Formation and Reactions of Chloro-methoxy- and -(2-methylpropoxy)-carbene [1]

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Chloro-methoxy- and -(2-methylpropoxy)-carbene are formed from 3-chloro-3-methoxy- and 3-(2-methylpropoxy)-diazirine, respectively. In the absence of carbene traps they fragment to give carbon monoxide and either methyl chloride or alkene and HCl. They add readily to electron-poor alkenes to give cyclopropanes, and react with alcohols to give alkyl formates. The influence of substituents on the reactivity of carbenes is discussed, and the reaction of alkoxychlorocarbenes with alcohols is related to the mechanism of base-catalysed halogenoform hydrolysis.

It is over a hundred years since Geuther [2] proposed that the alkaline hydrolysis of chloroform went by way of dichlorocarbene, and twenty-five since Hine [3] and his collaborators first postulated that in alcoholic solution dichlorocarbene reacts with alkoxide (or alcohol) to give an intermediate alkoxychlorocarbene, an hypothesis subsequently elaborated by the work both of his group [4] and that of Skell [5] and his co-workers. However, no unambiguous demonstration of the capture of an alkoxyhalogenocarbene by an alkene has been reported and this despite the many thousands of dihalogenocyclopropanations that have been carried out in alcoholic solution. Direct generation of chloro(methoxy)carbene (1) has been reported by Hine *et al.*,[6] using the base-promoted elimination of HCl from dichloromethyl methyl ether but no attempt at capture was made. The formation of anisole from the action of methyl-lithium on methyl trichloromethyl ether in the presence of cyclopentadiene is also plausibly explained as arising *via* (2) formed by the capture of (1) by cyclopentadiene,[7] but the evidence is not compelling. However, chloro(phenoxy)carbene (3), generated by the action of Bu^{t}OK on dichloromethyl phenyl ether, has been intercepted by simple alkenes to give the corresponding cyclopropanes (4).[8] All these procedures suffer from the disadvantage of being carried out in strongly basic media, which limits the possible alkyl groups on the carbene and the alkenes which may be employed. It seemed to us that an alternative route to (1) and its homologues would enable a proper definition of their properties, would be of synthetic value, and could shed some further light on the course of the alkaline hydrolysis of chloroform.

We here report that (1) may be conveniently generated using 3-chloro-3-methoxydiazirine (5a) as a precursor and that the method is also applicable to the formation of (6), and should be general for most groups for which the corresponding alcohol is accessible.

Synthesis of Diazirines.—A general route to 3-halogenodiazirines has been described by Graham,[9] involving oxidative cyclisation of amidinium salts using sodium hypohalite in dimethyl sulphoxide containing sodium and lithium halides. He briefly mentions that his method is applicable to *O*-methylisouronium hydrogensulphate and that it affords (5a).

O-Alkylisouronium salts may be prepared by the direct alkylation of urea using dialkyl sulphates,[10] and they may be converted to the hydrochlorides *via* the corresponding picrates.[11] This method is laborious, gives poor yields of hygroscopic salts, and is restricted by the availability of dialkyl sulphates. Urea is also *O*-alkylated by methyl and ethyl toluene-*p*-sulphonates and gives the non-hygroscopic toluene-*p*-sulphonate (tosylate) salts in good yield.[12] Attempts to extend this procedure to *O*-(2-methylpropyl)isouronium tosylate proved unsuccessful, either giving recovery of unchanged urea or formation of ammonium tosylate.

O-Alkylisouronium hydrochlorides have also been prepared by the alcoholysis of cyanamide using gaseous HCl as catalyst, but in many instances the salts could not be obtained crystalline from solution.[13] Modific-

ation of this procedure using anhydrous toluene-*p*-sulphonic acid afforded excellent yields of crystalline *O*-alkylisouronium tosylates from methanol, ethanol, and isobutyl alcohol. The method should be generally applicable to a wide variety of substituent groups.

The *O*-alkylisouronium tosylates were cyclised to the corresponding diazirines using Graham's method, with continuous removal of the diazirine as it was formed by evacuation of the reaction vessel through a series of traps. It was found essential to adhere closely to the directions in the Experimental section to avoid mishap during the preparation or use of these diazirines as they were unpredictably explosive when condensed as pure liquids. Yields averaged *ca.* 60%.

RESULTS AND DISCUSSION

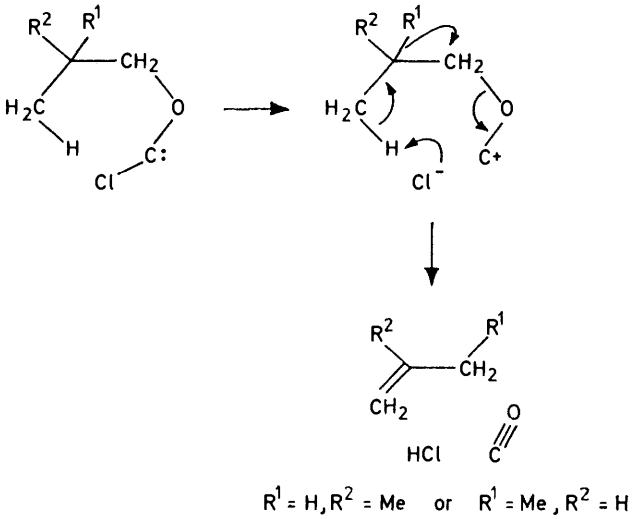
Diazirines have been used as carbene precursors since the discovery that the parent compound gives methylene.[14] However, it has become clear that in many instances isomerisation to diazo compounds precedes the loss of nitrogen.[15] Our study of the kinetics of the decomposition of (5a) strongly indicates that the formation of (1) occurs as a single step.[16] We will not reiterate those arguments here but the good agreement between our kinetics and those briefly reported by Moss and Shieh [17] for the decomposition of (5a) in the presence of alkenes lends further support to this conclusion. Further no pyrazoline was detected from the reaction of (5a) with any of the alkenes reported; pyrazolines would have been expected if chlorodiazomethoxymethane were an intermediate. In the remainder of this Discussion it has been assumed that (5a) gives (1) directly, although the possibility of a diazo compound as intermediate has not been ignored.

Fragmentation Reactions.—The work of Hine [4] and of Skell [18] indicates that alkoxychlorocarbenes fragment readily to give carbon monoxide, halide ion, and alkenes [equation (1)]. We find that in the gas phase or in

$$X-\ddot{C}-OR \longrightarrow X^- + C\equiv\overset{+}{O}-R \longrightarrow CO + R^+ \longrightarrow \text{Alkene} \qquad (1)$$

inert solvents (CCl_4 or Et_2O) both (1) and (6) follow this route, the methyl compound affording chloromethane and the isobutyl compound mainly isobutene (86%) together with but-1-ene (11%) and *trans*-but-2-ene (3%). That methane, ethane, and ethylene are not formed from (1), together with the fact that no products containing a CCl_3 group are formed in CCl_4 solution, confirm that these fragmentations occur by an ionic route, and not by a radical one, as has been invoked for dialkoxycarbenes.[19,20] In the methyl case it is unlikely that Me^+ is formed particularly in the gas phase and presumably nucleophilic attack by chloride ion occurs on $MeOC^+$ to give chloromethane and carbon monoxide. The lack of isobutyl chloride from (6) is a reflection of the ease of rearrangement of the isobutyl cation to give either the t-butyl or the 1-methylpropyl one. The preponderance of isobutene and but-1-ene in the products may be a reflection of the role of the chloride ion in the low dielectric medium, with elimination occurring mainly by way of the cyclic process depicted in Scheme 1.

Although this fragmentation has been written as a two-step process in equation (1), as favoured by Skell,[18] it would appear that the nature of the alkyl group affects the rate. During addition of (1) and (6) to ethyl



SCHEME 1

acrylate, the volume of permanent gas collected was 1.12 and 1.41 equivalents, respectively, showing that (6) undergoes a substantially higher proportion of fragmentation in competition with addition than does (1). While it is possible that this may be due to a slower rate of cycloaddition for (6), one would anticipate that the effect of the remote alkyl group on the rate of cycloaddition would be relatively minor, and it seems more probable that an increased rate of fragmentation is responsible. This is readily accommodated if, as R becomes more complex, the transition state for fragmentation is shifted towards a single stage process [equation (2)].

With neither (1) nor (6) was any product formed which could be attributed to an intramolecular rearrangement or insertion in the intermediate carbene [equation (3)], although both these paths have been invoked in other reactions where alkoxychlorocarbenes were putative intermediates.[21] Although dimethoxycarbene gives methyl acetate, which is formally an example of the first of these possibilities, this has been shown to arise by a radical cleavage–recombination path.[20] This would suggest that the origin of the acids and/or esters formed in the reaction of benzyl oxide, benzophenone, and benzaldehyde with CCl_2 lies in a carbonium ion rearrangement of the type $R-O-C^+$ to $R-\overset{+}{C}=O$. We ascribe this lack of intramolecular reaction in (1) and (6) to the increased stabilisation of $ROC\ddot{C}l$ caused by the mesomeric effect of the oxygen lone pair (7).

With both (5a and b), decomposition under the above conditions also gave significant amounts of the *cis*- and *trans*-azines (8a and b), and (5b) also formed a *ca.* 1 : 1 mixture of the *cis*- and *trans*-1,2-dichloro-1,2-bis-(2-methylpropoxy)ethene (9b), the formal dimer of the carbene (6). These products would seem to arise *via* attack of the intermediate carbene on the starting diazirine, either at the N=N bond [equation (4)] or at the C–N one [equation (5)]. We ascribe the greater preponderance of reaction (5) in the isobutoxy case to a steric effect of the alkyl group in the initial diazirine (5b) inhibiting attack on the N=N bond, although this is clearly not the only factor involved in this partition, for, in the presence of ethyl acrylate, the methoxydiazirine (5a) gives dimer (9a) (see Experimental section). That the alkenes (9) are not artefacts of the work-up procedure used (g.l.c.) produced by pyrolysis of the azines (8) is shown by the fact that the azines are stable to the conditions employed.

Addition Reactions.—In the presence of ethyl acrylate, (5a and b) gave the corresponding cyclopropanes (10a and b) as a mixture of *E*- and *Z*-isomers in isolated yields of 25 and 9%, respectively. We were unable to separate the two isomers of (10a), but integration of the methoxy signal in the ^{1}H n.m.r. spectrum showed it to be a 3 : 1 mixture. The stereochemistry was assigned on the basis of the shielding effect of the ethoxycarbonyl group on the methoxy protons, estimated by using Dreiding models and the calculated shielding maps of Pople for the carbonyl group.[22] This indicated that the methyl of a *syn*-methoxy should experience a slight shielding effect compared with that of an *anti*-one, and so we conclude that the major isomer has the *Z*-stereochemistry. The cyclopropyl ^{1}H n.m.r. signals formed an ABC system and they were analysed using the LAOCOON programme. The results are given in Table 1. These indicate that the cyclopropyl proton *cis* to the ethoxycarbonyl group is shifted to lower field in the *E*-

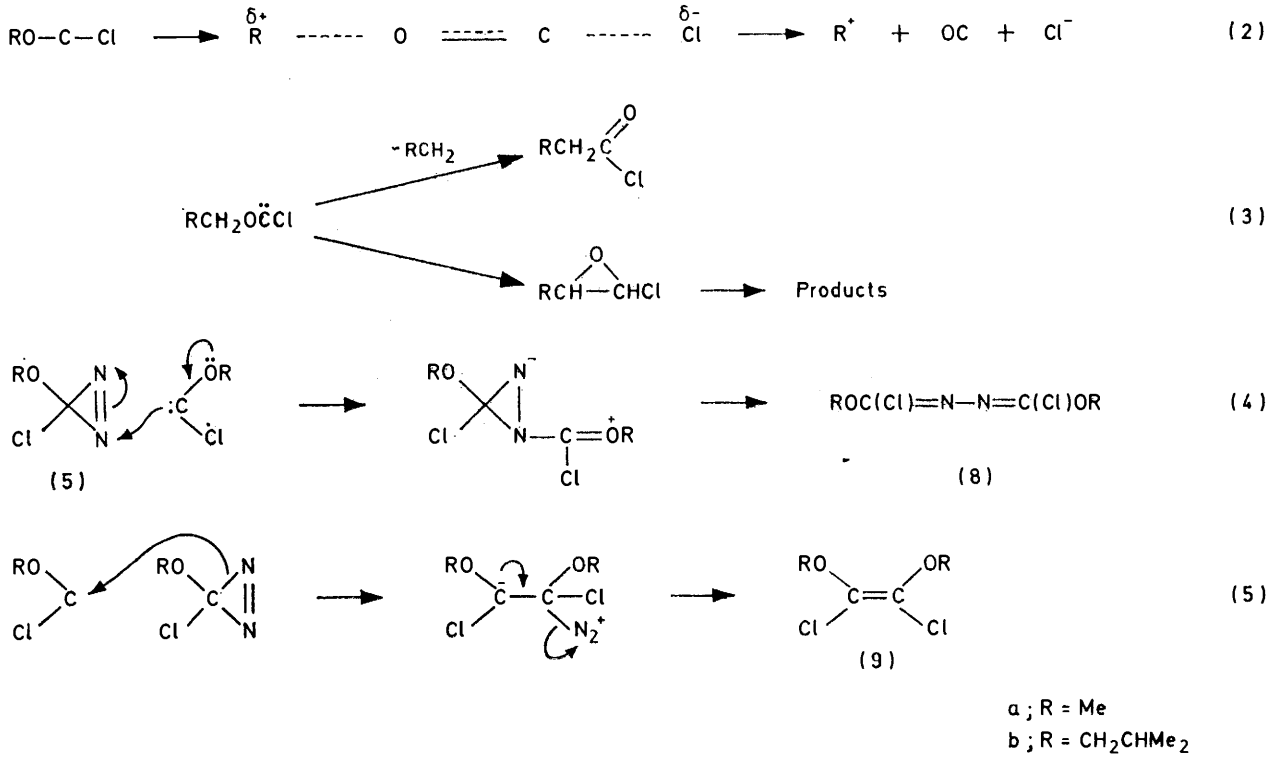


TABLE 1

^{1}H N.m.r. spectra of cyclopropanes (10)

Compound	Isomer	Chemical shift (τ) 1-H	3a-H	3b-H	CH_2R	R	Other	Coupling constant (Hz) $J_{1,3a}$	$J_{1,3b}$	$J_{3a,3b}$
(10a)	*E*	7.74	8.46	8.11	6.60		5.85 (q), 8.70 (t)	9.2	7.0	−6.4
(10a)	*Z*	7.89	8.45_5	8.21	6.56		5.85 (q), 8.70 (t)	9.7	7.3	−6.4
(10b)	*E*	7.80	8.50	8.16	6.58,[a] 6.68	8.12 (n),[b] 9.08 (d)	5.86 (q), 8.70 (t)	9.0	7.0	−6.2
(10b)	*Z*[c]	7.8_5	8.4_5	8.2_0	6.5	8.1 (m), 9.06 (d)	5.83 (q), 8.79 (t)	10	7	−6
(10c)	*E*	7.98	8.24	8.19	6.35			10.3_5	6.7	−7.0
(10c)	*Z*	8.01	8.19	8.29	6.52			10.5	7.0	-6.7_5

[a] AB quartet, J_{AB} 8.8, J_{vicA} 6.8, J_{vicB} 6.2 Hz. [b] Nine lines, J_{HMe} 6.5 Hz. [c] Not analysed by LAOCOON.

isomer, in agreement with other examples where a chlorine causes a larger shift of the proton *trans* to it than does methoxy.[23] The isomers of (10b) were separated by preparative g.l.c., and the stereochemistry was assigned on the basis of the difference in the OCH_2 signal. This gave the same result as that based on the position of the cyclopropyl proton *cis* to the ethoxycarbonyl group. Decomposition of (5a) in the presence of acrylonitrile gave a mixture of the *E*- and *Z*-cyclopropanes (10c) in 40% yield. They were separated by preparative g.l.c., and the stereochemistry assigned on the basis of the anisotropic and electrostatic effect of the cyano group,[24] which should cause a deshielding of the methoxy protons *syn* to it. It is to be noted that

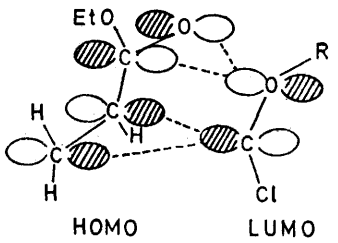
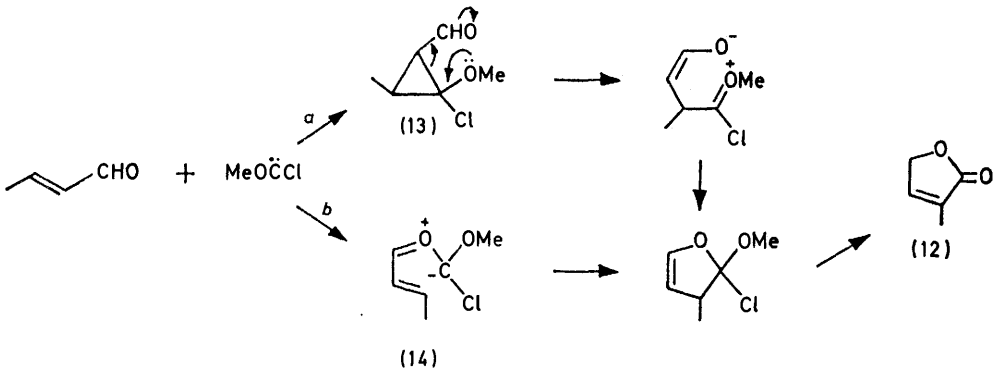


FIGURE 1

here too the effect of the *anti*-group on the proton *cis* to the cyano group is larger in the case of chlorine (*E*-isomer) than that of methoxy (*Z*-isomer), in concordance with the related esters. The ratio of *E*- to *Z*-isomers was 75 : 25, 90 : 10, and 55 : 45 respectively for the three cyclopropanes (10a—c), indicating that addition occurs with the methoxy group predominantly *syn* to the ester or nitrile group. This orientation is that to be expected on the basis of a Frontier Orbital controlled cycloaddition, where a favourable secondary orbital interaction would exist between the carbonyl (or nitrile) group of the alkene and the alkoxy substituent on (1) or (6) (Figure 1). The smaller orienting effect of the nitrile is consistent with that observed in Diels–Alder reactions.[25] Chloromethoxycarbene (1) was also trapped with dimethyl fumarate to give the cyclopropane (11) in 21% yield, together with azine (8a), and these were separated by column chromatography. The ^1H n.m.r. spectrum of (11) showed two 3 H singlets at τ 6.32 and 6.33 for the methoxycarbonyl groups, a singlet at 6.45 for the methoxy group, and a 2 H singlet at 7.18 for the cyclopropane protons. This degeneracy of the ring protons is rather unexpected and attempts to split it using $Eu(fod)_3$ were unsuccessful, the signals being simply shifted and unaccetably broadened. Attempts to replace the chlorine by hydrogen using Bu_3SnH under a variety of conditions were also unsuccessful, (11) being recovered unchanged in all cases. The *trans*-stereochemistry of (11) seems certain on the basis of the two signals from the methoxycarbonyl groups. This stereospecific addition would normally be taken to indicate that (1) reacts in the singlet state and that addition is concerted. However, the fact that the more stable *trans*-cyclopropane is formed does not preclude a two-step addition, for $(MeO)_2C$: adds to both fumarate and maleate to give the same product, *trans*-3,3-dimethoxycyclopropane-1,2-dicarboxylate,[26] and fluorenylidene reacts similarly.[27] Attempts to confirm that the addition takes place with retention of stereochemistry in other cases proved fruitless. Thermolysis of (5a) in the presence of dimethyl maleate gave azine, dimethyl methoxysuccinate, but no cyclopropane. Nor was any cyclopropane formed from either crotonaldehyde or *trans*-stilbene. Trapping with crotonaldehyde gave mainly (9a) together with some (8a) and a compound identified as 3-methyl-2,5-dihydrofuran-2-one (12) on the basis of its i.r. (1 760 and 1 660 cm^{-1}, butenolide), ^1H n.m.r. [τ (100 MHz) 2.97 (1 H, vinyl, sextet, J 1.8 Hz), 5.34, (2H-OCH_2, quintet J 1.8 Hz), and 8.11 (3 H, allylic Me, quartet, J 1.8 Hz)], and mass spectra. Unfortunately, no product containing a cyclopropane ring was detected. The formation of (12) may result from initial cyclopropanation to give (13), followed by a vinylcyclopropane type rearrangement (route *a* in Scheme 2). Alternatively it may be formed by initial attack at oxygen to give a carbonyl ylide (14), as has been proposed for CCl_2 and aldehydes,[21c] followed by the electrocyclic ring closure shown (route *b*). In view of the thermal stability of (10a—c) and (11) as well as the known [3,2] sigmatropic reactions of α-carbena allyl sulphides,[28] and of the ylides derived from allyl methyl ether with methoxycarbonylcarbene,[29] and from allyl sulphides



SCHEME 2

with allylidene,[30] we favour the second of these alternatives.

Decomposition of (5a) in cyclohexene solution gave a low yield of a compound tentatively identified as 2-chlorocycloheptanone, but this was not confirmed. In view of the recent results of Moss and Shieh [17] this would be a reasonable supposition.

Diphenylacetylene proved to be an efficient trap for (1) and afforded diphenylcyclopropenone in 40% yield. An i.r. spectrum of the crude reaction mixture showed a band at 1 850 cm^{-1} which would indicate that the initial adduct, 3-chloro-3-methoxy-1,2-diphenylcyclopropene, decomposed in solution by way of the cyclopropenium ion to give the cyclopropenone and methyl chloride.

Attempted trapping of (1) with *NN*-dimethylisobutenamine gave initially a bright yellow solution, but, on completion of the thermolysis of (5a), only an unidentifiable orange solid could be isolated.

Carbenes have been classified as falling into two general categories, being either electrophilic or nucleophilic, depending on their preference for addition to electron-rich or electron-poor olefinic π-bonds.[31] Our evidence shows that (1) reacts readily with the latter and less readily with the former, a difference that might be anticipated on the basis of a major contribution of the canonical form (7) to the resonance hybrid of alkoxychlorocarbenes. This should make them significantly more nucleophilic than the great majority of carbenes studied and in particular than $:CCl_2$. This enhanced nucleophilicity readily accounts for the failure to observe any products of the capture of alkoxychlorocarbenes by alkenes during dichlorocyclopropanation reactions. The evidence of Moss and Shieh,[17] however, shows that (1) also reacts with 2,3-dimethylbut-2-ene, isobutene, and *trans*-but-2-ene. This wide range of reactivity suggests that alkoxychlorocarbenes are probably the first examples of carbenes that may be described as ambiphilic. While any singlet carbene is inherently both an electrophile and a nucleophile, as can be seen from the singlet structure expressed as $R_2C^{\pm}$, its overall behaviour depends on whether, viewed in terms of the Frontier Orbital interactions involved in the transition state for addition to an alkene, the dominant term is that between LUMO (carbene) and HOMO (alkene) or that between HOMO (carbene) and LUMO (alkene), just as Diels–Alder reactions are described as normal or with inverse electron demand depending on the dominance of the HOMO (diene)–LUMO (dienophile) or LUMO (diene)–HOMO (dienophile) term during the reaction. A dominant LUMO (carbene)–HOMO (alkene) term then describes an electrophilic carbene, while a dominant HOMO (carbene)–LUMO (alkene) one describes a nucleophilic carbene.[32] A carbene could be expected to exhibit ambiphilic behaviour when these two interactions are of comparable importance and when the dominant one depends mainly on the nature of the substituents presents on the alkene. The relative behaviour of these three types of carbene can be summarised in terms of the graph of Figure 2.

So far all experiments to determine the relative rates of addition of carbenes to alkenes, which have led to the derivation of ' carbene selectivity indices ', m_{CXY},[33] have concentrated on alkenes at the left-hand side of Figure 2 and have used mainly electrophilic carbenes. Chloromethoxycarbene has $m^{calc.}$ 1.59, which falls between the values for $:CF_2$ ($m^{obs.}$ 1.48), a carbene which behaves in an electrophilic manner, and $:C(OMe)_2$ ($m^{calc.}$ 2.22) which behaves solely in a nucleophilic way, and it might therefore be expected to exhibit transitional behaviour.[34]

Substitution Reactions.—In order to gain some insight into the propensity of alkoxychlorocarbenes to undergo replacement of the chlorine, the reaction of (1) has been studied with methanol, propan-2-ol, isobutyl alcohol, and diethylamine, while that of (6) with methanol has also been examined. The product mixtures were

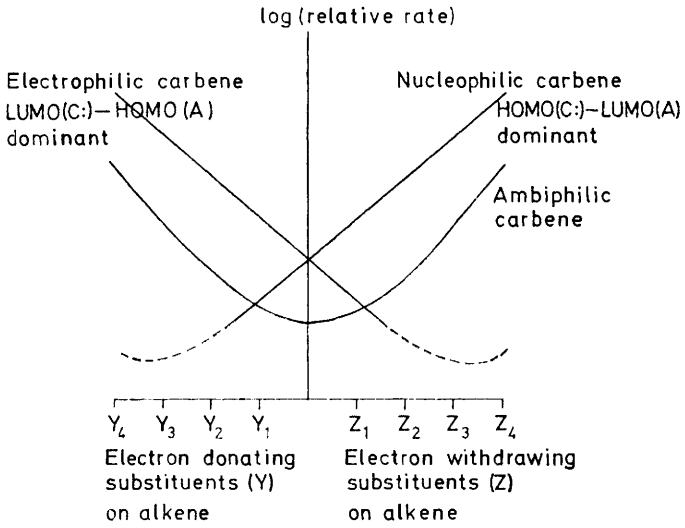


FIGURE 2

analysed by g.l.c. and the products identified by a combination of retention time comparison, combined g.l.c.–mass spectrometry, and trapping coupled with spectral analysis. The product analyses of the carbene–alcohol reactions are shown in Table 2. In each instance between 95 and 99% of the theoretical yield of nitrogen was obtained and no azine was formed. It is noteworthy that only in the reaction with propan-2-ol was any alkene produced, and then only in very minor amount. The products formed may all be readily rationalised by Scheme 3.

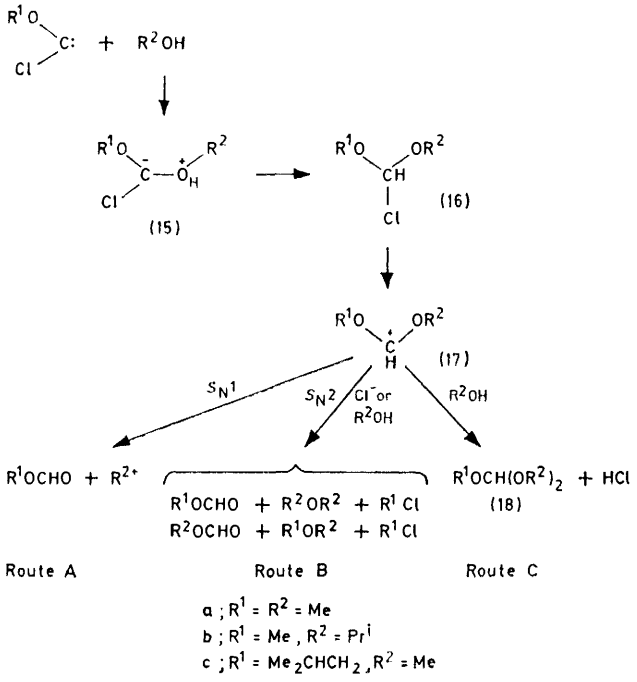
The initially formed carbene reacts to insert into the OH bond of the alcohol by way of the ylide (15) to generate the dialkoxychloromethane (16). Compounds of this type are known to decompose to give alkyl chlorides and formates,[35] but the formation of ethers has not been reported. We envisage three routes for their breakdown all *via* the carbocation (17). Depending on the nature of the alkyl groups involved, (17) may suffer S_N1 cleavage, S_N2 attack at alkyl, or addition at the cationic carbon to give the mixed orthoformate (18), which is then hydrolysed to formate and alcohols. (Unfortunately

TABLE 2

Products (mol % ratios) from 3-alkoxy-3-chlorodiazirine decomposition in alcohol solution

3-Alkoxy-group	MeO	MeO	MeO	Me_2CHCH_2O
Alcohol	MeOH	Me_2CHOH	Me_2CHCH_2OH	MeOH
		$MeCH{:}CH_2$ (0.3)		
	MeCl (22.6)	MeCl (3.4)	MeCl (23.6)	MeCl (15.9)
	MeOMe (3.0)			MeOMe (2.8)
		$MeOPr^i$ (0.8)	$MeOBu^i$ (1.3)	
		Pr^iCl (20.9)	Bu^iCl (7.5)	
		Pr^i_2O (6.0)	Bu^i_2O (1.0)	
	MeOCHO (74.4)	MeOCHO (trace)		MeOCHO (41.3)
		MeOH (32.6)	MeOH (17.2)	
		Pr^iOCHO (36.0)	Bu^iOCHO (49.4)	Bu^iOCHO (1.0)
				Bu^iOH (39.1)

the technique for the preparation of the diazirines renders it extremely difficult to obtain alcoholic solutions which are completely anhydrous and we were unable to prevent this hydrolysis.) The major formate isolated is

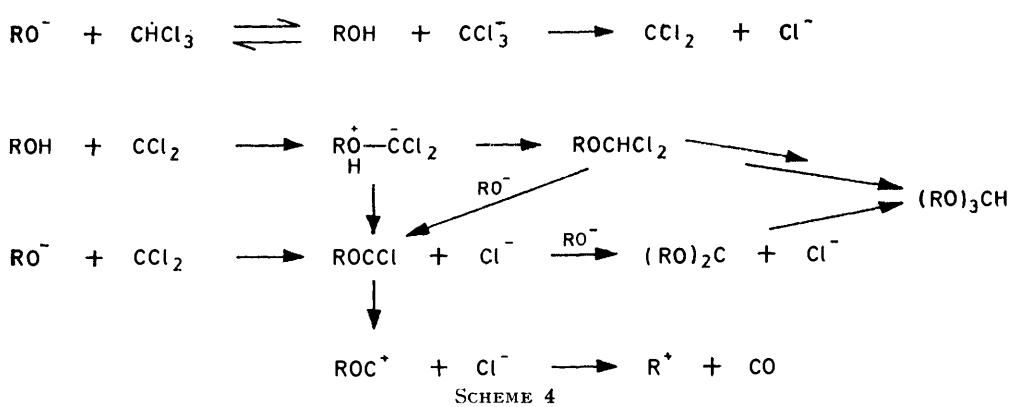


SCHEME 3

in all cases that of the solvent alcohol, as would be expected from the facile transesterification of alkyl formates in the presence of HCl. An examination of the products from the decomposition of (5b) in methanol (column 4, Table 2) shows that reaction of (6) with solvent to give (16c) occurs to the exclusion of the fragmentation process observed in the gas phase or CCl_4 solution. Further, they show that the breakdown of (17c) in methanol occurs with nucleophilic attack exclusively at the methyl group, as might be expected from the relative S_N2 reactivities of methyl and isobutyl compounds.[36] The absence of alkene also shows that (17c) decomposes only by routes *B* and *C*. That isobutyl chloride and di-isobutyl ether are formed from (17c) in isobutyl alcohol (column 3, Table 2), indicates that route *C* must be operative leading to the symmetrical ion (17; $R^1 = R^2 = Bu^i$). The formation of propene from (17b) in propan-2-ol shows that the carbonium ion route *A* must also exist, either directly from (17b) or *via* the symmetrical ion (17; $R^1 = R^2 = Pr^i$).

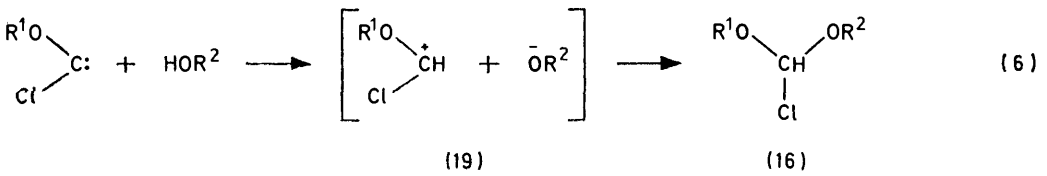
In the gas phase both (5a and b) gave (in addition to the fragmentation products) the corresponding formates formed by reaction of the carbenes (1) or (6) with water (Scheme 3; $R^2 = H$). For MeOCCl this was confirmed by thermolysing (5a) in chloroform saturated with water, when methyl formate was formed in 60% yield and much less fragmentation observed.

The lack of fragmentation from (6) in neutral alcoholic solution poses a problem in relation to the mechanism for the alkaline alcoholysis of chloroform, for it would indicate that (6) is intercepted by solvent more rapidly than it fragments and yet chloroform and sodium isobutoxide give 8—11% yields of alkenes.[3] The alcoholysis of chloroform is generally accepted to proceed by the stages shown in Scheme 4, with alkenes being formed by the fragmentation of the intermediate alkoxychloro-



SCHEME 4

carbene [equation (1)].[4,18] If one postulates that the capture of (6) by alcohol under neutral conditions occurs *via* nucleophilic attack of alcohol on (6) to give ylide (15),

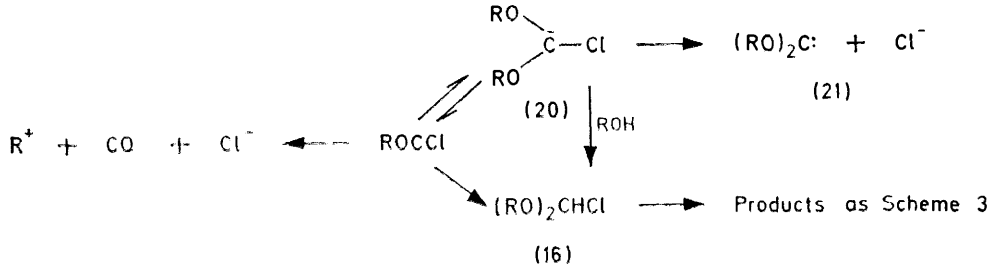


(19) (16) (6)

as is accepted for $:CCl_2$, then one would anticipate an even faster reaction with alkoxide ion, and hence that no fragmentation should be observed. The extent to which the alkaline methanolysis of chloroform gives fragmentation has been shown to vary with the base concentration, going from 19% (81% orthoformate) at 1M-sodium methoxide to 28% at 5M and to 35% (65% orthorformate) in saturated NaOMe solution.[37]

One possible explanation of this anomaly would be to postulate that (16) is formed by way of initial proton transfer [equation (6)] to give the intimate ion-pair (19), which then collapses.

to the destabilising effect of the oxygen on the negative charge combined with its stabilising influence on the carbene formed by loss of chloride.[6] The same arguments apply with equal or greater force to (20). The other possibility is that most of the fragmentation arises from the decomposition of the dialkoxycarbene (21). These are known to fragment to R^+, carbon monoxide, and alkoxide,[20] as well as to give orthoformates with alcohols.[40] Should this latter reaction occur by a process analogous to that of equation (5), this hypothesis could accommodate most of the results. Rate-determining proton transfer to $(RO)_2C:$ would be much more reasonable than to ROCCl, in view of its greatly increased nucleophilicity as expressed in its capture only by electrophilic alkenes.[26] However, the fact that the



SCHEME 5

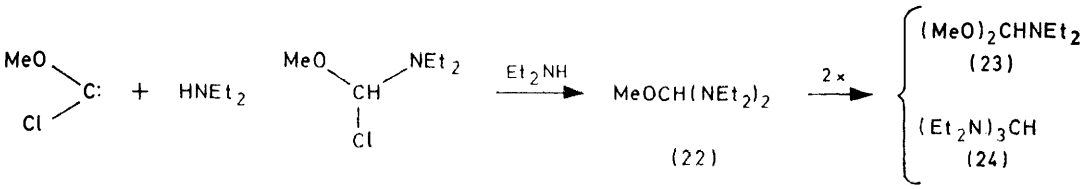
While this would accord well with the nucleophilic properties of alkoxychlorocarbenes as expressed by (7), it does not fit with the electrophilic properties shown in the reaction of (1) with 2,3-dimethylbut-2-ene, nor with the fact that not more than 14% of fragmentation is observed when (1) is trapped by diethylamine (in ether), which is less acidic than methanol by some 18 powers of ten,[38] while 1M-sodium methoxide gives 19% fragmentation with the less readily fragmented chloromethoxycarbene (1).[37]

Two other hypotheses may be advanced, of which the more reasonable is that the reaction of alkoxychlorocarbene with alkoxide to form (20) is reversible (Scheme 5). In view of our observation that the rate of fragmentation depends on the nature of R, this hypothesis would accord with the observation that the yield of CO in the alkaline alcoholysis of halogenoforms increases as R changes from primary to seondary to tertiary[5] and that the yield of orthoformate decreases as the basicity increases,[37] reflecting the decrease in protonation of (20) to give (16). However, this suggests that (20) is considerably more stable than has been thought and has an appreciably longer lifetime than $ROC\bar{C}l_2$, which has been considered to have not even a transient existence.[39] The difference between $ROC\bar{C}l_2$ and $\bar{C}Cl_3$ was ascribed yield of alkene depends on the halide involved (increasing from chloride to bromide)[39] would rule this out as the sole route to the formation of alkenes.

One final possibility, which we would favour, is that (20) is not formed at all, but that ROCCl gives (16) directly by a process requiring proton transfer to carbon and not *via* the ylide (15). The formation of MeOCCl from $MeOCHCl_2$ and NaOMe is a concerted elimination of HCl[6] and hence by the principle of microscopic reversibility its reaction with HCl should require concerted proton transfer to carbon. It would therefore be reasonable to postulate that the formation of (16) also requires proton transfer and is thus effectively a direct insertion into the OH bond of the alcohol. This explanation fits well with the kinetic investigation of Georgoulis and his collaborators,[37] which showed that at high base concentration in methanol, there is effectively no 'free' solvent, it all being tied up in the complexation sphere of the metal alkoxide. Hence the higher the base concentration the lower the 'free' solvent, and the larger the percent fragmentation.

Thermolysis of an ethereal solution of (5a) and diethylamine gave 1.14 equivalents of permanent gas, indicating some 14% of fragmentation, but no methyl chloride. The two-phase product solution gave *NN*-diethyl-

formamide dimethyl acetal (23) from the upper layer and a viscous, golden-yellow oil from the lower layer, which could not be identified. The acetal clearly arises by insertion of (1) into the NH bond of the diethylamine as in Scheme 6. The disproportionation of the intermediate (22) to give (23) and (24) has been reported previously.[41] Our failure to isolate (24) suggests that it gave rise to the unidentified oil. That no methyl chloride was formed is not unexpected as the amine would be expected to compete successfully for the intermediate $MeOC^+$ in competition with chloride ion.



SCHEME 6

EXPERIMENTAL

General.—I.r. and u.v. spectra were recorded on Unicam SP 200 and SP 800 spectrometers. ^1H N.m.r. spectra were measured at 60 MHz on a Perkin-Elmer R12 and at 100 MHz on a Varian Associates HA100 spectrometer, with tetramethylsilane as internal reference. Mass spectra were measured on an A.E.I. MS 12 instrument. Analytical g.l.c. was carried out on a Perkin-Elmer F11 instrument equipped with a flame ionisation detector. Peak areas were recorded using a Disc series 200 ball and disc integrator. Calibration factors were determined by standard techniques. Preparative g.l.c. was done on a Varian Aerograph A700 Autoprep, fitted with a thermal conductivity detector and using hydrogen as carrier.

Preparations.—Anhydrous toluene-*p*-sulphonic acid was prepared by heating the commercial monohydrate over P_2O_5 under vacuum. The anhydrous acid had m.p. 38—39° (lit.,[42] 38°), and was used without further purification.

*O-Alkylisouronium toluene-*p*-sulphonates.* The method used is an adaptation of that of Basterfield and Powell.[13b] Commercial cyanamide (4.2 g, 0.1 mol) was dissolved with stirring in the desired anhydrous alcohol (1.2 mol) contained in a flask maintained at 40°. Anhydrous toluene-*p*-sulphonic acid (17.2 g, 0.1 mol) was added in small portions with continuous stirring, (with methanol and ethanol a reflux condenser was necessary). The flask was then fitted with a drying tube and kept at 40° for 2 days. Removal of the solvent at reduced pressure, with stirring gave a paste which was triturated with ether (100 ml) to give the product as a microcrystalline solid. The salts may be recrystallised from the methyl ketone corresponding to the alcohol used, but this caused no change in m.p. from that of the crude product.

O-Methylisouronium toluene-*p*-sulphonate (92%) had m.p. 130—132° (lit.,[12] 134°), *O*-ethylisouronium toluene-*p*-sulphonate (87%), m.p. 80° (indefinite) (lit.,[12] 94°), and *O*-2-methlypropyl)isouronium toluene-*p*-sulphonate (92%) m.p. 39—45° (indefinite).

Diazirines. These were prepared by essentially the method of Graham.[9] **CAUTION**: As neat liquids, the diazirines, are unpredictably explosive at ambient temperatures, but in solution they can be handled safely. The details below should be adhered to closely to avoid accidents. It is most important that all traps should contain some solvent. Handled as described, we have had no accidents in over forty preparations.

3-Chloro-3-methoxydiazirine (5a). *O*-Methylisourea toluene-*p*-sulphonate (21 mmol), anhydrous lithium chloride (196 mmol), and dimethyl sulphoxide (100 ml) were placed in a three-necked flask (2 l), equipped with a pressure-equalising dropping funnel, magnetic stirrer, and exit tube fitted with a stopcock. The exit tube is connected to a train of three all glass traps containing 1, 2, and 1 ml respectively of redistilled di-n-butyl phthalate. A large glass U tube fitted with potassium hydroxide pellets was interposed between the first and second traps, and the traps were cooled to −35, −78, and −78° respectively. When the salts had dissolved, sodium hypochlorite solution (250 ml; 10—14% w/v available chlorine) containing sodium chloride (50 g) was placed in the dropping funnel, the flask cooled to 0°, and the whole apparatus evacuated to 1—2 Torr. The stirring rate was increased to maximum and the hypochlorite solution added dropwise to the flask over *ca.* 4 min. Considerable frothing occurs, which is controlled by adjusting the rate of addition and the stopcock on the exit tube. Evacuation was continued for 5 min after addition was complete. The traps were then isolated from the flask and the pump, and filled with dry nitrogen. The central trap, which contains most of the diazirine, is isolated, warmed to −35°, and cautiously agitated to form a homogeneous solution. The solution is stable and may be stored at −78° for several weeks, yield 60—68%, $\nu_{max.}$ 1 550, 1 470, 1 250, 1 050, and 970 cm^{-1}; $\lambda_{max.}$ (gas) 340—358 nm (ε 45), $\lambda_{max.}$ (hexane) 342 and 362 nm (ε 50 and 50); $\tau(CCl_4)$ 6.38 (s).

3-Chloro-3-(2-methylpropoxy)diazirine (5b). The above method was used, except that the traps were held at 0, −78, and −78° respectively, and that *O*-(2-methylpropyl)isouronium tosylate (6.05 g, 21 mmol) was used. The diazirine was of comparable stability to the methoxy homologue (5a), yield 50—67%, vapour pressure 15 mmHg at 0°, $\nu_{max.}$ 1 550, 1 240, and 1 030 cm^{-1}.

Fragmentation Reactions.—Chloromethoxycarbene in ether. Diazirine (1a) (13 mmol) was allowed to decompose in dry diethyl ether (10 ml), and the volatile products evolved collected by means of a pneumatic trough, after passing through a trap at −78°. After 48 h, 385 ml (corrected) of gas (17.2 mmol; 66% of two equivalents) had been collected. G.l.c. analysis (1 m; 5A molecular sieve) showed it to consist of nitrogen and carbon monoxide. The cold trap contents were analysed by g.l.c.–m.s. and shown to consist of diethyl ether (*m/e* 74), methyl formate (*m/e* 60), and methyl chloride (*m/e* 52 and 50). Removal of ether from the flask gave a liquid residue (280 mg; 23%) identified as *1,4-dichloro-1,4-dimethoxy-2,3-diazabuta-1,3-diene* (Found: C, 26.5; H, 3.3; N, 15.6. $C_4H_6Cl_2N_2O_2$ requires

C, 26.6; H, 3.3; N, 15.2%), *m/e* 188, 186, and 184 (ratio 1 : 6 : 9.5), $\nu_{max.}$ 2 930, 2 820, 1 625, 1 220, 1 170, and 810 cm^{-1}; $\tau(CCl_4)$ 6.03 (s, OMe) and 6.35 (s, OMe) (ratio 1 : 2), two isomeric forms After two years, needles, m.p. 51—51.5°, had crystallised out.

Decomposition in carbon tetrachloride solution gave results which were virtually identical. In the gas phase, substantially the same products were also formed, but in addition HCl was identified by its i.r. absorption. Addition of water vapour before decomposition resulted in an increase in the amount of methyl formate produced at the expense of the other organic products.

Chloroisobutoxycarbene in carbon tetrachloride. Diazirine (5b) (11.7 mmol) was allowed to thermolyse in carbon tetrachloride solution (3 ml) as for (5a). The temperature rose to *ca.* 50° due to the exothermic reaction. A gas (390 ml, 17.4 mmol, 149%) was collected. The cold-trap contents were analysed by g.l.c. (2 m 20% saturated $AgNO_3$ in diethylene glycol on Chromosorb P) which showed them to be but-1-ene (11%), *trans*-but-2-ene (3%), and isobutene (86%). *cis*-But-2-ene was not detected although it is separated from the other butenes by the column. Removal of solvent gave a liquid residue (317 mg) shown to consist of at least three components by g.l.c. The ^1H n.m.r. spectrum showed these to be *cis*- and *trans*-1,2-dichloro-1,2-bis-(2-methylpropoxy)ethene (9b) and two isomers of isobutyl chloroformate azine (8b) by comparison with the samples isolated in the reaction of (5b) with ethyl acrylate (see below), τ 5.85 (d, OCH_2 of azine, isomer A), 6.10 [d, OCH_2 of dimer (9b), isomer A], 6.20 [d, OCH_2 of azine (8b), isomer B], 6.40 [d, OCH_2 of dimer (9b), isomer B)], 8.00 (m, CH-Me_2), and 8.95 (d, Me_2CH). The stereochemistry of the dimers (9b) is tentatively assigned as isomer A *trans* and isomer B *cis* on the basis of the deshielding effect of the chlorine *versus* the oxygen. The ratio of the liquid products was 6 : 5 : 12.5 : 5.5 respectively for (8bA), (9bA), (8bB), and (9bB).

Thermolysis of (5b) in the gas phase (300 mmHg), monitored by i.r., showed that the major products were isobutene (3 070, 1 660, and 890 cm^{-1}), carbon monoxide (2 100 cm^{-1}), and isobutyl formate (2 970, 1 740, 1 460, 1 385, and 1 170 cm^{-1}).

Addition Reactions.—General procedure. The diazirine was condensed into a trap containing a small amount of solvent (*ca.* 3 ml) at −78°. This was allowed to warm to *ca.* −50° and added to a solution of the alkene in the same solvent contained in the decomposition apparatus (above). The mixture was allowed to warm to room temperature and gas evolution monitored to follow the thermolysis. Typically this was complete in 17—24 h. After removal of solvent, the residue was examined by t.l.c. or g.l.c. and then chromatographed.

With dimethyl fumarate. Diazirine (5a) (15 mmol) was treated with dimethyl fumarate (41.7 mmol) in CH_2Cl_2 (50 ml). After 24 h, gas (335 ml, 14.8 mmol) had evolved. Chromatography on silica gel afforded azine (8a) (2.8 mmol, 37%), dimethyl fumarate (36 mmol), and *dimethyl* trans-3-*chloro*-3-*methoxycyclopropane*-1,2-*dicarboxylate* (3.15 mmol, 21%), m.p. 87—87.5° (Found: C, 43.0; H, 4.9; Cl, 16.6. $C_8H_{11}ClO_5$ requires C, 43.1; H, 4.95; Cl, 16.0%), $\nu_{max.}$ 1 740, 1 320, 1 280, 1 200, 1 170, and 940 cm^{-1}, ^1H n.m.r., see text; *m/e* 224 and 222 (1 : 3), showing one chlorine.

With ethyl acrylate. (a) Diazirine (5a) (13.7 mmol) was treated with redistilled ethyl acrylate (26.6 mmol) in ether (50 ml). Gas (345 ml, 15.4 mmol) was evolved. Preparative g.l.c. (20 ft × 0.375 in, 15% polypropylene glycol on Chromosorb P gave (i) ethyl acrylate; (ii) 1,2-dichloro-1,2-dimethoxyethene (9a) (118 mg, 11%), $\nu_{max.}$ 1 740 1 485, 1 240—1 220, 1 165, 1 120, and 950 cm^{-1}, τ 6.40 (s), *m/e* 160, 158, and 156 (ratio 1 : 6 : 9), showing two chlorines; (iii) bis-(2-ethoxycarbonylethyl) ether; and (iv) ethyl 2-chloro-2-methoxycyclopropanecarboxylate (10a) as a mixture of *E*- and *Z*-isomers (610 mg, 25%), $\nu_{max.}$ 1 740, 1 385, 1 305, 1 180, 1 120, 1 050, and 1 030 cm^{-1}; *m/e* 180 and 178 (ratio 1 : 3), showing one chlorine, exact mass of 178 peak, 178.033, calc. for $C_7H_{11}ClO_3$: 178.039$_7$.

(b) Diazirine (5b) (14.0 mmol) and ethyl acrylate (25.6 mmol) was thermolysed in ether (25 ml). Gas (445 ml, 19.86 mmol) was evolved. Preparative g.l.c. (10 ft × 0.375 in, 15% Carbowax 20M on Chromosorb P) gave (i) ethyl acrylate; (ii) 1,2-dichloro-1,2-bis-(2-methylpropoxy)-ethene (9b (50 mg), isomer A, $\nu_{max.}$ (CCl_4) 1 735 and 1 300—1 250 cm^{-1}), τ 6.10 (2 H, d, *J* 7 Hz, OCH_2), 8.0 (1 H, m, $CHMe_2$), and 9.0 (6 H, d, *J* 7 Hz, Me_2CH), *m/e* 244, 242, and 240 (ratio 1 : 6 : 9), showing two chlorines; (iii) bis-(2-ethoxycarbonylethyl) ether; (iv) (9b) (54 mg), isomer B, $\nu_{max.}$ (CCl_4) 1 735 and 1 220 cm^{-1}, τ 6.40 (2 H, d, *J* 7 Hz, OCH_2), 8.0 (1 H, m, $CHMe_2$), and 9.0 (6 H, d, *J* 7 Hz, Me_2CH), *m/e* 244, 242, and 240 (ratio 1 : 6 : 9), (v) *ethyl* (E)-2-*chloro*-2-(2-*methylpropoxy*)*cyclopropanecarboxylate* (10b) (258 mg, 8%), $\nu_{max.}$ 1 730, 1 300, 1 190, 1 115, 1 050, and 1 030 cm^{-1}, *m/e* 222 and 220 (ratio 1 : 3), showing one chlorine, exact mass of 220 peak, 220.089, calc. for $C_{10}H_{17}ClO_3$: 220.086$_6$; and (vi) a 30 : 70 mixture of azine (8b) and the isomer (10b), τ 5.83 (q, OCH_2Me of ester), 5.89 (d, OCH_2CH of azine), 6.5 [d, OCH_2CH of (10b)], 7.5—8.3 (m, cyclopropyl protons and $CHMe_2$ of isobutyl groups), 8.79 (t, Me, of ester), 8.96 (d, Me_2CH of azine), and 9.06 [d, Me_2CH of (10b)].

With acrylonitrile. Diazirine (5a) (14.2 mmol) was treated with redistilled acrylonitrile (30 mmol) in ether (25 ml) and gas (325 ml, 14.5 mmol) was evolved. Preparative g.l.c. (10 ft × 0.375 in, 15% Carbowax 20M on Chromosorb P) gave (i) acrylonitrile; (ii) azine (8a) (23 mg), isomer A, τ 6.25 (s); (iii) azine (8a) (10 mg), isomer B, τ 6.05 (s), m.p. 51—51.5°, (iv) (E)-2-*chloro*-2-*methoxy*-*cyclopropanecarbonitrile* (10c) (408 mg, 22%), $\nu_{max.}$ 2 250, 1 290, 1 205, and 1 130 cm^{-1}, *m/e* 133 and 131 (ratio 1 : 3), exact mass of 131 peak, 131.010, calc. for C_5H_6ClNO: 131.013$_8$; (v) (Z)-2-*chloro*-2-*methoxycyclopropanecarbonitrile* (10c) (330 mg, 18%), $\nu_{max.}$ 2 250, 1 260, and 1 145 cm^{-1}, *m/e* 133 and 131 (ratio 1 : 3), exact mass for 131 peak: 131.015. No stereochemistry was assigned to the two azine isomers, but the single OMe signal in the ^1H n.m.r. spectrum indicates that each is one of the two possible symmetric isomers *syn,syn* and *anti,anti* and that the *syn,-anti*-isomer is not formed.

With crotonaldehyde. Diarizine (5a) (13.0 mmol) was treated with redistilled crotonaldehyde (26.2 mmol) in ether (25 ml) and gas (335 ml, 14.9 mmol) was evolved. Preparative g.l.c. (10 ft × 0.375 in, 15% Carbowax 20M on Chromosorb P) gave (i) crotonaldehyde; (ii) 1,2-dichloro-1,2-dimethoxyethene (9a) (144 mg, 14%); (iii) unidentified (27 mg); (iv) unidentified (14 mg); (v) azine (14 mg, 1.2%); and (vi) 2-methyl-2,5-dihydrofuran-2-one (12) (38 mg, 3%), $\nu_{max.}$ 1 760, 1 660, 1 210, 1 080, 1 061, and 940 cm^{-1}, *m/e* 98.027 1, calc. for $C_5H_6O_2$: 98.036 8.

With stilbene. Diazirine (5a) (12.5 mmol) and stilbene (22.2 mmol) in ether (125 ml) on thermolysis gave gas (315 ml, 14.05 mmol). Chromatography on silica gel gave a

quantitative recovery of stilbene. No other product was isolated.

With dimethyl maleate. Diazirine (5a) (13.4 mmol) and dimethyl maleate (42 mmol) in CH_2Cl_2 (50 ml) gave, on thermolysis, gas (300 ml, 13.4 mmol). Chromatography on silica gel gave azine (8a) (350 mg, 25%) and dimethyl methoxysuccinate (100 mg), together with recovered alkene, but no other product. Essentially the same results were obtained in ether (25 ml).

With cyclohexene. Diazirine (5a) (12.7 mmol) was thermolysed in cyclohexene (8.8 g, 107 mmol) and gave gas (340 ml, 15.2 mmol). Chromatography of the residue (1.14 g), which had a strong minty smell, afforded azine (8a), (235 mg, 20%) and an oil (130 mg) which had $\nu_{max.}$ 1 660, 1 450, 1 430, 1 210, 1 170, 1 070, and 801 cm^{-1}, and which gave a 2,4-dinitrophenylhydrazone, m.p. 140—141°. 2-Chlorocycloheptanone has a 2,4-dinitrophenylhydrazone with m.p. 140—141°.[43]

With NN-dimethyl-2-methylpropenamine. Diazirine (5a) (13.6 mmol) and enamine (26 mmol) reacted in ether (15 ml) to give gas (370 ml, 16.5 mmol). An orange solid separated which showed $\nu_{max.}$ 1 680 cm^{-1}, τ 6.6 (s) and 7.35 (s) (ratio 1 : 2), indicative of OMe and NMe groups, and no other signals. It did not react with bromine and could not be identified. The cold trap contained some chloromethane.

With diphenylacetylene. Diazirine (5a) (9.5 mmol) and diphenylacetylene (40 mmol) were thermolysed in ether (25 ml) and evolved gas (230 ml, 10.3 mmol). The crude product showed $\nu_{max.}$ 1 850 and 1 640 cm^{-1}. Chromatography on silica gel gave diphenylacetylene and 1,2-diphenylcyclopropenone (768 mg, 39%), m.p. 117—119° (lit.,[44] 121°), i.r. and u.v. spectra identical with published values, *m/e* 178 (M^+ — CO).

Substitution Reactions.—The same general procedure was followed as for the addition reactions, except that the contents of the cold trap were added to the solution and the whole analysed by g.l.c. without removal of solvent. Columns used were: 0.125 in ×2 m 15% Carbowax 20M on Chromosorb P, and 2 m 20% 1,3-bis-(2-cyanoethoxy)-propane on Chromosorb P.

Reactions with alcohols. The results are given in Table 2.

With water. Diazirine (5a) (12.8 mmol) was allowed to thermolyse in chloroform (300 ml) saturated with water. Gas (295 ml, 13.2 mmol) was evolved. The i.r. of the resultant solution was compared against standard solutions of methyl formate in $CHCl_3$ and found to contain 1.6 mg ml^{-1}, total formate 480 mg (62%). Titration of the solution against standard NaOH showed it to contain 10.92 mmol of acid, presumably HCl.

With diethylamine. Diazirine (5a) (14.4 mmol) was treated with redistilled diethylamine (26 mmol) in ether (15 ml). Gas (365 ml, 16.3 mmol) was evolved, and the cold trap contained only ether. The final solution comprised two layers, the upper slightly yellow and the lower golden-yellow and viscous. The upper layer was distilled to give *NN*-diethylformamide dimethyl acetal (161 mg), b.p. 40—50° at 20 mmHg, $\nu_{max.}$ 1 675 and 1 070 cm^{-1}, τ 5.6 [1 H, s, $CH(OMe)_2N$], 6.8 (6 H, s, OMe), 7.4 (4 H, q, *J* 7.5 Hz, NCH_2Me), and 9.0 (6 H, t, *J* 7.5 Hz, CH_3CH_2N): *m/e* 147 (M^+). The lower layer was dried at reduced pressure to remove ether and had $\nu_{max.}$ 1 670 cm^{-1}, τ 0.9 (s), 6.3br (q), 6.6 (s), and 8.6 (t), ratio *ca.* 1 : 12 : 3 : 18, *m/e* 184.

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