also undergoes ring opening and reclosure, the actual structure may be distorted, with an elongated bond or considerable deviation from the geometry of a regular trigonal bipyramid. Therefore the excess energy of a compound with a five-membered ring in the idealized geometry shown below might be even greater than the activation energy for pseudorotation here observed.

We conclude then that the activation energy of 22 kcal/mol, determined from the nmr spectra of the adduct of dimethyl phenyl phosphite and benzylidene acetylacetone, is associated with surmounting the barrier imposed by the strain rule. This energy is considerably greater than that required to place an alkyl or aryl group in apical position, *i.e.*, to surmount the barrier imposed by Muetterties' rule.[19] The activation energy for the opening of the ring in the adduct of phenyl dimethyl phosphite and benzylideneacetylacetone is also about 22 kcal/mol. But the two processes—ring opening and pseudorotation through an intermediate with the ring in diequatorial positions—have quite different consequences for the nmr spectra and are thus distinct. The former results in mixing the signals from the methyl groups of the acetylacetone system, without mixing those of the methoxyl groups whereas the latter mixes the signals of the methoxyl groups without mixing those from the methyl groups.

(3) Finally, it must be noted that at high temperatures the phosphoranes under discussion partially dissociate to the compounds from which they were formed, *i.e.*, to an alkylideneacetylacetone and a phosphite or phosphonite. This process, however, is slow compared to those previously discussed. The rates can be measured by conventional, rather than nmr techniques and are accompanied by activation free energies in the range of 30 kcal/mol.

(19) Muetterties, Mahler, and Schmutzler[20] have offered evidence that the ring in tetramethylene trifluorophosphorane occupies diequatorial positions. In this compound, the barrier imposed by Muetterties' rule apparently exceeds that imposed by the strain rule. Since fluorine is so much more electronegative than oxygen, the contrast between the behavior of the oxyphosphoranes and that of the fluorophosphoranes appears reasonable.

(20) E. L. Muetterites, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963).

Acknowledgments. The author wishes to thank Professor F. H. Westheimer, who suggested this problem, for his help and encouragement. He also wishes to acknowledge with gratitude the Grant GP-6465X from the National Science Foundation that made this work possible.

On the Mechanism of Sulfonamide Cleavage by Arene Anion Radicals[1a]

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Abstract: In the cleavage of sulfonamides of secondary amines with arene anion radicals 2 moles of the reducing species are consumed rapidly, resulting in formation of amide and sulfinate anions. In the case of arenesulfinate ion a subsequent, much slower reduction converts this to arene hydrocarbon and a mixture of thiosulfate, sulfite, and sulfide salts. By analysis of competitive reactions, the rate law for the first step has been deduced as rate = k[anion radical][sulfonamide]. In the reaction of sodium naphthalenide (and probably sodium biphenylide) with the toluenesulfonamide of *p*-toluidine, electron transfer and cleavage are considerably faster than acid–base reaction with the acidic proton. Sodium anthracenide, however, reacts only as a base with this substrate. Gross structural effects on the scope of the reaction are discussed.

The discovery of the efficient cleavage of arenesulfonamides[2] and toluenesulfonate esters[3] with the anion radicals derived from aromatic hydrocarbons by treatment with alkali metals in ether solvents has prompted us to examine the mechanisms of these potentially useful reactions. Some results and conclusions concerning the anion radical cleavage of sulfonamides are presented in this paper.

Preliminary examination of the reaction of several sulfonamides with sodium naphthalenide at room temperature in 1,2-dimethoxyethane (DME) indicated a rather variable stoichiometry. One equivalent of sulfonamide would require from 2 to almost 6 equiv of anion radical for complete cleavage to the anion of the corresponding amine. It was found, however, that at low temperatures (−60 to −80°) complete cleavage of arenesulfonamides of secondary amines required exactly 2 equiv of sodium naphthalenide. The rate of reaction of a typical arenesulfonamide is still quite rapid at these temperatures, and with suitable apparatus it is possible to titrate the sulfonamide solution, reaching a faint green end point when all of the sulfonamide is consumed. In fact, this represents an excellent method for standardization of sodium naphthalenide or biphenylide solutions in DME. (Unfortunately, the same reactions in tetrahydrofuran (THF) solution usually develop a brown color that seriously interferes with determination of the end point.) In Figure 1 is shown a typical titration plot for reaction of N-methyl-N-phenyl-*p*-toluenesulfonamide (I) with sodium naph-

(1) (a) Supported in part by the Public Health Service (Research Grant No. R01-AM11419 from the National Institutes of Arthritis and Metabolic Diseases). (b) Alfred P. Sloan Research Fellow, 1968–1970.

(2) S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, W. D. Closson, and P. Wriede, *J. Am. Chem. Soc.*, 89, 5311 (1967).

(3) W. D. Closson, P. Wriede, and S. Bank, *ibid.*, 88, 1581 (1966).

thalenide in DME at −70°. This was obtained by adding measured amounts of sodium naphthalenide to solutions containing an excess of I and measuring the yield of amine by gas chromatography. In the example shown, the slope of the plot is 0.49 ± 0.1 with a correlation coefficient of 0.98. We suspect that the scatter is due more to the error in gas chromatographic analysis than to any other factor.

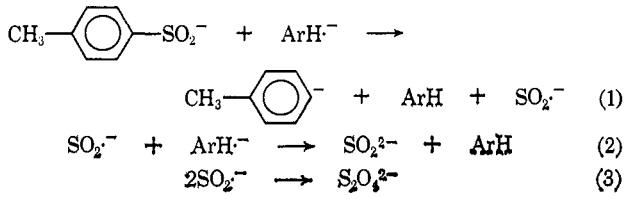
Analysis of the reaction mixtures obtained at low temperatures reveals only two products: the sodium salt of the amine and sodium arenesulfinate. *p*-Toluenesulfinate ion appears to react very slowly, if at all, with naphthalenide at temperatures in the vicinity of −70°. At 20–30°, however, it reacts further yielding toluene and a mixture of sulfur-containing salts. Qualitative analysis of this salt mixture by infrared and chemical means reveals the presence of sulfide, sulfite, and thiosulfate, in addition to a trace of sulfate ion; the latter probably derived from air oxidation during analysis. Unreacted toluenesulfinate is also usually present. Commercial sodium toluenesulfinate dihydrate slowly yields the same salt mixture and toluene on stirring with sodium naphthalenide in DME. This further reduction of sulfinate ion accounts, of course, for the larger amounts of naphthalenide consumed by arenesulfonamides at room temperature. In Table I are shown the results of two experiments in which N-ethyl-N-phenyl-*p*-toluenesulfonamide (II) was stirred with a large excess of naphthalenide for 12 hr.

Table I. Products from the Cleavage of N-Ethyl-N-phenyl-*p*-toluenesulfonamide with Sodium Naphthalenide in DME at 25° [a]

Expt no.	Molar ratio of arenide to sulfonamide	% yield[b] Toluene	Ethylaniline	Na_2S	Na_2SO_3	$Na_2S_2O_3$[c]
1	9	85	100	20	29	32
2	7	78	99	23	28	46

[a] Reaction time = 12 hr. [b] Yield based on sulfonamide. [c] Calculated on the basis of sulfur content.

Without doubt the inorganic salts are not produced directly from sulfinate ion but through one or more precursors. Bank and Noyd have reported that sulfur dioxide reacts with many arene anion radicals in THF to give sodium dithionite and products derived from it.[4] It was suggested that the reaction initially produces the sulfur dioxide anion radical which subsequently dimerizes to dithionite. Dithionite is known to disproportionate rapidly to thiosulfate and sulfite in the presence of moisture,[5] and thiosulfate and sulfite were the only anions other than dithionite identified by Bank and Noyd.[4] Under certain conditions sodium dithionite is converted to sulfide and sulfite,[6] but treatment of sodium dithionite with sodium naphthalenide in DME for 2 hr at 25°, quenching the solution with a little water, and isolation of the salts in the manner used for the reactions with sulfonamides or sodium toluenesulfinate yielded no detectable sulfide ion. (Reaction of arenesulfonamides with naphthalenide or biphenylide at 25° yields hydrogen sulfide in concentrations easily evident to the nose when the reaction mixtures are treated with a little water.) It seems likely, then, that sulfide comes from a precursor other than dithionite, and a likely one is sulfoxylate ion (SO_2^{2-}) which is known to disproportionate rapidly to sulfide and sulfite.[6,7] Further reduction of the SO_2 anion radical would seem a plausible way of producing this ion. The difference in salt products from those formed by reduction of SO_2[4] may be due to concentration effects. If the initial reaction of toluenesulfinate is that shown in eq 1, the observed sluggishness



of the overall reaction suggests that the concentration of $SO_2\cdot^-$ would always be very low, possibly allowing reaction 2 to compete with the dimerization reaction (3). In the SO_2 reaction, initial reduction to $SO_2\cdot^-$ is apparently much faster than step 2 and presumably only products of step 3 are observed at normal concentrations. Alternative pathways for production of sulfoxylate might be a competing cleavage mode yielding *p*-tolyl radical and SO_2^{2-} initially, or a competing double reduction of toluenesulfinate, followed by cleavage to SO_2^{2-} and *p*-tolyl anion.

As mentioned previously,[2] no arenethiol appears to be produced in these reactions. Thus, from reaction of I and N-methyl-N-phenylbenzenesulfonamide with large excesses of sodium naphthalenide at 25°, no *p*-thiocresol or benzenethiol, respectively, could be detected by gc. (A yield of arenethiol of 0.5% could have been easily detected.) This is in contrast to the sodium–liquid ammonia cleavage of tosylamides.[8]

The stoichiometry of the fast step of the cleavage reaction does not put much limit on the rate expression or mechanism. Attempts to measure the absolute rate of reaction of a rather unreactive sulfonamide [N-methyl-N-phenylmethanesulfonamide, (III)] with sodium

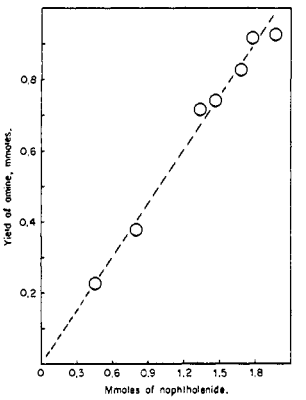


Figure 1. Titration of N-methyl-N-phenyl-*p*-toluenesulfonamide with sodium naphthalenide in DME at −70°. Least-squares slope, 0.49; correlation coefficient, 0.98.

(4) S. Bank and D. A. Noyd, *Tetrahedron Lett.*, 1413 (1969).
(5) T. Moeller, "Inorganic Chemistry, an Advanced Textbook," John Wiley & Sons, Inc., New York, N. Y., 1954, p 536.
(6) H. Bassett and R. G. Durrant, *J. Chem. Soc.*, (II), 1401 (1927).
(7) F. H. Pollard and D. J. Jones, Special Publication No. 12, The Chemical Society, London, 1958, p 363.
(8) J. Kovacs and U. R. Ghatak, *J. Org. Chem.*, **31**, 119 (1966).

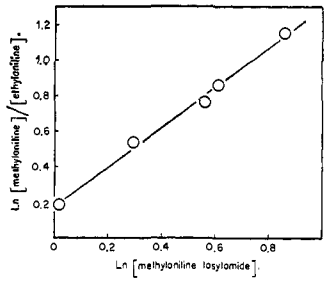


Figure 2. Ratio of yields of methylaniline and ethylaniline as function of N-methyl-N-phenyl-*p*-toluenesulfonamide concentration in competitive cleavage of the two tosylamides with sodium anthracenide in DME at 25°. Data from Table IV. Least-squares slope, 1.11; correlation coefficient, 0.994.

napthalenide at −70° or anthracenide at 25° gave somewhat ambiguous results (see Experimental Section) but did suggest that the reaction was approximately first order in each component. This suggests that either the rate-determining step is transfer of an electron from arenide to sulfonamide (eq 4) or that equilibrium is reached between arenide and sulfonamide anion radical followed by a slow breakdown of the latter (5). Both schemes require a second step that

$$\mathrm{ArH}\cdot^- + \text{sulfonamide} \xrightarrow{\text{slow}} \text{intermediate(s)} \xrightarrow[\text{fast}]{\mathrm{ArH}\cdot^-} \text{products} \quad (4)$$

$$\mathrm{ArH}\cdot^- + \text{sulfonamide} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{ArH} + [\text{sulfonamide}]\cdot^- \xrightarrow{\text{slow}}$$

$$\text{intermediate(s)} \xrightarrow[\text{fast}]{\mathrm{ArH}\cdot^-} \text{products} \quad (5)$$

rapidly consumes another molecule of arenide in order to satisfy the observed stoichiometry. If the initial equilibrium in (5) is rapid, a simple test can be made for its presence. It was found possible to measure, with a reasonable degree of accuracy, relative rates of cleavage of different arenesulfonamides of secondary amines by the competitive reaction method.[9] If eq 5 is correct, the relative rates of cleavage of a pair of arenesulfonamides under these conditions should be independent of the electron source. The data shown in Table II for the competitive cleavage of N,N-di-*n*-butyl-*p*-toluenesulfonamide (IV) and I indicate that this is clearly not the case. It was also found that the presence of 0.033 *M* anthracene had no detectable effect ($k_I/k_{IV} = 1.31$) on the selectivity of cleavage by naphthalenide, indicating that electron transfer from naphthalene to sulfonamide, while presumably being the slow step in the reaction, is still considerably faster than transfer to anthracene.

Table II. Relative Rates of Cleavage of N-Methyl-N-phenyl- (I) and N,N-Di-*n*-butyl-*p*-toluenesulfonamide (IV) by Arene Anion Radicals in DME at 25°

k_I/k_{IV}	Anion radical	$-\epsilon$ *vs.* SCE[a]
1.31 ± 0.06	Sodium biphenylide	2.70
1.26 ± 0.06	Sodium naphthalenide	2.50
10 ± 2	Sodium pyrenide	2.11
36 ± 4	Sodium anthracenide	1.96

[a] Half-wave reduction potential of arene in 75% aqueous dioxane: A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1968, p 178.

A test of the reaction order with respect to sulfonamide was performed as follows. If we have two sulfonamides S_1 and S_2 that react with arenide B to give amines A_1 and A_2, and we assume that the rate expressions can be written in the form

$$\frac{d[A_1]}{dt} = k_1[S_1]^{m_1}[B]^{n_1} \qquad \frac{d[A_2]}{dt} = k_2[S_2]^{m_2}B^{n_2} \quad (6)$$

Then if we make $[S_1]$ and $[S_2]$ constant by keeping them in large excess over [B] and if we assume that $n_1 = n_2$ as will be the case for structurally similar sulfonamides, it follows that

$$\frac{[A_1]}{[A_2]} = \frac{k_1}{k_2}\frac{[S_1]^{m_1}}{[S_2]^{m_2}} \cdot C \quad (7)$$

and if we hold $[S_2]$ constant and vary $[S_1]$, then

$$\ln \frac{[A_1]}{[A_2]} = m_1 \ln [S_1] + \ln \frac{k_1}{k_2} + C' = m_1 \ln [S_1] + C'' \quad (8)$$

and a plot of $\ln [A_1]/[A_2]$ *vs.* $\ln [S_1]$ should be linear with a slope of m_1, the reaction order with respect to S_1. For S_1 = I, S_2 = II, and B = sodium anthracenide, such a plot has a slope of 1.11 with a least-squares correlation coefficient of 0.994 and is shown in Figure 2.

Similarly, examination of the competition between a sulfonamide and aryl halide might allow one to determine the reaction order with respect to arenide ion. It is likely that the rate law for reaction of aryl halides with arene anion radicals is first order with respect to each reactant.[10] As above, it can be shown that a plot of ln [amine] [aryl halide]$_0$/[hydrocarbon][sulfonamide]$_0$ *vs.* ln [arenide] should have a slope of $n - 1$ where n is the reaction order with respect to arenide ion for the sulfonamide reaction.[11] Unfortunately, there is no way of knowing the concentration of arenide under the conditions of the competition reaction. The reactions are rapid, and using ordinary equipment it is impossible to make the solutions homogeneous before it is complete. However, making the assumption that the true average concentration of arenide at the time of reaction is *proportional* to the concentration of the arenide solution that is added to the competition mixture if we keep the volume of added solution, stirring speed, etc., constant, one can still hope to examine the relationship. For the system I, *p*-bromoanisole, and sodium biphenylide in DME at 25° the results illustrated in Figure 3 were obtained. While the results do not appear very impressive they are at least in line with the reaction being first order in arenide ion.

Using this same system, a further test of the preequilibrium mechanism was performed by measuring the relative yields of amine and anisole in the presence of

(9) (a) A. W. Francis, *J. Am. Chem. Soc.*, 48, 655 (1926); (b) G. A. Russell, "Technique of Organic Chemistry," Vol. VIII, Part I, S. L. Friess, E. S. Lewis, and A. Weissburger, Ed., 2nd ed, Interscience Publishers, New York, N. Y., 1961, Chapter 8.

(10) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 56, 343 (1960).

(11) It was shown that aryl halides give high and reproducible yields of aryl hydrocarbon on reaction with arenide ions, *e.g.*, 97 ± 2% toluene from *m*-chlorotoluene and sodium naphthalenide and 85 ± 2% anisole from *p*-bromoanisole and sodium anthracenide. Also, the yield is proportional to the extent of reaction and titration plots similar to Figure 1, with slopes close to 0.5, can easily be obtained.

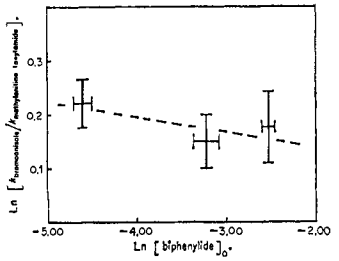


Figure 3. Ratio of reactivities of bromoanisole and methylaniline tosylamide as a function of initial biphenylide concentration in competitive cleavage of N-methyl-N-phenyl-*p*-toluenesulfonamide and *p*-bromoanisole with sodium biphenylide in DME at 25°.

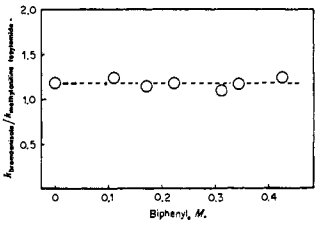


Figure 4. Ratio of yields of anisole and methylaniline as a function of free biphenyl concentration in competitive cleavage of N-methyl-N-phenyl-*p*-toluenesulfonamide and *p*-bromoanisole with sodium biphenylide in DME at 25°.

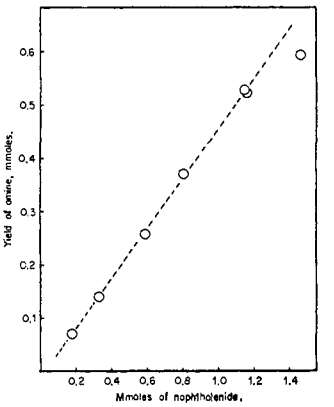


Figure 5. Titration of N-*p*-tolyl-*p*-toluenesulfonamide with sodium naphthalenide in DME at −70°. Data from Table III. Least-squares slope, 0.467; correlation coefficient, 0.999.

different concentrations of free biphenyl. If the pre-equilibrium mechanism were operating for cleavage of I (but not for reaction of bromoanisole), increasing the concentration of biphenyl should lower the yield of amine relative to that of anisole. As shown in Figure 4, no such effect is observed. Thus, it seems fairly certain that the rate law for cleavage of arenesulfonamides of secondary amines with the more reactive arene anion radicals is as shown in (9), and the rate-determining step is probably electron transfer from arenide ion to sulfonamide.

$$\frac{\mathrm{d[amine]}}{\mathrm{d}t} = k[\text{sulfonamide}][\mathrm{ArH}\cdot^-] \qquad (9)$$

Arenesulfonamides of primary amines have a quite acidic hydrogen attached to nitrogen, the basis of the Hinsberg technique for separation and characterization of amines.[12] Attempts to carry out competition experiments involving sulfonamides of primary amines, such as *N*-*p*-tolyl-*p*-toluenesulfonamide (V), were fruitless, the ratios of yields of products not being related in any obvious way to the ratios of reactants. Low temperature titration of V with sodium naphthalenide does furnish interesting information, however. A titration plot for a typical experiment is shown in Figure 5. The end point occurs when about 1 equiv of naphthalenide is added to the sulfonamide and the maximum yield of amine at −70° is around 44%. The slope of the titration plot is always in the range of 0.44–0.47, indicating that slightly more than 2 equiv of naphthalenide are used in producing 1 equiv of amine. The unreacted sulfonamide present after the end point is reached is in the form of its insoluble (in DME) sodium salt, which was isolated and characterized by ir. (This salt is cleaved rapidly by naphthalenide at room temperature.)[2] Samples that had been titrated past the green end point at −70 and then air quenched (a technique that destroys naphthalenide without producing dihydronaphthalenes)[13] showed the presence of dihydronaphthalenes in amounts corresponding to 5 ± 2% yield. (Since some dihydronaphthalene is produced by a slow reaction between naphthalenide and DME and traces of moisture in the DME solutions of V will produce it, careful, "blank" reactions were run simultaneously and the relatively small amounts of dihydro products so obtained subtracted from the amounts observed in the titrations.) If we assume that the mechanism of cleavage is similar to that of sulfonamides of secondary amines, *i.e.*, the slow step is initial electron transfer, these results can best be rationalized by the following set of reactions. Steps 11 and 14, the scavenging of

$$\mathrm{C_7H_7SO_2NHC_7H_7} + \mathrm{C_{10}H_8}\cdot^- \xrightarrow{k_1} \mathrm{C_{10}H_8} + \mathrm{C_7H_7SO_2}^{-/}\cdot + \mathrm{C_7H_7NH}\cdot^{/-} \qquad (10)[14]$$

$$\mathrm{C_7H_7SO_2}\cdot \text{ or } \mathrm{C_7H_7NH}\cdot + \mathrm{C_{10}H_8}\cdot^- \xrightarrow{k_2} \mathrm{C_{10}H_8} + \mathrm{C_7H_7SO_2}^- \text{ or } \mathrm{C_7H_7NH}^- \qquad (11)$$

$$\mathrm{C_7H_7SO_2NHC_7H_7} + \mathrm{C_7H_7NH}^- \xrightarrow{k_3} \mathrm{C_7H_7NH_2} + \mathrm{C_7H_7SO_2N}^-\mathrm{C_7H_7} \qquad (12)$$

$$\mathrm{C_7H_7SO_2NHC_7H_7} + \mathrm{C_{10}H_8}\cdot^- \xrightarrow{k_4} \mathrm{C_{10}H_9}\cdot + \mathrm{C_7H_7SO_2N}^-\mathrm{C_7H_7} \qquad (13)$$

$$\mathrm{C_{10}H_9}\cdot + \mathrm{C_{10}H_8}\cdot^- \xrightarrow{k_5} \mathrm{C_{10}H_9}^- + \mathrm{C_{10}H_8} \qquad (14)$$

$$\mathrm{C_7H_7SO_2NHC_7H_7} + \mathrm{C_{10}H_9}^- \xrightarrow{k_6} \mathrm{C_{10}H_{10}} + \mathrm{C_7H_7SO_2N}^-\mathrm{C_7H_7} \qquad (15)$$

neutral radicals by naphthalenide, and steps 12 and 15, neutralization reactions between strong acids and strong bases, would be expected to be very fast. If these assumptions are all valid, the ratio of sulfonamide cleaved to the amount of dihydronaphthalene produced would be equal to k_1/k_4. Alternatively, one may assign the deficiency in titration plot slope (from the value of 0.50 which should obtain if naphthalenide were only used up in the cleavage process) to destruction of naphthalenide by reaction 13 and obtain a similar measure of k_1/k_4. In either case, the value is approximately 10. The

(12) O. Hinsberg, *Ber.*, 23, 2962 (1890); O. Hinsberg and J. Kessler, *ibid.*, 38, 906 (1905).

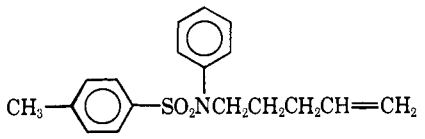
(13) A. LeBerre and P. Goasguen, *Bull. Soc. Chim. France*, 1838 (1963).

(14) Since there is no way, as yet, of telling which fragment produced in step 10 is anion and which is radical (or, for that matter, whether steps 10 and 11 are combined) the symbolism $\mathrm{XY} \rightarrow \mathrm{X}^{-/}\cdot + \mathrm{Y}\cdot^{/-}$ is used to indicate the ambiguity of the situation.

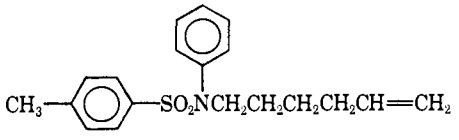
small amount of dihydronaphthalene could come, of course, from slow reaction with *p*-toluidine that builds up in the reaction mixture, but the regularity of the titration plot and the rough correspondence between the deviation of the slope of the plot from 0.50 and the yield of dihydronaphthalene argue in favor of direct acid–base reaction between V and naphthalenide. Also, considering the gross difference in acidity between V and *p*-toluidine (*ca.* 17 pK units), it would seem unlikely for naphthalenide to deprotonate the amine preferentially. (At room temperature, *p*-toluidine and most other primary and secondary amines rapidly protonate naphthalenide in DME, but at temperatures near that of Dry Ice neither *p*-toluidine nor N-methylaniline discharge the green color of the anion radical at any appreciable rate.) Finally, we must emphasize that the crucial assumption in the above treatment is that the slow step in cleavage of V is the initial electron transfer.

It is of interest to examine the behavior of other arenide ions toward V. Sodium anthracenide simply deprotonates it, yielding no detectable amount of amine. (Anthracenide will not cleave the sodium salt of V even at 25°.) Sodium biphenylide apparently does not deprotonate the sulfonamide at all, but this case is not as clear-cut. The difficulty lies in the fact that biphenylide cleaves the anion of V readily even at −70° and one cannot obtain a straightforward titration plot. Our conclusion that no deprotonation occurs rests only on the fact that partially titrated samples, or samples treated with an excess of biphenylide at −70° and then air-quenched, show no detectable amounts of dihydrobiphenyls on gc analysis. Assuming our conclusions are correct and assigning reasonable limits to the sensitivity of our gc analyses we conclude that the rates of electron transfer relative to proton transfer (k_1/k_4) are >100, ~10, and <0.01 for sodium biphenylide, naphthalenide, and anthracenide, respectively.

In an attempt to gain information about the initial step of the cleavage reactions, the reactions of the N-alkenyl-substituted sulfonamides VI and VII with sodium anthracenide in DME at 25° were examined.

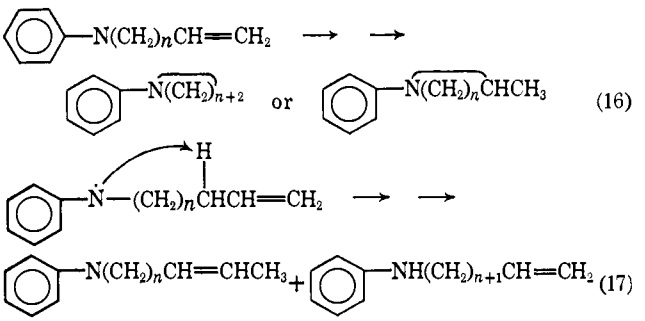


VI



VII

It was hoped that the amino radical, if formed, might either add to the double bond or abstract an allylic hydrogen (eq 16 and 17, respectively). A carbon radical of similar structure (the 5-hexenyl radical) is known to cyclize to cyclopentylmethyl radical at a rate competitive with that of further reaction with naphthalenide ion.[15] On the other hand, neutral amino radicals normally show little disposition to add to double bonds.[16]

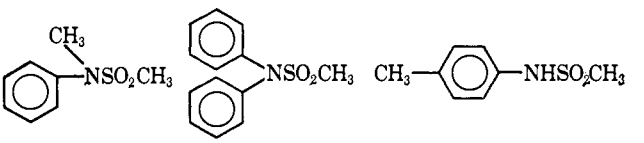


(16)

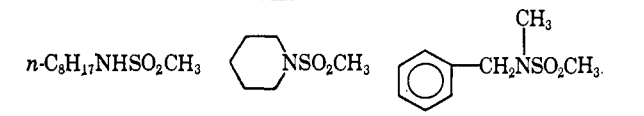
(17)

Unfortunately, neither VI nor VII yielded any detectable amino product other than the unrearranged secondary N-alkyenylanilines. The reacion of VI with sodium biphenylide at 25° also afforded only a near-quantitative yield of N-4-pentenylaniline. If formed, the neutral amino radical must be reduced faster than these possible side reactions. Since reduction of carbon radicals is probably very near the diffusion controlled limit,[15a] only modest sluggishness on the part of the amino radical would result in the observed behavior since one would expect the more electronegative nitrogen species to be reduced at least as fast.

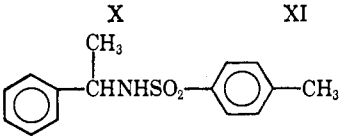
The scope of the cleavage reaction with respect to methanesulfonamides was examined further, since these seem to be more resistant to reaction with arenide ion than are arenesulfonamides.[2] In general, neither primary amine methanesulfonamides (which are simply converted to salts) nor purely aliphatic secondary amine derivatives can be cleaved with biphenylide, naphthalenide, or anthracenide. The requirements appear to be that the nitrogen be disubstituted and at least one of the groups be aryl. Thus, compounds III and VIII are cleaved in good yield (albeit slowly) even by sodium anthracenide, while IX, X, and XI are untouched even by



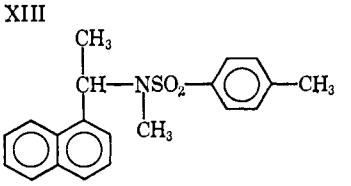
III VIII IX



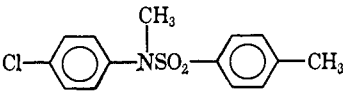
X XI XII



XIII



XIV



XV

(15) (a) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969); (b) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Am. Chem. Soc.*, 90, 7159 (1968).

(16) J. D. Hobson and W. D. Riddell, *Chem. Commun.*, 1178 (1968); R. S. Neale, *J. Org. Chem.*, 32, 3263 (1967); R. S. Neale and N. L. Marcus, *ibid.*, 32, 3273 (1967).

biphenylide at 25°. The benzylic methanesulfonamide, XII, yields toluene (90% yield) rather than amine after treatment with naphthalenide for 3 hr at 25°. (The free amine corresponding to XII was shown to be stable under the reaction conditions.) This is in contrast to the facile S–N cleavage of such N-benzylic toluenesulfonamides as XIII[2] and XIV.[17] Finally, it should be mentioned that N-*p*-chlorophenyl-N-methyl-*p*-toluenesulfonamide (XV) could be cleaved to N-methyl-*p*-chloroaniline in good yield by anthracenide (DME, 25°) without detectable dechlorination in contrast to results usually obtained with naphthalenide.[2]

Experimental Section

Solvents. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from lithium aluminum hydride and stored under nitrogen or argon prior to use.

Sulfonamides. Except when otherwise noted, these were prepared from the corresponding amine and appropriate sulfonyl chloride by vigorous stirring in aqueous sodium hydroxide (Schotten-Bauman technique).

N-Methyl-N-phenyl-*p*-toluenesulfonamide (I) had mp 92.5–93.5° (benzene–pentane) (lit.[18] mp 94°).

N-Ethyl-N-phenyl-*p*-toluenesulfonamide (II) had mp 84.5–85° (benzene–pentane), (lit.[18] mp 87°).

N-Methyl-N-phenylbenzenesulfonamide had mp 78–79.5° (methanol) (lit.[18] mp 79°).

N-Methyl-N-phenylmethanesulfonamide (III) had mp 77–77.5° (ethanol) (lit.[19] mp 76.6°).

N,N-Di-*n*-butyl-*p*-toluenesulfonamide (IV) had bp 130–135° (0.02 mm), $n^{20}D$ 1.5094 (lit.[20] $n^{20}D$ 1.5085). The material could be cleaved to N,N-di-*n*-butylamine in 97% yield by treatment with sodium naphthalenide in DME.

N-*p*-Tolyl-*p*-toluenesulfonamide (V) had mp 118–118.7° (ethanol) (lit.[18] mp 118°).

N-(4-Pentenyl)-N-phenyl-*p*-toluenesulfonamide (VI). 5-Bromo-1-pentene (15.7 g, 0.105 mole) was added to a mixture of 25 g (0.10 mole) of aniline tosylamide and 400 ml of 50% ethanol containing 2.5% KOH. The mixture was refluxed with stirring for 26 hr, then diluted with 200 ml of water and the organic material extracted with ether and methylene chloride. The organic extracts were combined, washed with water and 5% KOH solution, and concentrated. The residual oil was recrystallized from ether–pentane to give 21 g (0.067 mole, 67%) of white crystals: mp 40–41.5°, ir (liquid film) 1645 (w), 915 (s), 1350 (s), and 1170 cm^{-1} (s).

Anal. Calcd for $C_{18}H_{21}NO_2S$: C, 68.56; H, 6.71. Found: C, 68.11; H, 6.82.

N-(5-Hexenyl)-N-phenyl-*p*-toluenesulfonamide (VII). Crude 5-hexenyl-*p*-toluenesulfonate (prepared from the alcohol and tosyl chloride) (15.5 g, 61 mmoles) was added to a mixture of 12.4 g (50 mmoles) of aniline tosylamide, 60 ml of ethanol, and 100 ml of 5% KOH in water. The solution was refluxed for 43 hr and then concentrated to about half its volume under reduced pressure. On cooling, a white solid separated which was collected, washed with aqueous base, water, and then recrystallized from petroleum ether, yielding 7.1 g (21.5 mmoles, 43%) of white crystals, mp 64–65°.

Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04. Found: C, 69.32; H, 7.35.

N,N-Diphenylmethanesulfonamide (VIII). A solution of 35.7 g (0.211 mole) of diphenylamine in 65 ml of pyridine was treated with 21.5 g (0.188 mole) of methanesulfonyl chloride, added slowly at 0°. The reaction mixture was stirred for 20 hr at room temperature, and then mixed with 120 ml of 6.8 *N* aqueous HCl. The brown amorphous material was collected, washed with water, and recrystallized from methanol to give 13 g (0.0525 mole, 28%) of light brownish needles, mp 116.6–117°.

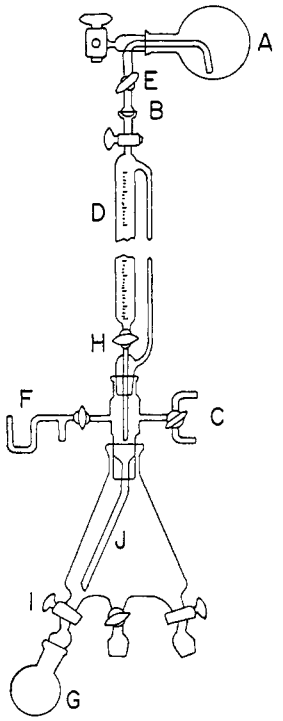


Figure 6. Apparatus ("octopus") for storage, titrations, and volume measurement of arene anion radical solutions.

Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.14; H, 5.30. Found: C, 63.26; H, 5.49.

N-*p*-Tolylmethanesulfonamide (IX) had mp 102–103.5° (benzene–pentane) (lit.[19] mp 102.5°).

N-*n*-Octylmethanesulfonamide (X) had mp 56.3–56.6° (pentane).

Anal. Calcd for $C_9H_{21}NO_2S$: C, 52.14; H, 10.21. Found: C, 51.94; H, 10.07.

N-Methanesulfonylpiperidine (XI) had mp 48.5–50° (carbon tetrachloride).

Anal. Calcd for $C_6H_{13}NO_2S$: C, 44.15; H, 8.03. Found: C, 44.35; H, 8.17.

N-Benzyl-N-methylmethanesulfonamide (XII) had mp 38–40° (ether).

Anal. Calcd for $C_8H_{13}NO_2S$: C, 54.24; H, 6.58. Found: C, 54.38; H, 6.78.

N-*p*-Chlorophenyl-N-methyl-*p*-toluenesulfonamide (XV). To a mixture of 232 g (0.825 mole) of N-*p*-chlorophenyl-*p*-toluenesulfonamide and 36 g (0.9 mole) of sodium hydroxide in 750 ml of water was slowly added 152 g (1.2 moles) of dimethyl sulfate. After addition was complete, the mixture was stirred for 2 hr while being heated at reflux. After cooling, a layer of oil separated and crystallized. Recrystallization of the solid from methanol yielded 50.2 g (0.169 mole, 20.5%) of off-white crystals, mp 94–94.5° (lit.[21] mp 96–97°).

Ttitrations with arenide ion solutions were carried out using the apparatus shown in Figure 6 or with a somewhat simpler apparatus in which the buret terminated in a syringe needle which could be inserted into a sealed flask through a septum. Operations with the two apparatus were very similar. Arenide ion solution, previously prepared in flask A from clean pieces of sodium and a slight excess of the appropriate hydrocarbon in DME or THF solution under nitrogen or argon, is attached at joint B, the apparatus filled with inert gas through C, and solution forced into buret D with inert gas, venting the excess pressure through a mercury pool at F. Solutions of substrates are attached at G and may be degassed through C before filling of the buret. Arenide solution may be added to any of several flasks through rotation of the lower assembly, and new flasks may be attached and degassed for each filling of the buret. Arenide concentrations in the range 0.05–0.15 *M* were used; at concentrations of 0.2 *M*, or higher, problems due to viscosity of the solutions arose. Solutions of arenide ions would last several days in flask A with little change in titer, and were stable

(17) J. Jacobus, M. Raban, and K. Mislow, *J. Org. Chem.* 33, 1142 (1968).

(18) Z. Rappoport, "Handbook of Tables for Organic Compounds Identification," 3rd ed, The Chemical Rubber Co., Cleveland, Ohio, 1967, Table XVIII.

(19) C. S. Marvel, M. D. Helfrick, and J. P. Belsley, *J. Am. Chem. Soc.*, 51, 1272 (1929).

(20) D. Klamann, G. Hofbauer, and F. Drahowzal, *Monatsh. Chem.*, 83, 870 (1952).

(21) J. Halberkann, *Ber.*, 54B, 1833 (1921).

in buret D for several hours. Initially, naphthalenide solutions were standardized by measuring the yield of dihydro- and tetrahydronaphthalene obtained on adding a measured amount of solution to water and THF,[22] and subtracting any minor amount of these species that might already be present, which could be determined by similar gc analysis of an air-quenched sample of titrant. Later, it was found more convenient and reproducible to standardize biphenylide and naphthalenide by titration of weighed amounts of I dissolved in DME and cooled to *ca.* −70° with a Dry Ice–acetone bath, and anthracenide by a similar titration of I at room temperature. A solvent blank is advisable. Normally, a series of such standardizations would have an average reproducibility of 2–3%.

Titration plots were obtained by adding measured amounts of previously standardized arenide solution to solutions containing *ca.* 1 mmole of substrate in 10 ml of DME, using the apparatus described above. After addition of the arenide solution, each was stirred (magnetically) for a few minutes, then quenched with water (or air), and the yield of product measured by appropriate gc technique. The data for a typical titration plot are given in Table III.

Table III. Titration of N-*p*-Tolyl-*p*-toluenesulfonamide with Sodium Naphthalenide in DME at −70°

Mmoles of naphthalenide	Yield of *p*-toluidine[a]	Amine/arenide
0.176	0.075	0.401
0.325	0.140	0.431
0.590	0.256	0.434
0.805	0.369	0.458
1.147	0.528	0.460
1.158	0.522	0.452
1.462[b]	0.592[b]	(0.467)[c]

[a] Each sample contained 1.30 mmoles of sulfonamide in 10 ml of DME. [b] Solution stayed green with this amount of naphthalenide. [c] Ratio from least-squares relationship of above data: amine = 0.467 (naphthalenide) −0.013; correlation coefficient = 0.999.

Competition reactions were carried out in a fashion very similar to that described above, except that DME solutions contained *ca.* tenfold excesses of the competing species, or, since the exact concentration of arenide was not too critical, by injecting arenide solution into a sealed flask containing the competing species in DME, by means of a syringe. The data for the competition between I and II for sodium anthracenide are shown in Table IV.

Table IV. Competition Data for Cleavage of N-Methyl-N-phenyltosylamide (I) and N-Ethyl-N-phenyltosylamide (II) with Sodium Anthracenide in DME at 25°

Amt, mmoles				
I[a]	II[a]	Anthracenide	Yield ratio of amines[b]	k_I/k_{II}
1.017	1.044	0.5	1.20	1.23
1.340	0.958	0.5	1.71	1.22
1.752	1.083	0.5	2.14	1.32
1.850	1.044	0.5	2.36	1.33
2.364	1.040	0.5	3.16	1.39
				1.30 ± 0.06

[a] Sulfonamides were combined and dissolved in 10 ml of DME. [b] Ratio of the yield of methylaniline to that of ethylaniline.

Kinetic measurements on rate of cleavage of III were carried out by mixing appropriate amounts of previously thermostated DME solutions of arenide and III (using a side-arm flask) and stirring the resulting solution magnetically in a constant-temperature bath. After a measured period of time, the solution was quenched with cold ethanol and the yield of amine measured by gc. A typical experiment is shown in Table V.

(22) S. Bank and W. D. Closson, *Tetrahedron Lett.*, 1349 (1965).

Table V. Rate of Cleavage of N-Methyl-N-phenylmethanesulfonamide (III) with Sodium Anthracenide in DME at 25° [a]

t, 10^3 sec	Yield of N-methylaniline, mol	10^4k_2, l./M sec[b]
2.50	0.77×10^{-3}	1.6
5.32	0.80×10^{-3}	1.0
28.10	7.98×10^{-3}	2.0
84.80	15.84×10^{-3}	2.2

[a] Concentration of III = 21.25×10^{-3} M, of anthracenide = 94.3×10^{-3} M, of anthracene = 17.9×10^{-3} M. [b] Graphically, a value of 2.3×10^{-4} l./M sec was obtained.

Cleavage of N-(4-Pentenyl)-N-phenyl-*p*-toluenesulfonamide (VI) with Sodium Anthracenide. In a 250-ml round-bottomed flask equipped with a side arm capped with a rubber septum was placed 1.32 g (4.19 mmoles) of VI dissolved in 12 ml of DME. Sodium anthracenide solution (36 ml, *ca.* 4 mmoles) was added through the septum with a syringe while the solution was stirred rapidly. After the addition was complete, a few drops of water was added to the yellowish brown solution and 1 ml was withdrawn and analyzed by gc (5 ft × 0.25 in. column, 20% SE-30 on 60–80 mesh Chromosorb W at a column temperature of 186°, flow rate of 40 ml/min). A sharp, symmetric peak with a retention time of 4.8 min was the only thing observed, other than solvent and anthracene. Acetylation with acetic anhydride caused the *complete* disappearance of this peak and the appearance of a new peak with a retention time of 9.5 min. It is therefore unlikely that any tertiary amine is present. From the rest of the reaction mixture the basic organic material was isolated by usual extraction techniques and found to be the material responsible for the peak with retention time of 4.8 min: ir (neat) 3420 (NH), 3060–3080 (aromatic H), 2970 (CH), 1645 (C=C), 1600 (benzene ring), 1520 (benzene ring), 1000 (C=CRH), 915 (C=CH_2), 750 and 700 cm^{-1} (benzene ring); nmr (neat) 7.10 (triplet, 2 H), 6.45 (multiplet, 3 H), 5.7 (multiplet, 1 H), 4.95 (doublet, 2 H), 3.25 (singlet, 1 H), 2.8 (triplet, 2 H), 1.85, (quartet, 2 H), 1.40 ppm (quartet, 2 H).

Cleavage of N-(5-Hexenyl)-N-phenyl-*p*-toluenesulfonamide (VII). Cleavage of VII with both sodium anthracenide and sodium biphenyl was carried out in a fashion similar to that described above, except that a 3:2 excess of arenide was used in each case. Similar gc analysis showed no evidence for formation of a tertiary amine in either case. The ir spectrum (neat) of the isolated amine was practically identical with that described above for N-(4-pentenyl)aniline, and its nmr spectrum was also in complete agreement for N-(5-hexenyl)aniline.

Reaction of N-*p*-Tolylmethanesulfonamide (IX) with Sodium Biphenylide. Titration of 0.231 g (1.25 mmoles) of IX with biphenylide solution at 25°, using the apparatus previously described, required *ca.* 1.5 mmoles of arenide to reach the blue end point. This color persisted for 20 hr. Quenching the solution with a little water and gc analysis of the reaction mixture revealed no *p*-toluidine (0.5% yield would have been detectable) but instead showed the presence of IX in essentially its original concentration. Similar results were obtained with naphthalenide and anthracenide.

Reaction of N-*n*-Octylmethanesulfonamide (X) with Sodium Naphthalenide. To 15 ml of *ca.* 0.4 M sodium naphthalenide solution under nitrogen was added 0.21 g (1.0 mmole) of X, and the resulting solution stirred at room temperature for 12 hr. The dark green solution was quenched with a little water, treated with 2 ml (*ca.* 20 mmoles) of acetic anhydride, and the mixture analyzed by gc. No more than 3% *n*-octylacetamide could be shown to be present, but X was shown to be present in essentially its original concentration. Similar results were obtained with biphenylide and anthracenide solutions. Also, N-methanesulfonylpiperidine (XI) showed no evidence for formation of piperidine on similar treatment with naphthalenide.

Cleavage of N,N-Diphenylmethanesulfonamide (VIII). Reaction of 1 mmole of VIII with *ca.* 6 mmoles of naphthalenide in a manner similar to that described above resulted in formation of diphenylamine in 94% yield (gc analysis). Similar results were obtained with anthracenide but required a reaction time of *ca.* 20 hr at room temperature before complete cleavage (99% yield of amine) was obtained.

Cleavage of N-Benzyl-N-methylmethanesulfonamide (XII). Treatment of 1 mmole of XII with *ca.* 7 mmoles of naphthalenide in the usual manner (3.5 hr reaction time at room temperature) resulted in the formation of toluene (*ca.* 90%, gc analysis), but no detectable

N-methylbenzylamine. The amine itself was shown to be stable under these reaction conditions.

Cleavage of N-Methyl-N-*p*-chlorophenyl-*p*-toluenesulfonamide (XV). Treatment of 1 mmole of XV with *ca.* 4 mmoles of sodium anthracenide in the usual manner (10 min reaction time, 25°) resulted in formation of N-methyl-*p*-chloroaniline (95% yield, gc analysis), but no detectable N-methylaniline.

Analysis of Salts from Cleavage Reactions. Salts were isolated either by filtration from air-quenched reaction mixtures or by extraction into aqueous solution, washing with ether, and concentration under reduced pressure. Sodium toluenesulfinate was identified by the Smiles test[23] and its concentration determined by comparison of the absorption of the Smiles test solution at 515 nm with a standard curve prepared from known concentrations of sulfinate ion. The ir (KBr) of the salts from an air-quenched reaction exhibited bands at 1140 (s), 665 (m), and 550 cm^{-1} (w) due to thiosulfate, and at 970 (s), 630 (m), and 490 cm^{-1} (m) due to sulfite, as well as bands due to adventitious carbonate. (The ir spectrum could be almost exactly duplicated using a mixture of sodium thiosulfate, sodium sulfite, and the ether insoluble residue of air-quenched sodium naphthalenide.) The characteristic bands at 510 and 420 cm^{-1} of dithionite ion do not appear in the ir spectrum of the salts. The identity of thiosulfate ion was confirmed through a positive test with Zwikker's reagent,[24] that of sulfide through lead acetate paper (and nose) test, and that of sulfite through formation and characterization of barium sulfite.

A semiquantitative measurement of the yield of sulfide, sulfite, and thiosulfate was performed as follows: the salt products from reaction of 1.2 mmoles of II were dissolved in 75 ml of water and acidified with hydrochloric acid to the phenolphthalein end point. A 1.0 *M* zinc acetate solution was then added till no more precipitate formed, and the zinc sulfide separated and washed with water by centrifugation. The zinc sulfide was then mixed with an excess of standard cupric sulfate solution, warmed to convert the sulfide to cupric sulfide (which was separated by centrifugation), and the excess cupric ion determined iodometrically. The original filtrate, containing sulfite and thiosulfate, was divided into two parts. One part was titrated with standard iodine solution to determine the sum of sulfite and thiosulfate present; the other part was mixed with 6 ml of 37% aqueous formaldehyde to complex the sulfite and the remaining thiosulfate determined iodometrically.

Gas Chromatographic Analyses. The determination of amines by gas chromatography is notoriously difficult. Two techniques were used to improve reproducibility and overall accuracy. One was to precondition the column at the temperature used by injecting large samples of the amine to be determined until the peak area for a given amount of the amine remained constant. This would have to be repeated after a few hours use of the column. The other technique was to convert the amines to the corresponding amides by treating the reaction mixtures with a large excess of either acetic or propionic anhydride. The amides gave more reproducible results (±3% average reproducibility) as compared to the amines (±5% average reproducibility) but were a little more difficult to separate from other components of the reaction mixtures. A Varian A-90 P instrument, equipped with thermal conductivity detector, was used for most of the analyses. Quantitative measurements were made using the internal standard technique and comparison with known mixtures. Peak areas were determined by cutting and weighing. Most of the analyses were performed on 5–8 ft × 0.25 in. columns of SE-30 or Carbowax 20M on 60–80 mesh Chromosorb W.

(23) A. I. Vogel, "Elementary Practical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1961, p 528.
(24) F. J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Co., New York, N. Y., 1947, p 386.

The Addition of Dihalocarbenes to 1-Germacyclopent-3-enes and to 1,1,3,4-Tetramethyl-1-silacyclopent-3-ene

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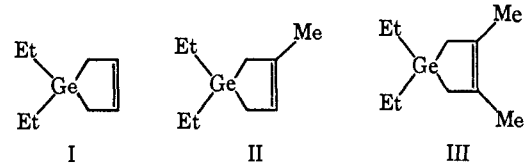
Abstract: The reaction of dichlorocarbene (generated *via* $CHCl_3$ + Me_3COK or $PhHgCCl_2Br$) with the 1,1-diethyl-1-germacyclopent-3-enes I, II, and III gave the expected 3,3-diethyl-6,6-dichloro-3-germabicyclo[3.1.0]-hexanes IV, V, and VI, but these were not very stable thermally. Only 3,3-diethyl-6,6-dichloro-3-germabicyclo-[3.1.0]hexane (IV) itself could be isolated as a pure substance. Methyl substituents on the germacyclopentene C=C bond (as in II and III) tended to decrease the stability of the CCl_2 adduct. The decomposition of these dichlorogermabicyclohexanes most likely proceeds *via* concerted C–Cl ionization and electrocyclic, disrotatory cyclopropane ring opening with concomitant *reversible* loss of HCl to give a 1,1-diethyl-4-chloro-1-germacyclohexa-2,4-diene or irreversible Ge–C cleavage to give a diethylchlorogermyl-substituted pentadiene ($Et_2ClGeCH_2CH{=}CCl{-}CH{=}CH_2$ in the case of IV). The 3,3-diethyl-6,6-difluoro-3-germabicyclo[3.1.0]hexane structure is much more stable than the analogous chloro system. 1,3,3,5-Tetramethyl-6,6-dichloro-3-silabicyclo[3.1.0]hexane was found to be unstable at room temperature.

The reaction of germanium(II) iodide with the appropriate 1,3-dienes, followed by treatment of the products with ethyl Grignard reagent, gave the novel 1,1-diethyl-1-germacyclopent-3-enes I, II, and III.[2a,b]

During a study of the action of various reagents on these compounds, two types of behavior were observed:



I II III

(1) (a) Fellow of the John Simon Guggenheim Memorial Foundation, 1968; (b) Postdoctoral Research Associate at M.I.T., 1967–1968; (c) National Science Foundation Graduate Fellow at M.I.T., 1967–1969.

(2) (a) P. Mazerolles and G. Manuel, *Bull. Soc. Chim. Fr.*, 327 (1966); (b) P. Mazerolles, G. Manuel, and F. Thoumas, *Compt. Rend.*, C, 267, 619 (1968).