyl)ethylene in 40 ml of dry benzene was added and stirring at the same temperature was continued for 4 hr.

Work-up as in the reactions with sulfones yielded 191 mg of neutral material which was chromatographed on a 3 × 90 cm alumina column. Fractions were eluted as follows: 1–4, 5% benzene in hexane; 5–12, 10% benzene in hexane; 13–24, 25% benzene in hexane; 25–26, 50% benzene in hexane; 27–28, benzene; and 29–32, chloroform. The only major peak, fractions 16–24, contained 115 mg (80%). An nmr spectrum of combined fractions 16–24 showed that it contained 1,1-diphenyl-2-(4-methoxyphenyl)ethylene and none of the other anisyldiphenylethylenes.

Preparation of 2-Anisyl-2,2-diphenylethylamine. In a 3-l., round-bottomed flask fitted with a stirrer, nitrogen inlet, and condenser with capillary outlet was placed a suspension of 13.3 g (0.35 mole) of lithium aluminum hydride in 1.5 l. of dry ether under nitrogen. After addition of 104.8 g (0.350 mole) of anisyldiphenylacetonitrile,[5] the mixture was stirred for 24 hr. About 100 ml of water was then added dropwise to produce a claylike, crystalline precipitate. The ether was decanted and the precipitate extracted with additional ether. The ether solutions were washed with water and dried over sodium sulfate. Evaporation of the ether yielded 102 g of yellow crystalline material. Recrystallization from ether gave 56.9 g (54%) of 2-anisyl-2,2-diphenylethylamine, mp 92.0–93.5°.

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98. Found: C, 83.24; H, 6.95.

Preparation of Ethyl N-(2-Anisyl-2,2-diphenylethyl)carbamate. In a 3-l., round-bottomed flask fitted with a condenser with Drierite tube and a stirrer were combined 45.5 g (0.150 mole) of 2-anisyl-2,2-diphenylethylamine, 17.2 ml (19.5 g, 0.180 mole) of ethyl chloroformate, and 25.2 ml (18.2 g, 0.180 mole) of triethylamine in 1.5 l. of absolute ethanol. After 1-hr stirring at reflux, nearly all of the volatile material was distilled and the residue dissolved in 1 l. of ether and 0.5 l. of water. The ether phase was washed with saturated sodium chloride solution and dried over sodium sulfate. Evaporation of ether yielded 57.8 g of oily material. Recrystallization from 95% ethanol yielded 39.6 g (70%) of ethyl N-(2-anisyl-2,2-diphenylethyl) carbamate, mp 74–76°.

Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71. Found: C, 76.66; H, 6.72.

Preparation of Ethyl N-Nitroso-N-(2-anisyl-2,2-diphenylethyl)carbamate. A general method given by White[6] was used. To a solution of 15.02 g (0.0400 mole) of ethyl N-(2-anisyl-2,2-diphenylethyl)carbamate in 200 ml of acetic anhydride and 40 ml of glacial acetic acid in an ice bath cooled, round-bottomed flask with stirrer was added 69.0 g (1.00 mole) of sodium nitrite in small portions over 4 hr. Stirring was continued for 6 hr more at 0° and the mixture was allowed to warm gradually over 0.5 hr to about 15° with stirring. The mixture was poured onto 400 g of ice and ether extracted. The ether solution was washed, in turn, with water, 5% sodium carbonate solution, and saturated sodium chloride solution and dried over sodium sulfate. Removal of the ether *in vacuo* at 25° left 16.2 g of yellow-green oil. This unpurified ethyl N-nitroso-N-(2-anisyl-2,2-diphenylethyl)carbamate was used directly in the next preparation.

Preparation of 2-Anisyl-2,2-diphenyldiazoethane. To a solution of 16.2 g (0.040 mole) of crude ethyl N-nitroso-N-(2-anisyl-2,2-diphenylethyl)carbamate in 200 ml of dry ether in an ice–salt cooled, round-bottomed flask with a stirrer was added 9.45 g (0.080 mole) of sodium methoxide monomethanolate and 40 ml of methanol. The mixture was stirred with ice–salt cooling for 4 hr. The mixture was poured onto 400 g of ice, washed with cold saturated sodium chloride solution, and dried over anhydrous potassium carbonate. The ether was removed *in vacuo* at 25° to give 11.8 g of orange oil. Recrystallization from ether–isopentane yielded 6.87 g (55%) of 2-anisyl-2,2-diphenyldiazoethane, mp 60–65° with decomposition.

Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 79.93, 79.95; H, 5.93, 5.87; N, 9.45.

Reaction of 2-Anisyl-2,2-diphenyldiazoethane with Copper. To a solution of 60 mg (1.91 mmoles) of crude 2-anisyl-2,2-diphenyldiazoethane in 10 ml of carbon tetrachloride was added 200 mg of copper powder.[22] The mixture was stirred for 3 hr at room temperature and 0.5 hr at reflux. Filtration of the copper and removal *in vacuo* of the solvent left 540 mg of transparent oil. This was subjected to chromatography on a 3 × 90 cm alumina column slurry packed in hexane. Fractions (250 ml) were eluted as follows: 1–2, hexane; 3–6, 5% benzene in hexane; 7–14, 10% benzene in hexane; 15–26, 25% benzene in hexane; 27–30, chloroform. Fractions 16–25 contained a total of 436 mg (80%). Analysis of nmr showed that this was 31.7% *cis*- and 31.5% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 36.8% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 314 mg (1.00 mmole) of pure crystalline 2-anisyl-2,2-diphenyldiazoethane in 5 ml of carbon tetrachloride was treated with 100 mg of copper powder with stirring at room temperature for 5 hr. The product was 287 mg (100%) of clear oil, which nmr analysis showed to contain 30.6% *cis*- and 30.8% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 38.6% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a third run a solution of 314 mg (1.00 mmole) of crystalline 2-anisyl-2,2-diphenyldiazoethane in 10 ml of carbon tetrachloride was treated with 100 mg of copper powder with stirring for 4 hr at room temperature. The product was 288 mg (101%) of clear oil, shown by nmr integration to be 29.2% *cis*- and 32.0% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 38.8% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Reaction of 2-Anisyl-2,2-diphenyldiazoethane with *p*-Toluenesulfonic Acid. To a solution of 300 mg (0.95 mmole) of crude 2-anisyl-2,2-diphenyldiazoethane in 2 ml of benzene was added 17 mg (0.10 mmole) of *p*-toluenesulfonic acid in 8 ml of benzene. The mixture was stirred for 30 min at room temperature although it appeared to be completely decolorized after less than 5 min. It was washed with 10% sodium bicarbonate solution followed by water and dried over sodium sulfate. Evaporation of the benzene afforded 273 mg of clear oil which was chromatographed on a 3 × 90 cm alumina column slurry packed in hexane. Fractions (250 ml) were eluted: 1–2, hexane; 3–4, 5% benzene in hexane; 5–12,

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[22] Luco brand, No. 16 natural copper bronze, analyzing for 99.5+% copper: Leo Uhlfelder Co., New York, N. Y.

25% benzene in hexane; 13–20, 50% benzene in hexane; 21–28, benzene; and 29–36, chloroform. Fractions 15–21 contained 242 mg (89%), which was shown by nmr analysis to contain 35.3% *cis*- and 29.2% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 35.5% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 2 mg (0.01 mmole) of *p*-toluenesulfonic acid in 8 ml of benzene was added to a solution of 314 mg (1.00 mmole) of pure crystalline 2-anisyl-2,2-diphenyldiazoethane in 2 ml of benzene. After stirring for 30 min at room temperature, work-up as above yielded 278 mg (97%) of clear oil. Nmr analysis showed this material to be 35.9% *cis*- and 30.9% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 33.2% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Stability of 1,1-Diphenyl-2-(4-methoxyphenyl)ethylene in the Presence of *p*-Toluenesulfonic Acid. A solution of 2.0 mg (0.01 mmole) of *p*-toluenesulfonic acid in 8.0 ml of benzene was added to a solution of 286 mg (1.00 mmole) of 1,1-diphenyl-2-(4-methoxyphenyl)ethylene in 2 ml of benzene. After stirring for 30 min the solution was washed with 10% sodium bicarbonate solution and water and then dried over sodium sulfate. Evaporation of the benzene yielded 278 mg (97%) of the starting ethylene, mp 83–85°.

Thermal Rearrangement of 2-Anisyl-2,2-diphenyldiazoethane in Benzene at Reflux. In a round-bottomed flask with a condenser, a solution of 314 mg (1.00 mmole) of crystalline 2-anisyl-2,2-diphenyldiazoethane in 10 ml of benzene was heated at reflux for 6 hr. Removal of the benzene yielded 286 mg (100%) of transparent oil. Nmr analysis showed the presence of 24.0% *cis*- and 25.7% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 50.3% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene. To check on its purity this material was subjected to alumina chromatography carried out just as in the *p*-toluenesulfonic acid reaction above. Fractions 15–22 gave 283 mg (99%) of ethylenes.

In a second run a solution of 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of benzene was heated at reflux for 4 hr. The yield was 284 mg (99%) of transparent oil, which was shown by nmr analysis to contain 21.5% *cis*- and 25.1% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 53.4% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Thermal Rearrangement of 2-Anisyl-2,2-diphenyldiazoethane in Xylene at Reflux. The procedure was the same as for the thermal rearrangement above except that a gas buret was connected to the top of the condenser. A solution of 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of xylene was heated at reflux for 30 min. The volume of gas became stationary and, after cooling, corresponded to 22.5 ml corrected for temperature and atmospheric pressure. Removal of the xylene left 288 mg (101%) of transparent oil, which was shown by nmr analysis to be 25.9% *cis*- and 27.3% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 46.8% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of xylene was again heated at reflux for 30 min. The stationary gas volume corresponded to 22.8 ml (corrected). The yield was 286 mg (100%) of transparent oil. Nmr analysis showed the presence of 26.0% *cis*- and 26.8% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 47.2% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Thermal Rearrangement of 2-Anisyl-2,2-diphenyldiazoethane in Xylene at 80°. A solution of 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of xylene was heated in an oil bath at 80–82° for 2 hr. Removal of the xylene left 285 mg (100%) of transparent oil. Nmr analysis showed that 24.2% *cis*- and 26.8% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 48.9% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene were present.

In a second run 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane dissolved in 10 ml of xylene was again heated in an 80–82° bath for 2 hr. The stationary gas volume corresponded to 22.5 ml (corrected). The yield was 286 mg (100%) of transparent oil, which nmr analysis showed to contain 24.5% *cis*- and 28.1% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 47.4% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Thermal Rearrangement of 2-Anisyl-2,2-diphenyldiazoethane in Tetrahydrofuran at Reflux. Using the same procedure as in the other thermal rearrangements above, a solution of 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran was heated at reflux for 8 hr. The stationary gas volume corresponded to 22.0 ml (corrected). Evaporation of the solvent left 290 mg of dark oil. Chromatography on alumina exactly as in the thermal rearrangement run in benzene above yielded fractions 15–21 which contained 270 mg (94%) of ethylenes. This material was shown by nmr analysis to be 28.2% *cis*- and 29.5% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 32.4% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran was heated at reflux for 10 hr. The stationary gas volume corresponded to 22.8 ml (corrected) and the yield was 289 mg (101%) of oil. Nmr analysis showed the presence of 28.2% *cis*- and 27.5% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 44.3% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Reaction of 2-Anisyl-2,2-diphenyldiazoethane with Lithium Chloride. Using the same general procedure as for the thermal reactions above, a solution of 47 mg (1.1 mmoles) of lithium chloride and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran was heated at reflux for 20 hr. The solution was washed with water and dried over potassium carbonate. Evaporation of the solvent yielded 286 mg of oil. Chromatography of 200 mg of this material on alumina exactly as in the thermal rearrangements afforded fractions 16–21 which contained 190 mg (95%) of olefins. Nmr analysis showed that this contained 19.7% *cis*- and 21.0% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 59.3% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 47 mg (1.1 mmoles) of lithium chloride and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran was heated at reflux for 8 hr. After work-up 289 mg (101%) of oil remained. Nmr analysis indicated the presence of 21.3% *cis*- and 22.0% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 56.7% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a third run a solution of 47 mg (1.1 mmoles) of lithium chloride and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran again was heated at reflux for 8 hr. The stationary gas volume corresponded to 23.0 ml (corrected) and the yield was 288 mg (101%) of oil. Nmr analysis showed that there was 22.5% *cis*- and 23.1% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 54.4% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene present.

Reaction of 2-Anisyl-2,2-diphenyldiazoethane with Lithium Perchlorate. Using the same procedure as for the reaction with lithium chloride above, a solution of 117 mg (1.1 mmoles) of lithium perchlorate and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran was heated at reflux for 30 min. The stationary gas volume corresponded to 23.7 ml (corrected). The solution was washed with water and dried over sodium sulfate. Removal of the solvent afforded 277 mg (97%) of clear oil, which was shown by nmr analysis to contain 26.5% *cis*- and 28.6% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 44.9% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 117 mg (1.1 mmoles) of lithium perchlorate and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of tetrahydrofuran was heated at reflux for 90 min. The stationary gas volume corresponded to 24.8 ml (corrected) and the yield was 281 mg (98%) of transparent oil. Nmr analysis indicated that this was 26.7% *cis*- and 27.8% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 45.6% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

Reaction of 2-Anisyl-2,2-diphenyldiazoethane with 1,4-Diazabicyclo[2.2.0]octane. Using the same general procedure as for the thermal rearrangements above, a solution of 0.54 g (5.0 mmoles) of 1,4-diazabicyclo[2.2.2]octane and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of benzene was heated at reflux for 4 hr. The stationary gas volume corresponded to 22.4 ml (corrected). The solution was washed with 5% hydrochloric acid followed by water and dried over sodium sulfate. Evaporation of the benzene left 284 mg of dark oil. Chromatography on alumina as in other diazoethane reactions above gave fractions 11–17 which afforded 230 mg (80%) of olefins. Nmr analysis showed this material to contain 21.8% *cis*- and 23.2% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 55.0% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

In a second run a solution of 0.54 g (5.0 mmoles) of 1,4-diazabicyclo[2.2.2]octane and 314 mg (1.00 mmole) of 2-anisyl-2,2-diphenyldiazoethane in 10 ml of benzene was heated at reflux for 4 hr. The stationary gas volume corresponded to 23.1 ml (corrected). Work-up gave 286 mg which was subjected to alumina chromatography as before, giving fractions 13–19, which afforded 232 mg (81%) of olefins. Nmr analysis indicated the presence of 24.1% *cis*- and 23.2% *trans*-1,2-diphenyl-1-(4-methoxyphenyl)ethylene and 52.7% 1,1-diphenyl-2-(4-methoxyphenyl)ethylene.

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The Radiation Chemistry of Biochemical Disulfides. I. The Low-Dose X-Radiolysis of Cystine[1]

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Abstract: All ninhydrin-positive products resulting from exposure of dilute solutions of cystine in sulfuric acid to moderate doses (1,000–80,000 rads) of X-rays have been separated, identified, and determined quantitatively. Cysteic acid is the major product under all conditions. Yields vary with cystine concentration, dose rate, photon energy, and slightly with acidity, at low cystine concentrations. A mechanism for cysteic acid production is presented and a kinetic interpretation is given. These accommodate the concentration and dose-rate effects and are consistent with the photon energy effect and the amounts of hydrogen peroxide formed along with the cysteic acid.

Organic sulfur compounds are of considerable importance in radiation biochemistry. The activity of many biochemical intermediates (sulfhydryl enzymes, coenzyme A, lipoic acid, methionine, thiamin, etc.) depends upon the chemical integrity of sulfur groups and such groups are known to be very radiation sensitive. Disulfide groups of cystine units are essential to the secondary–tertiary structure of many enzymes and proteins. Radiolytic disturbance of such groups may well be more important in radiation inactivation of enzymes than direct destruction of active sites. Many sulfur compounds show some ability to protect living systems against radiation damage and lethality. It is noteworthy that, while cysteamine, cysteine, and cystamine are among the most effective of such compounds, cystine has no radiation-protective properties.

The radiation chemistry of cystine, cystine peptides, and cystamine has received some study, but little comprehensive quantitative determination of all the organic products has been reported. Mechanisms have been proposed for processes leading from initial radicals to final products but these have not been tested and most of them show little analogy with known reactions. Early work[2] with cystine using heavy radiation doses (10^5–10^6 r) gave simple inorganic compounds (SO_4^{2-}, S, NH_3, etc.) as the major products. More recent and sophisticated studies[3] with somewhat lower radiation doses (8×10^4 r) under conditions minimizing radiolysis of initial products gave mainly cysteic acid along with some cysteinesulfinic acid and cystine dioxide[4] and a little cysteine and alanine. Much radiobiological and radiation biochemical interpretation has been based on the above results.

This complete change in products as a result of a moderate change in radiation dose indicates the need for direct determination of products at typical radiobiological lethal doses (500–1000 r). We now report the quantitative determination of all the nonvolatile ninhydrin-positive products and hydrogen peroxide produced in dilute solutions of cystine upon X-irradiation with doses as low as 1000 rads.

Experimental Section

Radiation-chemical yields are rather small. At $G \sim 1$, deposition of 1000 rads produces about 10^{-9} mole of product per milliliter of solution. Yields of minor products are correspondingly smaller. It is very difficult to detect, identify, and assay all products over a wide range of independent variation of such parameters as disulfide concentration and excess acidity, dose, dose rate, etc. Accordingly, we have used two approaches. In the first, all ninhydrin-positive products were identified and assayed over a wide total-dose range while concentration, acidity, and dose rate were varied interdependently so as to permit such assay. In the second, a limited number of products was assayed over a wide range of independent variation of irradiation conditions.

Ninhydrin-Positive Products (Table I). Preliminary experiments showed that the expected[3] radiolysis products cysteic acid, cysteinesulfinic acid, cystine dioxide, alanine, and unchanged cystine[5] are well separated by electrophoresis on cellulose acetate[6] in formic acid (40 g/l., pH 2) during 12–16 min at 25 v/cm. Color development utilized a ninhydrin reagent similar to that of Moore and Stein[7] but more concentrated. The cellulose acetate strips were dried under a warm air stream on glass plates, saturated with the reagent, sandwiched *in vacuo* between glass plates, and heated for 4–5 min at 90–95°. Reproducible color development was authenticated with specimens of pure materials and relative color yields

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[2] P. Markakis and A. L. Tappel, *J. Am. Chem. Soc.*, **82**, 1613 (1960).

[3] D. W. Grant, S. N. Mason, and M. A. Link, *Nature*, **192**, 352 (1961).

[4] This compound, earlier commonly called cystine disulfoxide, almost certainly is a thiosulfonate (*cf.* J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951); T. C. Owen and R. R. Crenshaw, *Proc. Chem. Soc.*, 250 (1961). However, the structure is not completely proved and the name cystine dioxide used here is brief, self-explanatory, and at least not incorrect.

[5] Cysteine is oxidized to cystine during electrophoresis. However, cysteine yields were extremely small up to 100 μM cystine and were determined spectrophotometrically using a modified phosphotungstate reagent (*cf.* O. Folin and J. M. Looney, *J. Biol. Chem.*, **51**, 421 (1922); K. Shinohara, *ibid.*, **109**, 665 (1935).

[6] "Sepraphore III" cellulose acetate, Gelman Instrument Co., Ann Arbor, Mich.

[7] S. Moore and W. H. Stein, *J. Biol. Chem.*, **176**, 367 (1948).