Evidence for Protonation of Typically Electrophilic Carbenes by Methanol

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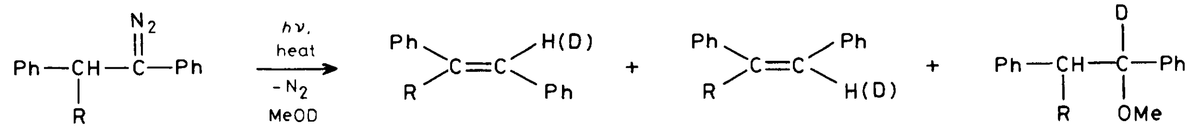
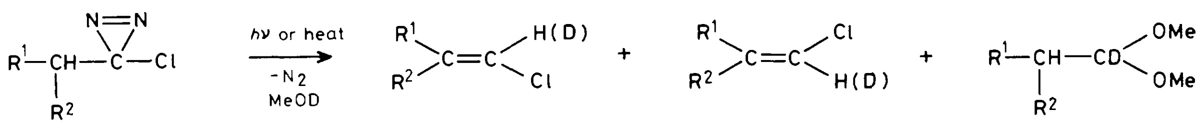
Deuterium was incorporated in the alkenes formed by 1,2-H migration in phenyl- and chloro-carbenes generated in MeOD.

A variety of carbenes react with alcohols to give ethers.[1] At least three plausible reaction paths are conceivable:[2] (a) one-step insertion into the O–H bond, (b) electrophilic attack of the carbene at oxygen, followed by proton transfer, and (c) protonation of the carbene to give a carbocation. Kirmse[3] presented evidence which demonstrated that cycloheptatrienylidene, a typically nucleophilic carbene,[4] undergoes protonation in alcohols with formation of the stable tropylium ion. More recently, Kirmse,[5] Skattebøl,[6] and Warner[7] showed that 'foiled'[8] carbenes also undergo protonation in alcohols to generate nonclassical homoallylic cations. Electrophilic carbenes, on the other hand, are likely to follow path (b) as



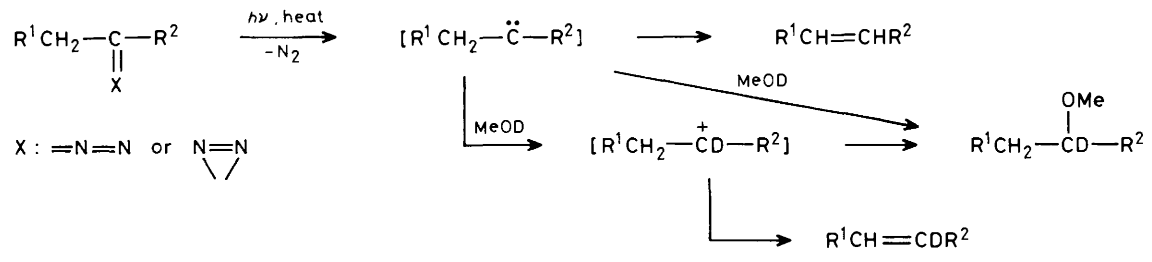
(1) (2E) (2Z) (3)

Scheme 1



(4) (5E) (5Z) (6)

Scheme 2



Scheme 3

Table 1. Photolysis[a] and thermolysis[b] of diazo compounds (1) in MeOD.

					% Yield[c] (% D Incorp.)[d]		
Entry	(1)	R	hν or heat	T/°C	(2E)	(2Z)	(3)
1	**a**	H	hν	20	25.6(10.6)	18.3(10.6)	57.1
2	**b**	Me	hν	20	8.0(14.6)	12.9(14.9)	79.1
3	**b**	Me	Heat	70	37.6 (0.2)	28.3 (4.1)	34.1
4	**b**	Me	BF_3·OEt_2[e]	20	2.5(83.5)	6.9(85.8)	90.6

[a] Irradiations were carried out on 10 mM degassed solutions of (1) through a Corning CS-052 filter with a 300 W high-pressure Hg lamp. [b] Thermolyses were performed in a degassed and sealed Pyrex tube. [c] Determined by g.c. Total product yields are 70—85%. [d] Determined by g.c.–mass spectrometry. [e] A catalytic amount of BF_3·OEt_2 was added.

exemplified by the work on cyclopentadienylidene.[3] In this report we report experimental evidence which demonstrates that typical electrophilic carbenes, *i.e.*, chloro- or phenylcarbene, also undergo protonation, at least partially, when generated in an alcohol.

Photolysis of 1,2-diphenyldiazoethane (**1a**)[9] in MeOD at 20 °C in Pyrex tubes afforded the stilbenes (**2a**) and 1-deuterio-1,2-diphenylethyl methyl ether (**3a**) (Scheme 1). These products apparently arise from a 1,2-H shift and O–D insertion of the photolytically generated singlet 1,2-diphenylethylidene. Deuterium (>10%) was incorporated in both *E*- and *Z*-stilbenes. Similarly incorporation of about 15% of deuterium was found in 1,2-diphenylpropene (**2b**) formed on photolysis of 1,2-diphenyldiazopropane (**1b**)[9] in MeOD (Table 1).

In order to clarify the origin of the observed deuterium incorporation, several control experiments were carried out. First, Lewis acid-catalysed decomposition of the diazopropane was carried out in MeOD. The propenes were formed with about 85% deuterium incorporation (entry 4, Table 1). This indicates that the carbocation, an obligatory intermediate derived from either carbene or diazo compound, undergoes proton elimination to give the alkene. Secondly, the carbocation may also be formed by protonation on the diazo carbon atom followed by loss of N_2 from the resulting diazonium ion under the photolytic conditions, and so thermolysis of the diazo compound was carried out in MeOD at 70 °C in a sealed tube (entry 3, Table 1). In spite of the expectation that the diazonium process would be favoured at higher temperature, the deuterium incorporation into the alkene formed in the thermolysis was greatly reduced compared with the photolytic run.[10] This indicates that the cation was derived mostly from the singlet carbene in the photolytic run.†

More convincing evidence was obtained in the photolysis of the 3-chlorodiazirines (**4**),[11] compounds which are known to be resistant to strong acids and are decomposed only by 80% sulphuric acid.[12] Thus, irradiation of 3-benzyl-3-chlorodiazirine (**4a**) in MeOD afforded β-chlorostyrenes (**5**) and β-phenylacetaldehyde dimethyl acetal (**6**) (Scheme 2), all of which have been shown[11] to be derived from the corresponding chlorocarbene. Deuterium was again incorporated in the chlorostyrenes. Similar deuterium incorporation was also found for other chloroalkenes (**5b**—**d**) formed by photolysis of the chlorodiazirines (**4b**—**d**). Deuterium incorporation in the alkenes formed by thermolysis was again greatly reduced (Table 2).

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† It is not possible, however, to exclude the possibility of proton transfer to the photoexcited precursor as a minor pathway.

Table 2. Photolysis[a] and thermolysis[b] of 3-chlorodiazirine (**4**) in MeOD.

						% Yield[c] (% D Incorp.)[d]		
Entry	(**4**)	R^1	R^2	$h\nu$ or heat	T/°C	(**5E**)	(**5Z**)	(**6**)
1	**a**	Ph	H	$h\nu$	20	15.2(6.7)	10.7 (6.7)	74.1
2	**b**	Ph	Me	$h\nu$	20	38.9(2.0)	28.3 (5.5)	32.8
3	**b**	Ph	Me	Heat	70	50.3(0.3)	25.6 (0.3)	24.1
4	**c**	$PhCH_2$	H	$h\nu$	20	12.7(4.9)	22.4(13.9)	64.9
5	**d**	PhO	H	$h\nu$	20	12.3(1.2)	71.5 (0.9)	16.2

[a—d] See footnotes a—d in Table 1.

Moreover, no deuterium incorporation into the alkenes was observed when the alkenes (**2**) and (**5**) were irradiated in MeOD or when the photolyses of the carbene precursors (**1**) and (**4**) were carried out in non-hydroxylic deuteriated solvents, *e.g.*, $CDCl_3$ and C_6D_6. Photochemical transformation of the ethers (**3**) and (**6**) to give the alkenes (**2**) and (**5**) was also excluded by control experiments. All these facts clearly demonstrate that both chloro- and phenyl-carbenes generated in an alcohol either undergo 1,2-H migration to give an alkene or are protonated by the alcohol to give carbocations, which subsequently eliminate a proton to give the alkene or undergo nucleophilic trapping by the alcohol to give the ether (Scheme 3). Inspection of the product distribution in Tables 1 and 2 as a function of deuterium content immediately indicates that the extent of deuterium incorporation into the alkene increased as more O–H insertion products were formed. This is consistent with the above view since increase in extent of O–H insertion should indicate an increase in the proportion of the carbocationic route to the alkene. It should be noted, however, that the present results do not necessarily indicate that all the ether is formed *via* protonation of the carbene. More probably, some of the carbene undergoes electrophilic attack on the oxygen lone pair of electrons [path (b)] since the carbenes investigated here are recognised to be typical electrophiles. At least partial, although not exclusive, formation of the cation by protonation of the carbene is not unreasonable in the light of the well known stabilization of cations by the effect of chlorine or phenyl groups.[13,14]

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