This change in medium will tend to cause proton transfer in the transition state to be rather less complete than in the case of an entirely aqueous solution. The surprising point about kinetic solvent deuterium isotope effects for ortho ester hydrolysis is that they are larger than unity. This must indicate that, even if proton transfer is involved in the transition state, the transfer must be nearly complete. This is consistent with the observation of large Brønsted α values for general acid catalysis of ortho ester hydrolysis.[15,16]

While the above results suggest that proton transfer is involved in the transition state for ortho ester hydrolysis, it is unlikely that this process is solely rate determining. This would require that the decomposition of the protonated intermediate and the diffusion apart of the reaction products be much faster than the diffusion-controlled loss of a proton. In addition, it would require that the Brønsted α value for general acid-catalyzed ortho ester hydrolysis be unity; observed values are near 0.7.[15,16] All the data are best rationalized by depicting the first step in ortho ester hydrolysis as involving unimolecular carbon–oxygen bond cleavage concerted with proton transfer to the leaving group from the hydrated proton or other acid.

It ought to be specifically recognized that, for the case of phenyl orthoformate hydrolysis, protonation need not necessarily occur on oxygen. It is possible that the most basic site of this molecule is at aromatic carbon and the proton transfer to the aromatic rings may, then, be involved in the transition state.

Registry No.—Phenyl orthoformate, 16737-44-3.

Carbenoid Decomposition of Aryldiazomethanes with Lithium and Zinc Halides. A Convenient Method for the Synthesis of Arylcyclopropanes[1]

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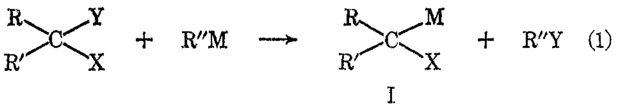
Received June 17, 1968

The carbenoid decompositions of phenyl-, *p*-tolyl-, and *p*-anisyldiazomethane catalyzed by lithium salts and zinc halides were investigated. The yields, stereochemistry, and relative rates of cyclopropane formation with olefins were studied and compared with other carbenoid systems. In all cases the thermodynamically less stable *syn* isomer was formed predominantly. The isomer ratios were found to be influenced by both cation and anion of the catalyst and also to be a function of the aryl substituents. Rates of the zinc halide catalyzed decompositions of the diazo compounds were measured by stopped-flow methods. The lifetimes of the organozinc intermediates were estimated by flow techniques. The preparative aspects of the zinc salt catalyzed reactions were explored and found to be superior to other methods of synthesizing arylcyclopropanes.

Considerable evidence has been accumulated in this and other laboratories that many reactions initially thought to be characteristic of divalent carbon compounds are also given by certain organometallics.[3-8] The common structural feature of the latter reagents is the binding of an electropositive element, usually a metal of group I or II, and an electronegative element or group to the same carbon atom. Because reactivities are qualitatively similar to those expected for carbenes, the name carbenoids has been suggested for such compounds.[4]

Several methods for the preparation of carbenoids have been reported, but the majority may be classified as acid–base reactions on alkyl halides as shown in reaction 1. Another method involves the reaction of diazoalkanes with metal salts. Many examples of this reaction type were examined by Wittig and collaborators, who postulated the formation of metal organic compounds according to reaction 2.[9]



(1)

(2)

It is worthwhile pointing out, however, that the proposed structures of carbenoids are based on rather circumstantial evidence and that a formulation such as I should be regarded as the simplest possible description which is in reasonable agreement with most of the observed chemistry. On the other hand, there exists a considerable body of evidence suggesting that I is an oversimplification and that specific solvent complexes and perhaps dimeric or even polymeric forms of I would be better descriptions of the actual structures.[4,6,10]

Since carbenoids are usually short-lived reaction intermediates, only a few of which have been isolated at very low temperatures,[6] little direct structural evidence has been reported so far. Also, very few quantitative studies exist which may serve as a basis of simple structure–reactivity relationships. For example, little is known about the effect on reactivity of changing either the cationic (M) or the anionic (X) leaving groups. Or even more fundamental, it is not even known whether methods 1 and 2 really do give the same carbenoid when all of the substituents and leaving groups are identical.

In a previous study carried out in this laboratory,

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[1] Supported by National Science Foundation Grants GP-4214 and GP-7043.

[2] Uniroyal Predoctoral Research Fellow, 1967–1968.

[3] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **82**, 5723 (1960).

[4] G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).

[5] G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).

[6] G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

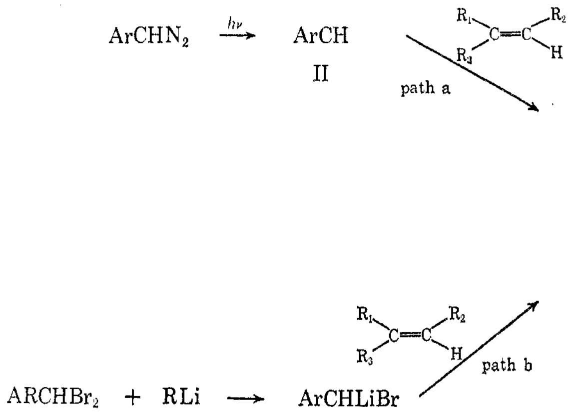
[7] E. Müller, H. Kessler, and B. Zeeh, *Fortschr. Chem. Forsch.*, **7**, 128 (1967).

[8] D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1965).

[9] (a) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961); (b) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

[10] G. L. Closs and C. H. Lin, to be published.

reactivities of arylcarbenes were compared with those of the corresponding arylcarbenoids by examining the additions of these reagents to olefins in the cyclopropane-forming reaction.[4] Specifically arylcarbenes (II) were produced by photolyses of the corresponding aryldiazomethanes while the arylcarbenoid systems III were generated from the benzal bromides in halogen–lithium exchange reactions with alkyllithiums (reaction 3a and b). Stereoselectivities as expressed by the ratios of the epimeric cyclopropanes IV and V were measured as well as relative addition rates to a set of olefins with varying degree of alkyl substitution. It was found that the product ratios in the carbene reactions were significantly different from those observed in the carbenoid system with the latter usually exhibiting greater selectivity.



(3)

In the present study we have generated arylcarbenoids from the corresponding aryldiazomethanes with a number of salts, particularly lithium and zinc halides. The aim of this work was to explore the preparative aspects of the reactions as well as to obtain information on the influence of both cationic and anionic leaving groups in carbenoid chemistry.

Results

Product Studies.—Because of the obvious comparative value with reaction **3b**, lithium halide catalyzed decomposition of diazo compounds was investigated first. In preliminary experiments it was found that anhydrous lithium bromide catalyzes the carbenoid decomposition of diazomethane and that methylene transfer to double bonds occurs with modest efficiency. For example, up to 20% norcarane can be isolated from a reaction mixture containing cyclohexene. Polymethylene accounts for the remainder of the product balance.

The reaction with phenyldiazomethane under identical conditions was found to be very slow and cyclopropane formation in the presence of olefins proceeded with poor yields. Nitrogen elimination is faster from p-tolyldiazomethane although the yields of cyclopropanes are still poor. The major product of the reaction is 4,4′-dimethylstilbene in addition to small quantities of 4,4′-dimethylbenzalazine. The cyclopropanes were isolated by chromatography and quantitative analyses were carried out by gas–liquid partition chromatography (glpc). The products were characterized by direct comparison with samples prepared by methods previously described.[3] In all cases the cyclopropanes were formed by stereospecific *cis* additions and, when epimer pairs were possible, both compounds were identified. The configurational assignments (*syn* for the isomer in which the aryl group has the *cis* relationship to the largest number of alkyl groups) are based on nmr and equilibration studies as previously reported.[4] The third row of Table I gives the *syn/anti* isomer ratios of cyclopropanes obtained from additions to four olefins. For comparison, the corresponding ratios observed in reactions with photolytically generated carbenes are listed in the first row, while the second row of the table gives the results from the lithium–halogen exchange reaction 3b. The ratios differ somewhat from those reported in ref 4 because, in contrast to the older work, reaction conditions were chosen to be similar to those of the lithium bromide catalyzed reactions.

Table I

syn/anti Ratios of Carbenoid Additions to Olefins
(R = p-Tolyl)[a]

	Reactant			
Method				
RCHN$_2$ + $h\nu$	1.2	1.7	1.2	1.2
RCHBr$_2$ + CH$_3$Li	1.3	2.3	1.3	1.6
RCHN$_2$ + LiBr	2.0	7.5	2.4	0.8
RCHN$_2$ + LiClO$_4$		12.0	1.8	
RCHN$_2$ + ZnCl$_2$	3.5	6.6	1.3	4.2
RCHN$_2$ + ZnBr$_2$	4.9	8.5	1.5	4.9
RCHN$_2$ + ZnI$_2$	5.4	21.0	2.6	5.9
RCHN$_2$ + MgBr$_2$		10.0		
RCHN$_2$ + CoBr$_2$	3.4	18.0	2.5	
C$_6$H$_5$C(=N$_2$)CH$_3$ + ZnCl$_2$		2.0		

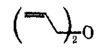
[a] The *syn* configuration is defined as the configuration in which the largest number of alkyl groups has a *cis* relationship with the phenyl group.

Other lithium salts, such as lithium perchlorate and lithium iodide, also function as catalysts in the decomposition of p-tolyldiazomethane. Cyclopropane yields, however, were not any better than in the lithium bromide experiments.

Excellent yields of cyclopropanes were obtained in reactions catalyzed by zinc halides. At room temperature decolorization of the diazo compounds is essentially instantaneous. Both stoichiometric and catalytic quantities of zinc halides give good yields of cyclopropanes. Table II lists the results obtained for a variety of olefins and three aryldiazomethanes. The stereoselectivities of the reactions are included in the table and for comparative purposes are also listed in Table I.

TABLE II

REACTION OF ARYLDIAZOMETHANES ($RC_6H_4CHN_2$) WITH ZINC HALIDES IN THE PRESENCE OF OLEFINS[a]

R	Olefin	ZnX_2	Yield,[b] %	*syn/anti* isomer ratio
p-H		$ZnCl_2$	70	2.8
p-H		$ZnCl_2$	90	3.0
p-H		$ZnBr_2$	70	4.7
p-H		$ZnBr_2$	70	
p-Me		$ZnBr_2$	52	1.5
p-Me		ZnI_2	60	21
p-Me		$ZnBr_2$	50	4.9
p-MeO		$ZnCl_2$	50	6.7
p-MeO		ZnI_2	40	4.4
p-MeO		$ZnBr_2$	37	53
p-MeO		$ZnCl_2$	37	34
p-MeO		$ZnCl_2$	16	2.7
p-MeO		$ZnBr_2$	14	
p-MeO		$ZnCl_2$	5	

[a] Zinc halides were used in stoichiometric amounts. [b] Based on $ArCHN_2$ used.

The decomposition of phenyl- and *p*-tolyldiazomethane in ether in the absence of olefins gave *cis*- and *trans*-stilbenes and 20% a product (VI) derived from insertion into the α-CH bond of ether. No evidence for insertion into the β-CH bond was found. The insertion reaction must be slow compared with olefin addition because VI was not found in runs containing olefins.

$$ArCH_2\overset{CH_3}{\overset{|}{C}}HOC_2H_5$$

VI

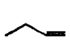
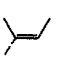
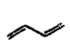
Other catalysts which were tried in the addition reaction were magnesium bromide and cobaltous bromide. Both were found to catalyze carbenoid cyclopropane formation with the latter being much more efficient than the former. The *syn/anti* isomer ratios of the *cis*-butene adducts as obtained by these catalysts are included in Table I.

Other aryldiazomethanes included in this study were diphenyldiazomethane, 9-diazofluorene, and 1-phenyldiazoethane. With zinc salts as catalysts, olefin adducts were obtained from diazofluorene and 1-phenyldiazoethane in modest yields, while, in agreement with earlier observations,[11] only traces of cyclopropanes were formed from diphenyldiazomethane and zinc salts.

Kinetic Studies.—The relative rates of the additions of the various reactive intermediates to a set of olefins were determined by standard competition methods with excesses of olefins. The results, normalized to *trans*-2-butene, are listed in Table III, which also includes the corresponding relative addition rates of the free carbene as generated by photolysis and the rates obtained from the benzal bromide–alkyllithium system. Temperature and solvent systems are comparable in all relative rate studies listed in the table.

TABLE III

RELATIVE RATES OF CARBENOID OLEFIN ADDITIONS (R = *p*-TOLYL)[a]

	Reactant					
Method						
$RCHN_2 + h\nu$	0.89	1.00	1.76	0.83	2.40	1.7
$RCHBr_2 + CH_3Li$	0.72	1.00	1.35	1.35	1.50	1.9
$RCHN_2 + LiBr$	0.28	1.00	1.65	3.62	9.6	16.0
$RCHN_2 + ZnCl_2$	0.43	1.00	1.44	1.82	2.0	1.2
$RCHN_2 + ZnBr_2$	0.44	1.00	2.11	2.54	2.7	1.4
$RCHN_2 + ZnI_2$	0.51	1.00	4.96	3.90	5.0	1.5
$RCHN_2 + CoBr_2$	0.37	1.00	2.93	2.55	2.20	

[a] Each system is independently normalized to *trans*-2-butene.

Information on the lifetime of possible reaction intermediates in the zinc halide catalyzed reactions was obtained in several ways. First in a qualitative experiment, phenyldiazomethane in ether was allowed to react at −55° with zinc chloride until the red color of the diazo compound had disappeared. Introduction of *cis*-2-butene to this mixture and subsequent warming gave 30% of the cyclopropane adducts. Stopped-flow and continuous-flow methods were used to estimate the rates of formation and decomposition of the reactive intermediate. The reaction of phenyldiazomethane with zinc chloride was monitored by following the absorption at 490 mμ in a stopped-flow spectrophotometer. Measurements of the disappearance of the diazo-stretching frequency in the infrared region (2058 cm^{-1}) gave results essentially identical with those obtained from the visible spectrum. The reaction was found to be pseudo first order, following the rate law, $v = k_2[ArCHN_2][ZnCl_2]_0$, where $[ZnCl_2]_0$ is the initial zinc chloride concentration. Table IV lists the results of the kinetic runs for phenyldiazomethane and *p*-tolyldiazomethane.

Semiquantitative information on the lifetime of the reactive intermediate was obtained in continuous-flow experiments. The intermediate was generated by mixing efficiently two syringe driven ether solutions, one containing aryldiazomethane and the other zinc chloride, in a four-jet mixing chamber. The resulting solution travelled with known velocity through a capillary into a flask containing excess cyclohexene. The final reaction mixture was analyzed by glpc for norcaranes. The residence time of the solution in the capillary was varied by changing the motor speed of the syringe drive. The yields of norcaranes obtained from phenyldiazomethane and *p*-tolyldiazomethane as function of residence time are recorded in Table V. A meaningful kinetic analysis of the data would be possible only if both of the following conditions were

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(11) D. E. Applequist and H. Babad, *J. Org. Chem.*, **27**, 288 (1962).

Table IV

Rates of Reactions of Aryldiazomethanes with Zinc Chloride in Ether at 20°

$[ArCHN_2]$, M	$[ZnCl_2]_0$, M	k_1,[a] sec^{-1}	k_2,[b] l. M^{-1} sec^{-1}	Method[c]
		$C_6H_5CHN_2$		
0.0075	0.0084	0.199	24	A
0.0075	0.0084	0.192	23	A
0.0075	0.0184	0.375	20	A
0.0075	0.0184	0.374	20	A
0.0075	0.0553	1.61	29	A
0.0075	0.0553	1.52	28	A
0.0075	0.0955	2.47	26	A
0.0075	0.0955	2.65	28	A
0.0021	0.0100	0.24	24	B
		p-$CH_3C_6H_4CHN_2$		
0.0050	0.043	24.0	555	A

[a] Pseudo-first-order rate constants. [b] $k_2 = k_1/[ZnCl_2]_0$. [c] Method A, reaction monitored by absorption change at 490 mμ; method B, monitored at 2058 cm^{-1}.

Table V

Yields of 7-Arylnorcaranes Generated in Flow Experiments at 20°

Time, sec[a]	0.12	0.57	1.17	1.86	2.6	4.4
% yield of 7-phenylnorcarane[b]	71	78	73	62	58	56
Time, sec[a]	0.25	0.39	1.1	3.3		
% yield of 7-(*p*-tolyl)norcarane[c]	36	21	3	0.3		

[a] The time listed is the calculated residence time of the solution between mixing of the zinc chloride and aryldiazomethane solution and the quenching with cyclohexene. [b] Concentration of phenyldiazomethane, 0.012 *M;* zinc chloride, 0.053 *M.* [c] Concentration of *p*-tolyldiazomethane, 0.0063 *M;* zinc chloride, 0.027 *M.*

met: (i) the reaction time of the aryldiazomethane with zinc chloride must be very short relative to the residence time of the solution in the capillary; (ii) the trapping of the intermediate by cyclohexene must be quantitative and must occur rapidly compared to other decay processes. Neither of these assumptions can be expected to hold. This is especially true for the first assumption as a comparison of Table IV and V shows. Consequently no attempts were made to analyze the data in terms of specific rate constants. However, it can be stated with confidence that under the reaction condition chosen, the lifetime of the intermediate generated from *p*-tolyldiazomethane ($t_{1/2} \simeq 0.2$ sec) is significantly shorter than that of the intermediate derived from phenyldiazomethane ($t_{1/2} \simeq 10$ sec).

Discussion

Because of poor yields, the lithium bromide catalyzed decompositions of aryldiazomethanes in the presence of olefins has little value for the preparation of arylcyclopropanes. However, the results obtained on the stereochemistry of the addition and the relative rate studies are of interest because they demonstrate that two different intermediates are generated in the lithium bromide catalyzed reaction (3a) and in the lithium–halogen exchange reaction (3b) although they lead formally to the same intermediate. The stereoselectivity of the species generated by lithium bromide is generally larger and its relative addition rates to a set of olefins show a larger spread than those observed for reaction 3b. The relative rate data suggest that the intermediate formed in the lithium bromide catalyzed reactions has a more pronounced electrophilic character. This difference in reactivity is in agreement with a reaction path outlined in reaction 4. The lithium salts

$$\begin{aligned} \mathrm{ArCHN_2 + LiBr} &\longrightarrow \mathrm{ArCHLi\overset{+}{N}_2\,Br^-} \\ &\qquad\quad \mathrm{VII} \\ \mathrm{VII} &\longrightarrow \mathrm{Ar\overset{+}{C}HLi\,Br^- + N_2} \\ &\qquad\quad \mathrm{VIII} \\ \mathrm{VIII} &\longrightarrow \mathrm{ArCHLiBr} \\ \text{olefins} + \mathrm{VIII} &\longrightarrow \text{cyclopropanes} \end{aligned} \qquad (4)$$

function as Lewis acids with the formation of an α-lithiodiazonium ion pair (VII) which can be expected to lose nitrogen rapidly to form the α-lithiocarbonium ion pair VIII. The latter may collapse to carbenoid III or may itself react in carbenoid additions. The fact that lithium perchlorate catalyzes the carbenoid additions suggests strongly that an ion pair like VIII would be able to form cyclopropanes presumably *via* a bridged transition state similar to the one suggested for other carbenoid reactions.[4] On the other hand it is entirely possible that the difference in reactivities of the two reaction intermediates should be attributed to a different degree of aggregation of either the carbenoid with itself or with lithium salts.

The zinc halide catalyzed decomposition of aryldiazomethane in the presence of olefins appears to have potential as a preparative method. With simple olefins the yields are generally as good or better than those obtained with previously described methods.[4,12] It is the simplicity of the reaction which makes it superior to photochemical methods giving the equivalent products. Furthermore, the reaction is valuable for the preparation of the thermodynamically less stable *syn* isomers which are the predominant reaction products particularly with zinc iodide as a catalyst. The corresponding *anti* isomers can always be obtained from the *syn* compounds by base-catalyzed isomerization.[4,13]

The predominant *syn* stereochemistry of all reaction types studied in this investigation is in agreement with previously studied aryl carbenoid systems.[4,13,14] For a given catalyst and olefin, for example, zinc bromide and *cis*-2-butene, electron-donating groups in the aryl substituent increase the *syn/anti* ratio from 4.7 for the unsubstituted phenyl ring to 8.5 in the *p*-tolyl and to 53 in the *p*-anisyl system. A qualitatively similar but much less pronounced trend has been observed for the addition of the free arylcarbenes as generated by photolysis from the aryldiazomethanes, and has been attributed to either charge transfer or dipolar interactions in the transition state.[4,14] The current results are in agreement with this model although steric factors caused by the metal halide may be partly responsible for the predominant *syn* addition. If the aryl substituent is kept constant but the halide ion of the zinc salt is varied it is found that chloride ion

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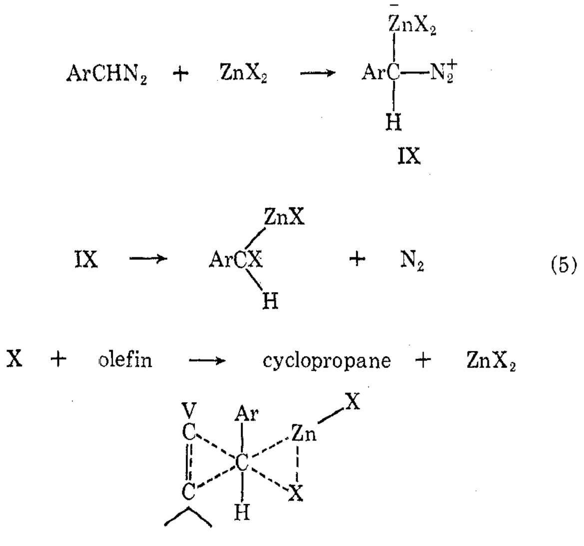
[12] (a) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 1579 (1966); (b) H. Kristinsson, *Tetrahedron Lett.*, 2343 (1966).

[13] R. A. Moss, *J. Org. Chem.*, **30**, 3261 (1965).

[14] G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Amer. Chem. Soc.*, **84**, 4985 (1962).

causes the smallest *syn/anti* ratio and iodide the largest with bromide ion in between. A similar trend is observed in the relative rate data in which among the zinc salts the iodide give the largest spread. Presumably both trends have the same origin, namely, an increasing electron deficiency on the carbenoid carbon reflecting greater carbon–halogen bond breaking in the transition state with increasing atomic number of the halide ion. This would lead to a more pronounced electrophilic behavior, and if charge transfer or dipolar attractions are responsible for the stereochemistry, to greater *syn/anti* isomer ratios. The influence of substituents on the phenyl ring on the *syn/anti* ratios is also consistent with this interpretation.

The over-all mechanism of the zinc halide catalyzed reaction is probably close to that represented in reaction 5 and analogous to that proposed by Wittig and Schwarzenbach.[9a] The first step represents a Lewis acid–base reaction and its velocity should be influenced by the basicity of the diazo compound. This is experimentally observed in the much greater decomposition rate of *p*-tolyldiazomethane compared to phenyldiazomethane. The loss of nitrogen from intermediate IX is presumably very fast since infrared monitored stopped flow experiments failed to detect any intermediate with a shifted diazo band. The reaction of X with the olefin probably proceeds through a similar transition state (XI) as that proposed for the Simmons–Smith reaction.[15]



$$\mathrm{ArCHN_2 + ZnX_2 \longrightarrow Ar\overset{\overset{-}{Z}nX_2}{\underset{H}{C}}{-}N_2^+}$$

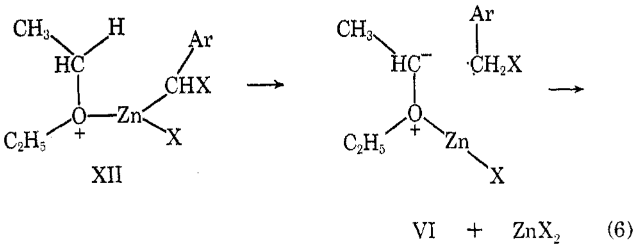
$$\mathrm{IX \longrightarrow Ar\overset{ZnX}{\underset{H}{C}}X + N_2} \qquad (5)$$

$$\mathrm{X + olefin \longrightarrow cyclopropane + ZnX_2}$$

XI

It should be pointed out that the observation that the intermediate X in the *p*-tolyl series has a shorter lifetime than the unsubstituted molecule requires also a faster olefin addition for the *p*-tolyl carbenoid, since the yields of cyclopropanes are comparable in both series. This is in spite of the fact that *p*-tolyl carbenoid appears to give a greater stereochemical discrimination and might therefore be assigned a greater stability. This suggests a note of caution against the generally accepted practice of assigning ground-state stabilities of reaction intermediates by comparing abilities to discriminate among various substrates. Of course, absolute rates and discriminating abilities are determined by the energies of the ground states as well as the transition states, and in the absence of information on one it is highly dubious to speculate about the other.

The unusually high yield of ether insertion product VI produced in the absence of olefins deserves some comment. A similar product is formed in the Simmons–Smith reaction[15] but in extremely low yield. The high specificity for the α position of the ether molecule suggests a collapse of the etherate complex XII according to reaction 6.



Experimental Section

Infrared spectra were determined on a Beckman IR-7 instrument in carbon tetrachloride solutions. Mass measurements were made by peak matching on a MS-9 mass spectrometer. The nmr spectra were recorded on Varian A-60A or A-56-60 spectrometers using solutions in carbon tetrachloride with internal tetramethylsilane (TMS) as standard. Chemical shifts are reported in parts per million (ppm) downfield from TMS, with the number in parentheses indicating the number of protons causing the signal. The letter immediately following the parentheses designates the multiplicity of the signal: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Gas–liquid partition chromatography (glpc) was carried out by use of an Aerograph A-90-P instrument, equipped with a thermoconductivity detector. Columns were made from various stationary phases on Chromosorb W packed into 0.25-in.-diameter copper tubing of various lengths.

Gaseous olefins were Matheson reagent grade or Phillips 66 99% grade and were used without further purification. Liquid olefins were distilled from sodium and filtered through an alumina column before use. Aryldiazomethanes were prepared as described previously.[4,5]

Norcarane.—Lithium bromide (1.0 g) was dried in a three-necked flask by heating to 140° (0.002 mm) for 4 hr. Dried nitrogen was then admitted and the lithium bromide was dissolved in dried ether (10 ml). To the resulting solution was added diazomethane (7 mmol) in cyclohexene (20 ml) in small portions allowing the mixture to decolorize after each addition. The total addition time was 3 hr. The resulting solution was washed with water and the interphase of polymethylene was filtered off. The solution was analyzed by glpc on an 8-ft column containing TCP as stationary phase. Norcarane was identified by trapping and comparison of its nmr and ir spectra with those of an authentic sample. The yield (1.33 mmol, 19%) was determined by standardization of the glpc trace.

Decomposition of *p*-Tolyldiazomethane with Lithium Bromide.—Lithium bromide (1.0–1.3 g) was dried under reduced pressure (0.01 mm) at 140°. Ether (40 ml) was added and the resulting mixture was stirred for 15 min. The flask was then equipped with a Dry Ice condenser and the olefin (20 ml) was distilled into the flask. *p*-Tolyldiazomethane in *n*-pentane (2 *M*) was added in small portions to the magnetically stirred mixture. The addition of the solution (1 ml) was carried out over a period of 8–10 hr, while the reaction mixture was held at 0°. The reaction mixture was worked up washing with water followed by removal of the solvent and filtration in pentane over a short alumina column. Separation of the isomeric cyclopropanes was carried out by glpc on an 8-ft silicon 710 column. Identification of the products was made by glpc retention times and trapping of the compounds and comparison of the nmr spectra with those of authentic samples. Yields of cyclopropanes were between 1 and 5% as determined by standardized glpc runs. The isomer ratios as listed in Table I were determined from the glpc peak areas.

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[15] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); H. E. Simmons and E. P. Blanchard, *ibid.*, **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

Syntheses of Arylcyclopropanes from Aryldiazomethanes and Zinc Halides. Method A.—Zinc halide (10 mmol) was heated in a three-necked flask under reduced pressure (0.1 mm) until the salt began to fuse. After cooling a Dry Ice condenser and addition funnel were attached and ether (10 ml) was introduced dissolving the zinc halide. Gaseous olefins (15 ml) were then distilled into the flask by cooling it to −10° while liquid olefins were introduced through the addition funnel. Aryldiazomethane (10 mmol) was dissolved in anhydrous ether and was added dropwise to the magnetically stirred solution. Nitrogen evolution and decolorization were instantaneous. After addition was complete (10 min), stirring was continued for another 5 min. The solvents were then removed under reduced pressure and the residue was washed with water (5 ml) and extracted with pentane. The product was isolated by distillation under reduced pressure and quantitative analysis was carried out by glpc.

Method B.—The procedure was essentially the same as the one described above except that an ether solution of zinc halide was added with a syringe in catalytic amounts. Zinc halide consumed was usually less than 10% of the aryldiazomethane used. The reaction mixture was worked up in the same manner as described above. Previously described arylcyclopropanes[4] were identified by comparison of their glpc retention times on the appropriate columns[4] and nmr spectra with those of authentic samples. Yields are listed in Table II. Newly synthesized arylcyclopropanes are described below.

1-Phenyl-2-vinylcyclopropane was obtained in 70% yield from phenyldiazomethane, butadiene, and zinc chloride using method B at −10°. The stereoisomers were separated on a 34-ft QF-1 column at 170° with the *syn* isomer having the shorter retention time. Spectral properties of the syn isomer are as follows: nmr 7.1 (5) broad s, 4.65–5.15 (3) m, 2.0–2.5 (1) m, 1.6–2.1 (1) m, 0.8–1.35 (2) m; ir 1640 (medium), 900 cm^{-1} (strong). Mass spectrum calcd for $C_{11}H_{12}^+$: 144.0939. Found: 144.0941. Spectral properties of the *anti* isomer are as follows: nmr 7.0–7.15 (5) m, 4.75–5.7 (3) m, 1.3–2.0 (2) m, 0.9–1.3 (2) m, ir 1640 (medium), 900 cm^{-1} (strong). Mass spectrum calcd for $C_{11}H_{12}^+$: 144.0939. Found: 144.0940.

7-*p*-Anisylnorcarane was obtained in 37% yield from *p*-anisyldiazomethane, cyclohexene, and zinc chloride at −10° using method A. Glpc analysis on a 9-ft QF-1 column indicated that practically all the product has the *syn* configuration: nmr 7.1 (2) d, 6.7 (2) d, 3.7 (3) s, 0.3–2.1 (11) m. Mass spectum calcd for $C_{14}H_{18}O^+$: 202.1358. Found: 202.1363.

Treatment of the *syn* isomer with potassium *t*-butoxide as described previously[4] gave the *anti* isomer which had the longer retention time on the QF-1 column: nmr 6.8 (2) d, 6.6 (2) d, 3.67 (3) s, 0.95–2.15 (11) m. Mass spectrum calcd for $C_{14}H_{18}O^+$: 202.1358. Found: 202.1357.

1-(*p*-Anisyl)-2,2,3-trimethylcyclopropane was obtained in 40% yield from *p*-anisyldiazomethane, 2-methyl-2-butene, and zinc iodide at −10° using method B. The two isomers were separated on a two-stage column containing SF-96 and QF-1 with the *anti* isomer having the shorter retention time: nmr (*syn* isomer) 7.04 (2) d, 6.7 (2) d, 3.74 (3) s, 1.5–1.8 (1) m, 1.2 (3), s, 0.9 (6) d; nmr (*anti* isomer) 7.0 (2) d, 6.7 (2) d, 3.74 (3) s, 1.18 (6) broad s, 0.75 (3) s.

1-(*p*-Anisyl)-2-vinylcyclopropane was obtained from *p*-anisyldiazomethane, butadiene, and zinc chloride in 50% yield at −10° using method A. The stereoisomers were separated on a 6-ft SFXF-1150 column with the *syn* isomer having the shorter retention time. Spectral properties of the *syn* isomer are as follows: nmr 7.02 (2) d, 6.67 (2) d, 4.7–5.15 (3) m, 3.67 (3) s, 1.9–2.4 (1) m, 1.5–2.0 (1) m, 0.8–1.3 (2) m. Mass spectrum calcd for $C_{12}H_{14}O^+$: 174.1045. Found: 174.1048. Spectral properties of the *anti* isomer are as follows: nmr 6.92 (2) d, 6.66 (2) d, 4.7–5.7 (3) m, 3.72 (3) s, 0.8–2.0 (4) m. Mass spectrum calcd for $C_{12}H_{14}O^+$: 174.1045. Found: 174.1050.

2-(*p*-Anisyl)cyclopropylmethylallyl ether was obtained in 16% yield from *p*-anisyldiazomethane, diallyl ether, and zinc chloride at 30° using method A. The isomers were separated on a 6-ft SE-30 column with the *syn* isomer having the shorter retention time. Spectral properties of the *syn* isomer are as follows: nmr 6.97 (2) d, 6.55 (2) d, 5.35–5.85 (1) m, 4.75–5.15 (2) m, 3.62 (5) m, 2.85–3.1 (2) m, 1.85–2.25 (1) m, 1.1–1.5 (1) m, 0.5–1.1 (2) m. Mass spectrum calcd for $C_{14}H_{18}O_2^+$: 218.1307. Found: 218.1304. Spectral properties of the *anti* isomer are as follows: nmr 6.77 (2) d, 6.54 (2) d, 5.5–6.0 (1) m, 4.9–5.3 (2) m, 3.8–3.0 (2) m, 3.65 (3) s, 3.3 (2) d, 0.7–2.0 (4) m. Mass spectrum calcd for $C_{14}H_{18}O_2^+$: 218.1307. Found: 218.1304.

1-(*p*-Anisyl)-2,2,3,3-tetramethylcyclopropane was obtained in 14% yield from 2,3-dimethyl-2-butene, *p*-anisyldiazomethane, and zinc bromide at −30° using method B. Final purification was achieved by trapping from a 3-ft SF-96 column: nmr 6.95 (2) d, 6.66 (2) d, 3.70 (3) s, 1.45 (1) s, 1.22 (6) s, 0.90 (6) s. Mass spectrum calcd for $C_{14}H_{20}O^+$: 204.1514. Found: 204.1501.

2-(*p*-Anisyl)methylenecyclopropane was obtained in 5% yield from allene, *p*-anisyldiazomethane, and zinc chloride using method A. The product was purified by glpc on a 6-ft SFXF-1150 column: nmr 6.94 (2) d, 6.63 (2) d, 5.4–5.6 (2) m, 3.7 (3) s, 1.0–2.5 (3) m. Mass spectrum calcd for $C_{11}H_{12}O^+$: 160.0888. Found: 160.0882.

Delayed Addition of 2-Butene to the Reaction Mixture of Phenyldiazomethane and Zinc Chloride.—Zinc chloride (2.5 g, 20 mmol) was dried and dissolved in ether (230 ml) as described under method A. The resulting solution was cooled from −50 to −60° and phenyldiazomethane (4.7 mmol) in ether (10 ml) was added in small portions over a period of 90 min. After the addition was complete the color of the diazo compound was allowed to disappear and the solution was then cooled to −70°. *cis*-2-Butene (14 ml) was introduced and the reaction mixture was allowed to warm to room temperature within 20 min. *syn*- and *anti*-1-phenyl-*cis*-2,3-dimethylcyclopropanes were isolated as described under method A in 30% yield.

Relative Rates of Lithium Bromide Catalyzed Additions.—Lithium bromide (1.0 g), dried as described above, was dissolved in anhydrous ether (40 ml). Two olefins (approximately 12 g) were then admitted in known mole ratios which were determined by weighing in closed cold traps. The flask was equipped with a Dry Ice condenser to prevent escape of the olefins. *p*-Tolyldiazomethane (1.3–1.5 mmol) in pentane (1 ml) was added in small portions to the magnetically stirred solution. The reaction temperature was kept at 0° and the total addition time was between 6 and 10 hr. The excess olefin was then allowed to evaporate and the reaction mixture was filtered through a short (3 in.) alumina column which was washed with pentane to avoid fractionation. Analysis of the cyclopropanes was carried out by glpc and the relative rates were calculated from the peak areas using the relationship $k_1/k_2 = (O_2/O_1)(A_1/A_2)$, where O_2/O_1 are the olefin mole ratios and A_1/A_2 are the standardized glpc peak areas of the respective cyclopropanes. The following stationary phases were used to analyze the cyclopropanes obtained from the following olefin pairs: QF-1, *cis*-2-butene–*trans*-2-butene, isobutene–1-butene, 1-butene–*trans*-2-butene, silicone 710, *trans*-2-butene–isobutene, *cis*-2-butene–isobutene, 2-methyl-2-butene–*trans*-2-butene; Carbowax 20M, butadiene–*trans*-2-butene.

Relative Rates of Cyclopropane Formation from *p*-Methylbenzal Bromide, Olefins and Methyllithium.—The procedure was essentially the same as the one described in ref 4 with the following modifications. *p*-Methylbenzal bromide (1 mmol) was dissolved in anhydrous ether (40 ml) under a protective atmosphere of dry nitrogen. To this solution were then added two olefins (10–12 g) in known mole ratios which were determined by weighing in closed cold traps. Methyllithium (2 mmol) in ether (2 ml) was added to the well-stirred solution which was kept at 0° over a period of 15 min. Work-up of the solution followed the previously described procedure.[4] Analysis by glpc and calculation of the relative rates were performed as described above. The results are listed in Table III.

Relative Rates of Cyclopropane Formation from *p*-Tolyldiazomethane, Olefins, and Zinc Halides and Cobaltous Bromide.—Zinc halide (1 mmol) dissolved in anhydrous ether (19 ml) was introduced into a flask fitted with a Dry Ice condenser containing two olefins (10 ml) in a known mole ratio determined by weighing. The solution was cooled to −10° and *p*-tolyldiazomethane (1 mmol) in anhydrous ether (2 ml) was added dropwise with rapid stirring. A few minutes after the addition was complete most of the excess olefins and solvents were evaporated, the salts washed out with water (5 ml), and the residue was analyzed by glpc. All olefins listed in Table III were run against *trans*-2-butene and double checked with isobutene. Stationary phases for the glpc analysis for the adduct were SE-30 except for the following pairs: *trans*-2-butene–1-butene, *trans*-2-butene–butadiene, isobutene–1-butene, and isobutene–butadiene which were analyzed on QF-1 columns. In the case of cobaltous bromide as a catalyst, owing to lower solubility, a saturated ether solution was used and the reaction was allowed to proceed over a period of 10 min.

Rates of Reactions of Aryldiazomethanes with Zinc Chloride in Stopped-Flow Apparatus.—The stopped-flow spectrometer was similar to those described previously[16] and consisted of a Beckman DU monochromator, a four-jet mixing chamber constructed of Hastalloy-C2 with a quartz exit tube serving as absorption cell (0.7 mm i.d.), a photomultiplier (EMI 6256S) with associated power supply, John Fluke Mfg. Co., Model 409A, a Tektronix RM 503 oscilloscope with time base, and a Fairchild camera using Polaroid film. The solutions were pressed through the mixing chamber by a motor-driven syringe drive equipped with magnetic clutch. The mixed solution was taken up in a 50-ml syringe whose barrel activated the time sweep of the scope and disengaged the clutch. Syringes and mixing chamber were jacketed and were kept at 20° by circulating water. The individual runs were carried out by carefully filling the syringes with the solutions of aryldiazomethane and zinc chloride in ether with the concentrations stated in Table IV, care being taken to avoid gas bubbles. The time base of the oscilloscope was chosen to observe the reaction over several half-lives and the results were evaluated from the Polaroid photographs. The results are listed in Table IV.

Infrared monitored runs were carried out on a Beckman IR-7 instrument using a standard Beckman sodium chloride cell. The top exit of the cell was fitted with a Teflon four-jet mixing chamber connected to two syringes which were operated manually. The bottom exit of the cell was connected to another syringe with polyethylene tubing. The flow was stopped manually by clamping the exit tubing. The spectrometer was set at the maximum of the diazo-stretching vibration absorption band (2058 cm^{-1}) and after the flow of the solution had been stopped the decay of this band was monitored by recording a trace on the fast-moving recorder chart. The results listed in Table IV are the average of several runs. In another experiment the region between 2500 and 1700 cm^{-1} was rapidly scanned to detect any band possibly to be associated with an intermediate. None was found.

Continuous-Flow Experiments.—The continuous-flow apparatus consisted of a motor-driven syringe drive equipped with two calibrated syringes connected with polyethylene tubing to a four-jet mixing chamber constructed of Hastalloy C-2. The exit of the mixing chamber was attached to exchangeable capillaries (0.4 cm i.d.) varying in length from 2 to 26 cm. The capillary tip dipped into a flask containing well-stirred cyclohexene. The syringe drive mechanism was equipped with an electrical timer activated by a switch at the beginning of the run and stopped by another switch at the end of the syringe drive. The residence time (τ) of the solution in the capillary was calculated according to $\tau = al/Vt$, where a is the cross section of the capillary, l is its length, V is the total volume delivered during the experiment, and t is the time of the run.

Runs were carried out with phenyldiazomethane and *p*-tolyldiazomethane with zinc chloride in the concentrations stated in Table V. The reaction mixture was then analyzed by calibrated glpc for norcaranes and the yield calculated in a standard manner. The results are listed in Table V.

Isolation of 1-Phenyl-2-ethoxypropane.—The combined reaction mixtures of the stopped-flow experiments with phenyldiazomethane were washed with water and the solvent was evaporated. The residue was extracted with carbon tetrachloride and bromine in carbon tetrachloride was added to a slight excess to precipitate unsaturated products. The solution was filtered and analyzed by glpc on a 5-ft SE-30 column. The major component was trapped in the conventional manner: nmr 7.1 (5) s, 3.2–3.7 (3) m, 2.85 (1) d of d, 2.5 (1) d of d, 1.1 (3) t, 1.08 (3) d. Mass spectrum calcd for $C_{11}H_{16}O^+$: 164.1201. Found: 164.1207.

1-*p*-Tolyl-2-ethoxypropane.—The combined reaction mixtures of the stopped-flow experiments with *p*-tolyldiazomethane were worked up as described above and the product was isolated by glpc on a 5-ft SE-30 column: nmr 7.0 (4) s, 3.15–3.7 (3) m, 2.3–3.0 (2) m, 2.3 (3) s, 1.12 (3) t, 1.05 (3) d. Mass spectrum calcd for $C_{12}H_{18}O^+$: 178.1358. Found: 178.1345.

Registry No.—*sym*-1-Phenyl-2-vinylcyclopropane, 17955-08-7; *anti*-1-phenyl-2-vinylcyclopropane, 17955-09-8; *sym*-7-*p*-anisylnorcarane, 17955-10-1; *anti*-7-*p*-anisylnorcarane, 17955-11-2; *sym*-1-(*p*-anisyl)-2,2,3-trimethylcyclopropane, 17955-12-3; *anti*-1-(*p*-anisyl)-2,2,3-trimethylcyclopropane, 17955-13-4; *sym*-1-(*p*-anisyl)-2-vinylcyclopropane, 17955-14-5; *anti*-1-(*p*-anisyl)-2-vinylcyclopropane, 17955-15-6; *sym*-2-(*p*-anisyl)cyclopropylmethylallyl ether, 17955-16-7; *anti*-2-(*p*-anisyl)cyclopropyl methylallyl ether, 17955-17-8; 1-(*p*-anisyl)-2,2,3,3-tetramethylcyclopropane, 17953-95-6; 2-(*p*-anisyl)methylenecyclopropane, 17953-96-7; 1-phenyl-2-ethoxypropane, 17953-97-8; 1-*p*-tolyl-2-ethoxypropane, 17953-98-9.

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Chlorination of Unsymmetrical Sulfides[1]

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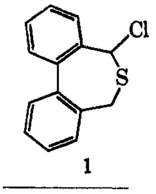
Received July 15, 1968

The chlorination of unsymmetrical aliphatic sulfides by N-chlorosuccinimide (NCS) in carbon tetrachloride has been investigated. The resulting mixtures of α-chloro sulfides have been analyzed using nmr spectrometry. The reaction of benzyl *t*-butyl sulfide and benzyl *p*-methoxybenzyl sulfide with sulfuryl chloride results in carbon–sulfur bond cleavage; reaction of these substrates with NCS affords α-chloro sulfides. Ratios of chlorinated products from the reactions of ethyl methyl sulfide with NCS and sulfuryl chloride also indicate significant differences between these chlorinating agents.

The chlorination of unsymmetrical sulfides has not been studied extensively. Chlorination of benzyl methyl sulfide by sulfuryl chloride[2] or chlorine[3] gives chlorobenzyl methyl sulfide as the only observed product. A powerful directive influence of an α-chloro substituent has also been observed; chlorination of α-chloro sulfides generally leads to exclusive polyhalogenation at one carbon atom.[4] Only two exceptions to this general behavior have been reported. Mixtures of dichloro sulfides are formed in the sulfuryl chloride chlorination of dibenzothiepin **1** and chloromethyl *p*-nitrobenzyl sulfide (**2**).[4d,e] Böhme and Gran isolated



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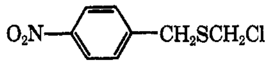

2

$CH_3SCHClCH_3$

3

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