

Carbenes and the O–H Bond: Norbornenylidenes

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Bicyclo[2.2.1]hept-2-en-7-ylidene **10** and bicyclo[2.2.1]hept-5-en-2-ylidene **21** are shown to react with methanol by way of proton transfer, with formation of norbornenyl cations.

The insertion of carbenes into O–H bonds, leading to ethers, has been primarily discussed in terms of stepwise mechanisms:¹ (a) electrophilic attack of the carbene on the oxygen atom followed by proton transfer (ylide mechanism) and (b) protonation of the carbene to give a carbocation (ion pair) followed by nucleophilic substitution (carbocation mechanism). A concerted process (c) cannot be excluded *a priori* but has not received definitive experimental support.

Attempts at observing the insertion of dialkylcarbenes into O–H bonds are often frustrated by rapid intramolecular reactions. Even in neat alcohols, 2-norbornylidene **1** was found to give nortricylene **2** and norbornene **3** rather than norbornyl ethers.² Dimethylcarbene,³ diadamantylcarbene,⁴ adamantylidene,⁵ and homocubylidene⁶ have been trapped with alcohols, although the reaction mechanism is not clear.

To date, 2-bicyclo[2.1.1]hexylidene **4** stands out as the only dialkylcarbene for which protonation-induced rearrangements have been demonstrated by means of deuterium and methyl labels.²

As compared with **1**, the norbornenylidenes **10**⁷ and **21**⁸ show diminished intramolecular reactivity. Moreover, protonation of **10** and **21** should be facilitated by homoallylic stabilization of the resulting carbocations **11** and **22**, respectively.⁹ Owing to delocalisation of the positive charge, the carbocations will give products that cannot originate from the carbenes. As a prerequisite for such studies, the carbene precursors had to tolerate alcohols. In contrast to previous work,^{7,8} we generated the norbornenylidenes by photolysis of diazirines.

Spiro(bicyclo[2.2.1]hept-2-en-7,3'-diazirine) **9** was obtained in low yield (5–10%) by application of the standard

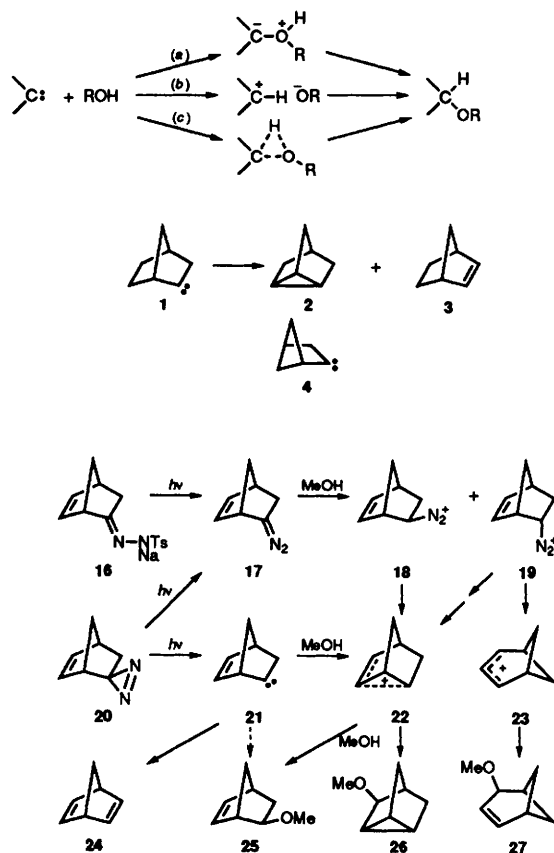


Table 2 Product distributions (%) obtained from photolyses of **16** and **20** in methanol (20 °C)

Entry	Substrate, additive	24	25	26	27
1	16 , 0.2 mol dm ⁻³ NaOMe	0.2	36.2	61.8	1.8
2	20	2.1	33.9	63.1	0.8
3	20 , 0.2 mol dm ⁻³ FN	3.7	32.7	63.6	—
4	20 , 1.0 mol dm ⁻³ FN	4.0	32.1	64.7	—
5	20 , 2.0 mol dm ⁻³ FN	4.1	31.6	65.7	—
6	20 , 0.2 mol dm ⁻³ DEF	3.7	33.2	63.1	—
7	20 , 1.0 mol dm ⁻³ DEF	3.2	34.1	61.9	—
8	20 , 2.0 mol dm ⁻³ DEF	2.8	35.6	60.2	—

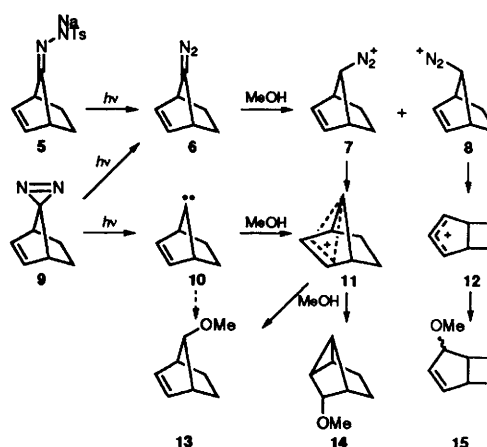


Table 1 Product distributions (%) obtained from photolyses of **5** and **9** in methanol (20 °C), Ts = tosyl

Entry	Substrate, Additive	13	14	15 ^a
1	5 , 0.2 mol dm ⁻³ NaOMe	43.3	8.4	48.3
2	5 , 1.0 mol dm ⁻³ NaOMe	48.6	12.4	39.0
3	9	92.6	4.7	2.6
4	9 , 0.2 mol dm ⁻³ NaOMe	85.0	13.1	1.9
5	9 , 1.0 mol dm ⁻³ NaOMe	72.7	24.4	2.8
6	9 , 0.2 mol dm ⁻³ Ph ₂ CO	82.0	3.9	14.1
7	9 , 1.0 mol dm ⁻³ FN ^b	86.6	13.4	—
8	9 , 1.0 mol dm ⁻³ DEF ^c	84.8	15.2	—

^a *exo:endo* ≈ 20:1. ^b Fumaronitrile. ^c Diethyl fumarate.

procedure ($\text{H}_2\text{NSO}_3\text{H}$, NH_3 , then HgO)¹⁰ to bicyclo[2.2.1]hept-2-en-7-one. The benzylimine route¹¹ afforded a stable *N*-benzylidiaziridine (60%), but the overall yield of **9** was not improved. The preparation of spiro(bicyclo[2.2.1]hept-5-ene-2,3'-diazirine) **20** from bicyclohept-5-en-2-one proceeded more smoothly (standard procedure, 21% yield). Small samples of the diazirines were conveniently purified by gas chromatography.

Upon photoexcitation of diazirines, extrusion of nitrogen to give carbenes is accompanied by isomerisation to give diazo compounds.¹² In order to generate 7-diazobicyclo[2.2.1]hept-2-ene **6** in methanol, the tosylhydrazone salt **5** was irradiated. Protonation of **6** leads to mixtures of the epimeric diazonium ions **7** and **8** which decompose by distinct reaction paths.¹³ The *anti* species **7** gives rise to the 7-norbornenyl cation **11** while dediazination of the *syn* isomer **8** proceeds by way of the bicyclo[3.2.0]heptenyl cation **12**. The product ratio (**13** + **14**):**15** indicates a 7:8 ratio close to unity (Table 1, entries 1 and 2). Only 2–3% of **15** was obtained from direct photolyses of the diazirine **9**, suggesting the intervention of 4–6% of **6** (entries 3–5). Isomerisation to the diazo compound is less significant for **9** than for the majority of 3,3-dialkyldiazirines.^{2,12} This may be due to the small bond angle at C-7 which favours sp^3 over sp^2 hybridisation. Triplet sensitisation enhances the formation of **6** (entry 6), as was observed for other spirobicyclic diazirines.² Potent dipolarophiles scavenge **6** prior to protonation, thus eliminating the diazonium route (entries 7 and 8). The ethers **13** and **14** are thus shown to originate predominantly (entries 3–5) or exclusively (entries 7 and 8) from the carbene **10**. On the other hand, both **13** and **14** are formed stereospecifically, in a ratio depending on the concentration of methoxide. Analogous data have been reported for the methanolysis of *anti*-7-norbornenyl tosylate.¹⁴ Thus the immediate precursor of **13** and **14** is clearly identified as the 7-norbornenyl cation **11**. The **13**:**14** ratios obtained from **5** and **9** are similar (entries 2–5). Therefore, the ylide mechanism and (or) concerted O–H insertion cannot contribute significantly to the formation of **13**. We conclude that the reaction of 7-norbornenylidene **10** with methanol proceeds by way of proton transfer.

With minor modifications, the 5-norbornen-2-yl system conforms to an analogous pattern. Upon photolysis of the tosylhydrazone salt **16** in methanol, protonation of the diazo compound **17** generates the diazonium ions **18** and **19** which react predominantly by way of the 5-norbornen-2-yl cation **22** to give **25** and **26**. However, a small fraction of **19** proceeds with participation of C-7 to give **23** and, eventually, **27**¹⁵ (Table 2, entry 1). Photolysis of the diazirine **20** in methanol also produces some **27** (entry 2) while none is formed in the presence of dipolarophiles (entries 3–8). Scavenging of the diazo compound **17** was confirmed by detection of an adduct with diethyl fumarate ($70 \pm 4\%$, entries 6–8). Norbornadiene **24** appears to originate from **21** rather than **22** (compare entries 1, 2, and 3–5). The low yield of **24** can be attributed to highly strained transition states for both *exo*- and *endo*-3,2-H shifts.¹⁶ The nearly constant ratio of **25**:**26** in all runs points to the carbocation **22** as the ultimate intermediate of both the diazonium ion and carbene routes. Moreover, these data exclude product formation from tight ion pairs, in some

contrast to our observations with **4**.² The delocalised charge of **22** appears to favour solvation over ion pair collapse.

We have demonstrated the ability of norbornenylidenes to accept a proton, thus adding to the number and variety of carbenes that prefer the carbocation mechanism in their reactions with O–H bonds. As for **10**, this result was anticipated in studies of carbene rearrangements leading to 7-norbornenylidene.¹⁷ Our analysis of the former circuitous route is fully confirmed by the present straightforward approach to **10**.

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