hydrogen donor; much better, in fact, than are most of the RH compounds. By measuring the yields of methane and chloromethane from reaction of acetyl peroxide in mixtures of chloroform and carbon tetrachloride, we obtained these ratios of rate constants: $k_H/k_{Cl} = 160$; $k_H/k_{Cl}' = 53$; $k_{Cl}'/k_{Cl} = 3.2$, where k_H is the rate constant for abstraction of hydrogen from $CHCl_3$, k_{Cl}' is that for abstraction of chlorine from $CHCl_3$, and k_{Cl} is that for abstraction of chlorine from CCl_4. Thus, even fairly short chain lengths for reactions 6 and 7 could produce sufficient $CHCl_3$ to seriously affect the apparent k_H/k_{Cl} value obtained for RH. These conclusions are in accord with the findings of DeTar[15] who studied the hexyl radical using reaction with CCl_4 as the standard. He also found that for aliphatic solvents, $\cdot CCl_3$ reacts with RH to produce $CHCl_3$ and RCl in a reaction with an appreciable chain length.

The difficulty in using CCl_4 as the standard substrate for aliphatic but not for aromatic solvents can be rationalized by a consideration of the heats of reactions 6 and 7. For RH equal to ethane, the heats are -8 and $+2$ kcal/mol, for reactions 6 and 7, respectively; for toluene as RH, the heats are $+5$ and -11.[14] Thus, the chain sequence 6 and 7 is blocked for aromatic donors by the high enthalpy, and consequently high activation energy, of reaction 6. It would appear that this difficulty could be circumvented by using a standard substrate which has a higher bond strength than does CCl_4; unfortunately, this does not appear to be the case. Berezin and Dobish[9b] used the reaction of methyl radicals with tritiated heptane as their standard reaction. However, Table I of their publication[9b] shows that their values of the relative rate constant for hydrogen abstraction also are quite solvent dependent. At present, therefore, there is no satisfactory method for putting the relative rate constants for abstraction of hydrogen from aliphatic and aromatic solvents on the same scale.

This has one important consequence. The relative rate constants measured by Edwards and Mayo are widely quoted and are compared with data for the reaction of methyl radicals in the gas phase. It is often pointed out that the only solvent which appears to give a relative rate constant in solution which does not parallel the gas phase data is cyclohexane.[4d,7b,15,16] This solvent is, in fact, the only solvent studied by Edwards and Mayo which is saturated. It would appear, therefore, that the Edwards and Mayo value of k_H/k_{Cl} for cyclohexane is not reliable; in fact, we find that this value is solvent dependent.

Finally, it is interesting to consider a consequence of the simple mechanism indicated by eq 1 and 2. If eq 1 is the only important methane-producing reaction, and if all the *free* methyl radicals[12b] react either with the hydrogen donor RH or with CCl_4, then one should be able to calculate k_H/k_{Cl} as in eq 8 where M_0 has the same

$$k_H/k_{Cl} = \frac{CH_4/CO_2 - M_0}{[CH_4/CO_2]_{ps} - CH_4/CO_2} R_0 \qquad (8)$$

meaning as before and $[CH_4/CO_2]_{ps}$ is the relative yield of methane obtained in the pure hydrogen donor as solvent.[17] We find that eq 3 and 8 give essentially the same values of k_H/k_{Cl} for aromatic substrates but give very different values for aliphatic donors. This again indicates the solvent dependence of the relative k_H values in aliphatic solvents. Clearly, it is better to calculate k_H/k_{Cl} values using eq 3, but the agreement between eq 3 and 8 gives confidence that this system does yield a simple partition of free methyl radicals between reaction with RH or CCl_4 in aromatic solvents.

Registry No.—Methyl radical, 2229-07-4; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; *p*-phenoxytoluene, 1,706-12-3; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *p*-chlorotoluene, 106-43-4; *p*-bromotoluene, 106387; *m*-chlorotoluene, 108418.

Acknowledgment.—We wish to thank Dr. Donald F. Hunt, then at the Massachusetts Institute of Technology and now at the University of Virginia, for the mass spectrographic analyses.

(14) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
(15) D. F. DeTar and D. V. Wells, *J. Amer. Chem. Soc.*, **82**, 5839 (1960).
(16) Reference 6a, p 70.
(17) We have measured the value of CH_4/CO_2 in these pure solvents: toluene, 0.730; *p*-xylene, 0.682; *p*-bromotoluene, 0.495 (also see ref 8e). We have used the toluene value for toluene, ethylbenzene, and cumene, the xylene value for both xylenes, and the bromobenzene value for all other solvents in eq 8.

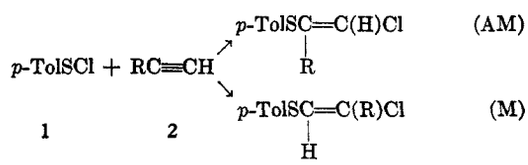
Additions of Sulfenyl Chlorides to Acetylenes. XII.[1a] Addition to *t*-Butylacetylene[1b]

V. CALÓ, G. SCORRANO, AND G. MODENA[1c]

Istituto di Chimica Organica, Università di Bari, Padova, Italy

Received September 3, 1968

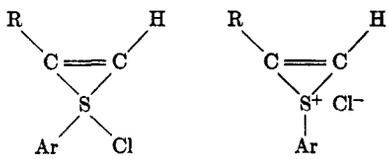
Both Markovnikov (M) and anti-Markovnikov (AM) orientations have been observed in the addition of *p*-toluensulfenyl chloride to acetylenes[2] depending on the nature of the acetylene and on the solvent (with



R = alkyl, 100% AM in all solvents;[3,4] with R = phenyl, 100% AM in ethyl acetate, 29% AM and 71% M in acetic acid). The effects are such that the phenyl substitution at the acetylenic carbons and good hydrogen bonding solvents[5] favor a shift from AM to M addition.

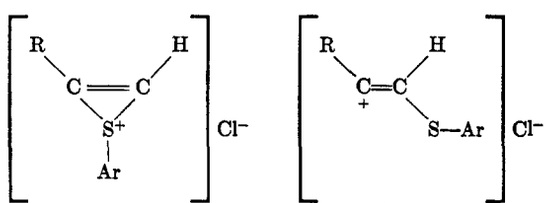
(1) (a) Part XI: L. Di Nunno and G. Scorrano, *Ric. Sci.*, **38**, 343 (1968). (b) This work has been supported by a grant from the Consiglio Nazionale delle Ricerche, Roma. (c) To whom all correspondence should be addressed at the Istituto di Chimica Organica, Via Marzolo, 1, Padova, Italy.
(2) V. Caló, G. Modena, and G. Scorrano, *J. Chem. Soc., C*, 1339 (1968).
(3) Small amounts of M-type adducts have been observed in the addition to alkylacetylenes of *o*-nitrobenzensulfenyl chloride[2] and dimethylaminosulfenyl chloride.[4]
(4) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **33**, 2111 (1968).
(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell Publishers, London, 1953; K. B. Wiberg "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, Chapter 3; A. J. Parker, *Quart. Rev.* (London), 163 (1962); R. Alexander and A. J. Parker, *J. Amer. Chem. Soc.*, **89**, 5549 (1967); M. A. P. Dankleff, R. Curci, J. O. Edwards, and H. Y. Pyun, *ibid.*, **90**, 3209 (1968).

These results have been explained[2] in terms of a common intermediate which leads *via* internal collapse to the AM products, or *via* dissociation into chloride and organic ions to the M products. Following such hypothesis, the intermediate complex formed on reaction of the sulfenyl chloride with the acetylene may be tentatively represented as either a covalent species **3a** or a tight ion pair **3b**. Other resonances or equilibrium structures resembling **3a** and **3b** could also be formulated. The intermediate complex would then collapse to the products by a transition state characterized by little charge separation, yielding the AM adducts.[6] Alternatively **3**, under the influence of a



3a **3b**

good solvent for Cl^- and the stabilizing effect of R on the cation, may dissociate into a loose ion pair or into free ions (represented as **4a** and **4b**)[7] before collapsing to the final product. This product should have the M structure as expected for a two step polar addition. In other words, the transition state leading to the M adducts would be characterized by a much larger degree of charge separation than the one leading to the AM adducts.

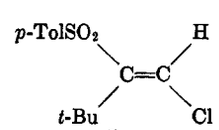
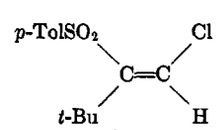
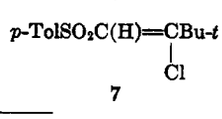


4a **4b**

We wish to report the results of the addition of **1** to *t*-butylacetylene in ethyl acetate and in acetic acid and to relate them to the above problem.

TABLE I

RELATIVE YIELDS OF ISOLATED OXIDATION PRODUCTS IN THE ADDITION OF *p*-TOLUENSULFENYL CHLORIDE TO *t*-BUTYLACETYLENE

	Ethyl acetate	Acetic acid
 **5**	96	88
 **6**	4	7
 **7**	0	5

(6) The collapse to AM adducts of **3a** or **3b** is not well understood. The formation of AM products is an experimental fact and might be due to an appropriate balance of short distance interactions of the groups present in the intermediate complex.

(7) It is not possible at this stage to say whether the cation is better represented by **4a**, and **4b**, or by an equilibrium among them.

The additions have been carried out as previously described.[2,8] After the usual work-up of the solution, the oily residue was distilled at reduced pressure (yield 90%) and oxidized with peroxybenzoic acid in chloroform. The sulfones were separated by column chromatography on silica gel. The oxidation as well as the chromatographic separation gave almost quantitative yields. The results are collected in Table I.[9] The structures of sulfones **5** and **6** have been assigned on the basis of the nmr spectra[2,10] ($CDCl_3$ solutions = CH; **5**, τ 2.24; **6**, τ 3.31) and from the known stereochemistry of reactions of this kind.[2,4,10-16] The stereochemistry of **7** has not yet been defined; by analogy with the results found in similar reactions[2,4,10-16] it should be the *trans* isomer ($ArSO_2$ to Cl).

As pointed out in a previous paper,[10] the presence of the *cis* isomer does not affect the discussion on orientation, since it is due to a successive *trans–cis* isomerization.

As the results above reported show, the preferred orientation of the addition to *t*-butylacetylene is once again the anti-Markovnikov one, but, at variance with the reaction of *n*-butyl- and ethylacetylene,[2,8] a small but significant amount of M adduct is formed in the present case.

In terms of the mechanism proposed for these reactions, it should mean that the *t*-butyl group is favoring the ionization of the intermediate complex **3** more than the other alkyl groups. This could be justified on the basis of the greater +I effect of *t*-butyl[17] in respect to *n*-alkyl. These results would indicate that the stabilizing effect of R on **4a** has to be preferentially inductive in character as observed in the formally similar case of the cyclopropenyl cations.[18] It could be argued, however, that the intervention of a hyperconjugative effect might have caused an opposite shift on the orientation; in our opinion a detailed analysis of the various factors involved in the system under investigation may not be straightforward at this stage.

Experimental Section[19]

Adducts of *t*-Butylacetylene to *p*-Toluenesulfenyl Chloride (1).—The reactions were run in ethyl acetate and acetic acid by adding dropwise to *t*-butylacetylene (0.11 mol in 200 ml of solvent) a solution of **1** (0.1 mol in 50 ml). The solutions were maintained at room temperature until the sulfenyl chloride color was essentially absent. The ethyl acetate solution was washed (water, dilute $NaHCO_3$, water), dried (Na_2SO_4), concentrated

(8) A. Dondoni, G. Modena, and G. Scorrano, *Boll. Sci. Fac. Chim. Ind. Bologna*, **22**, 26 (1964).

(9) When this work was completed we learned from G. Viehe (Union Carbide European Research Associates, Bruxelles, Belgium) that the reaction of concentrated benzene solutions of benzenesulfenyl chloride with *t*-butylacetylene yields a products mixture which composition parallels our results in acetic acid solvent (Halocarbon Chemistry Conference, Wayland, Mass., May 6–7, 1968, and personal communication).

(10) V. Caló, G. Modena, and G. Scorrano, *J. Chem. Soc., C*, 1339 (1968).

(11) F. Montanari, *Gazz. Chim. Ital.*, **86**, 735 (1956).

(12) W. E. Truce and M. M. Boudakian, *J. Amer. Chem. Soc.*, **78**, 2748 (1965).

(13) L. Maioli, G. Modena, and F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, **18**, 58 (1960).

(14) L. Benati, M. Tiecco, and A. Tundo, *ibid.*, **21**, 177 (1963).

(15) N. Kharasch and C. N. Yiannios, *J. Org. Chem.*, **29**, 1190 (1964).

(16) V. Caló and G. Scorrano, *Gazz. Chim. Ital.*, **98**, 545 (1968).

(17) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newmann, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956.

(18) A. W. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

(19) All melting points are uncorrected. The nmr spectra were measured on a Varian A-60 instrument and the shifts are from tetramethylsilane as an internal standard.

and distilled under reduced pressure (1 mm) giving 20.5 g (90%) of the sulfides. The oxidation by peroxybenzoic acid in chloroform gave, in almost quantitative yields, a mixture of ethylenic sulfones from which compounds **5** and **6** can be isolated by column chromatography on silica gel (eluents petroleum ether (bp 30–60°)–ethyl ether 2:1). The chromatographic separation was almost quantitative (over-all yields on sulfides >90%).

The acetic acid solution was poured in iced water and extracted with ether. The ethereal extract has been worked up as the ethyl acetate solution giving a mixture of the three sulfones **5**, **6** and **7** (see Table I).

Identification of Sulfones 5, 6, and 7.—The three sulfones, recrystallized from petroleum ether, gave satisfactory analyses for 1:1 adducts in the oxidized form [*Anal.* Calcd for $C_{13}H_{17}ClO_2S$: Cl, 12.99; S, 11.75. Found. (**5**, mp 84–85°): Cl, 13.00; S, 11.68. (**6**, mp 88–89°) Cl, 13.12; S, 11.71. (**7**, mp 83–84°) Cl, 13.15; S, 11.90]. Hydrogenation of **5** and **6** over 5% palladium–charcoal in ethanol (3.5 atm for 4 hr at room temperature) yielded the same (1,2,2-trimethyl)propyl *p*-tolyl sulfone (**8**). Hydrogenation of **7** yielded (3,3-dimethyl)butyl *p*-tolyl sulfone (**9**).

(1,2,2-Trimethyl)propyl *p*-tolyl sulfone (8) has been synthesized by oxidation of the corresponding sulfide **10** with peroxybenzoic acid in chloroform, mp 67–68° from methanol. *Anal.* Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39; S, 13.34. Found: C, 64.96; H, 8.39; S, 13.20.

(3,3-Dimethyl)butyl *p*-tolyl sulfone (9) was obtained by oxidation of the corresponding sulfide **11**, mp 97–98° from methanol. *Anal.* Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39; S, 13.34. Found: C, 64.82; H, 8.39; S, 13.28.

(1,2,2-Trimethyl)propyl *p*-tolyl sulfide (10) was obtained by reaction of *p*-bromobenzensulfonic acid (1,2,2-trimethyl)propyl ester[20] with sodium *p*-toluenethiolate in ethanol, bp 118–120° (1 mm). *Anal.* Calcd for $C_{13}H_{20}S$: C, 74.93; H, 9.68; S, 15.41. Found: C, 74.09; H, 9.44; S, 15.30.

(3,3-Dimethyl)butyl *p*-tolyl sulfide (11), obtained by reaction of 1-bromo-3,3-dimethylbutane with sodium *p*-toluenethiolate in ethanol, had bp 104–106° (1 mm). *Anal.* Calcd for $C_{13}H_{20}S$: C, 74.93; H, 9.68; S, 15.41. Found: C, 75.16; H, 9.59; S, 15.10.

Registry No.—*t*-Butylacetylene, 917-92-0; **5**, 19519-80-3; **6**, 19519-81-4; **7**, 19519-66-5; **8**, 19519-67-6; **9**, 19519-68-7; **10**, 19519-69-8; **11**, 19519-70-1.

Acknowledgments.—We thank Professor F. Taddei, Istituto di Chimica Organica e di Chimica Industriale, Bologna, for the nmr spectra.

(20) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 852 (1948).

Organosulfur Derivatives of Azulene. III. Di-1-azulyl Sulfide, Sulfoxide, and Sulfone[1a]

LANNY L. REPLOGLE, GERALD C. PETERS,[1b] AND JAMES R. MAYNARD

Department of Chemistry, San Jose State College, San Jose, California 95114

Received August 9, 1968

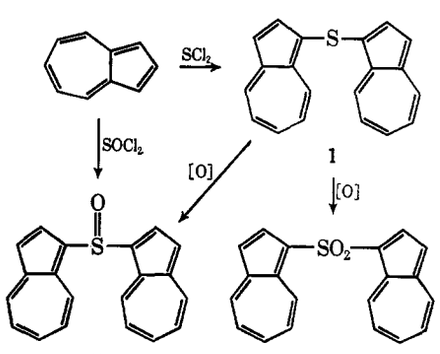
Earlier papers in this series have described the preparation and properties of some methyl and phenyl 1-azulyl sulfides[2] and the corresponding sulfoxides and sulfones.[3] This paper is concerned with the symmetrical derivatives di-1-azulyl sulfide (**1**), di-1-azulyl sulfoxide (**2**), and di-1-azulyl sulfone (**3**).

It is known that aromatics react with sulfur dichloride to form symmetrical diaryl sulfides[4] and with thionyl chloride to form symmetrical diaryl sulfoxides.[5] Azulenes react with benzenesulfenyl chloride to give phenyl 1-azulyl sulfides[2,6] and with methanesulfinyl and benzenesulfinyl chlorides to give methyl and phenyl 1-azulyl sulfoxides.[3] Also, it was reported[7] that the reaction of the sodium salt of 1-azulenesulfonic acid with thionyl chloride gave azulene-1-sulfonyl-3-sulfinyl dichloride. Therefore, it was expected that di-1-azulyl sulfide (**1**) and di-1-azulyl sulfoxide (**2**) should result from the reaction of azulene with sulfur dichloride and thionyl chloride, respectively.

Azulene reacted vigorously with sulfur dichloride in anhydrous ether at −78° to give an 18% yield of the blue, crystalline di-1-azulyl sulfide (**1**). The sulfide (**1**) was characterized by its elemental analysis, its nmr spectrum, which was characteristic of a 1-substituted azulene, and its visible spectrum with λ_{max} 598 mμ. Much unreacted azulene was recovered from this reaction as well as a considerable amount of polymeric green solid. Variations in reaction conditions such as different solvents (tetrahydrofuran, chloroform, or acetonitrile), different temperatures (−45 or −111°), or the inclusion of pyridine did not increase the yield of the sulfide (**1**).

A 21% yield of di-1-azulyl sulfoxide (**2**) was obtained from the reaction of azulene with thionyl chloride in acetonitrile at −45°. The sulfoxide (**2**), a purple, crystalline solid, had λ_{max} 557 mμ and a band at 9.75 μ (S=O) in its infrared (ir) spectrum. The sulfide (**1**) was isolated in very low yield from one of the reactions between azulene and thionyl chloride.[8] When the reaction was carried out at −70° in anhydrous ether, another product, a red solid which eluted before the sulfoxide (**2**), was isolated in low (*ca.* 4%) yield. This red solid was later identified as di-1-azulyl sulfone (**3**) (Scheme I). An attempt to form the sulfone (**3**)

SCHEME I



(1) (a) Supported in part by Grant GP-3885 from the National Science Foundation. (b) National Science Foundation Undergraduate Research Participant, 1967.

(2) L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, **30**, 2715 (1965).

(3) L. L. Replogle and J. R. Maynard, *ibid.*, **32**, 1909 (1967).

(4) A. Schöberl and A. Wagner, in "Houben-Weyl, Methoden der Organischen Chemie," Vol. 9, 4th ed, Georg Thieme Verlag, Stuttgart, Germany, 1955, p 216.

(5) H. H. Szmant, in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 158.

(6) K. Hafner, A. Stephan, and C. Bernhard, *Justus Liebigs Ann. Chem.*, **650**, 42 (1961).

(7) A. G. Anderson, Jr., D. J. Gale, R. N. McDonald, R. G. Anderson, and R. C. Rhodes, *J. Org. Chem.*, **29**, 1373 (1964).

(8) Diaryl sulfides can be formed in the reaction of phenols with thionyl chloride: A. Luttringhaus and K. Hauschild, *Chem. Ber.*, **72B**, 890 (1939).