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Bicyclo[2.2.2]octylidene

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Abstract—Bicyclo[2.2.2]octylidene is formed in four quite different ways. Reactions of the precursors do not complicate the chemistry of the carbene. The products are tricyclo[$2.2.2.0^{2.6}$]octane and bicyclo[2.2.2]octene, formed in approximately a 70:30 ratio. © 2001 Elsevier Science Ltd. All rights reserved.

In this letter we describe the reactions of bicyclo[2.2.2]octylidene produced in four ways. Although this carbene has been described only once before, and there is reasonable doubt that the method reported almost 40 years ago actually made the carbene,¹ it is surely legitimate to ask why we bother to reinvestigate this seemingly straightforward bicyclic alkylcarbene.

In Grob and Hostynek's paper of 1963,¹ it was demonstrated that decomposition of the tosylhydrazone of bicyclo[2.2.2]octanone in a solution of sodium in acetamide at 160°C (Bamford–Stevens conditions) led to tricyclo[2.2.2.0^{2,6}]octane (1) and bicyclo[2.2.2]octene (2) in a 70:30 ratio. A carbene was the presumed intermediate.

In recent years, the intramolecular chemistry of alkylcarbenes has been shown to be accompanied by substantial amounts of precursor chemistry. Indeed, this problem was recognized decades ago.^{2,3} Therefore, it is of interest to uncover the real chemistry of this model for many bicyclic carbenes; to see what the unpolluted carbene chemistry really is. Much more important, various bi- and polycycloalkylidenes have served as frameworks that enforce specific geometries on cycloalkylidenes and allow mechanistic details of carbene reactions to be uncovered. For example, Nickon and co-workers have cleverly used bridged bicyclo[2.2.1]heptylidenes to investigate the effect of the extent of overlap of a carbon–hydrogen bond with the carbenes empty 2p orbital on the ease of migration of adjacent hydrogens.⁴ Very recently, Creary and Butchko used the bicyclo[2.2.2]octane framework to investigate the effect of spectator substituents on the various carbon–hydrogen insertion reactions of several bicyclo[2.2.2]octylidenes.⁵ In this latter paper, the intervention of precursor chemistry was explicitly discussed and deemed unlikely. It is our aim in this letter to put the notion that bicycloalkylidenes are truly generated in Nickon and Creary's work to the test.

Why should one be uncomfortable with the idea that thermal or photochemical decomposition of alkyl diazo compounds, surely the most widely used of all sources of carbenes, might not give pure carbene chemistry? If one takes the decompositions of dimethyl diazirine or *tert*-butyl diazomethane as exemplars, it is clear that there is a lot to worry about.^{6,7} In each case, much of the chemistry attributed to carbenes is in fact the result of rearrangement of the precursor as the nitrogen leaves. Nor is it safe to assume that only photochemical decompositions are bedeviled by precursor chemistry.⁵ There are examples of thermal reactions in which the diazo compound leads to products on its own.⁸



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It is true that the dimethyl and *tert*-butyl systems differ from the bicyclic molecules in question here. As noted by Creary and Butchko,⁵ the acyclic precursors can easily adopt conformations in which migration of carbon or hydrogen can take place as nitrogen departs, whereas the bicyclic molecules can not. Therefore, it does not seem that concerted migration in either a 1.2 or 1,3 fashion should be particularly favorable. Nonetheless, rather than rely on the assumption that carbenes are involved, we thought it worthwhile to attempt to put the mechanistic experiments on a firmer basis. We compared the ratio of tricv $clo[2.2.2.0^{2,6}]octane$ (1) and bicyclo[2.2.2]octene (2) formed from 'bicyclo[2.2.2]octylidene' made in four ways, two suspect and two not.

For the two 'non-suspect' methods we take reactions of *tert*-butylcarbene as a model. Both carbon atom-mediated deoxygenation of the related ketone^{7,9} and passage of the geminate dihalo compound through Udo Brinker's 'methyllithium tube'¹⁰ led to pure reactions of *tert*-butylcarbene, at least as judged by comparison to reactions of an unimpeachable hydrocarbon carbene source.⁷ The ratio of **1:2** from these two reactions was compared to that from two 'suspect' sources, photolysis and flash vacuum pyrolysis (FVP) of the tosyl hydrazone salt. We are happy to report that all four new reactions gave the same ratio of 1:2 within experimental error.

It would seem that both thermal and photochemical decomposition of bicyclic tosyl hydrazone salts do give pure carbene chemistry. The precursor chemistry that intrudes in the acyclic examples does not appear here, presumably because the geometry for concerted migration is unfavorable. That **1** is the major product fits well with Creary's calculation that the activation energy for formation of **1** is 2.1 kcal/mol lower than that for formation of **2**.⁵

Of course, one cannot simply dismiss the possibility of precursor chemistry in all polycyclic molecules. When the geometry of a polycyclic molecule is favorable, as in homocubylidene for example,¹¹ precursor chemistry completely dominates carbene chemistry. Again, it is a question of overlap; when a bond can align with the breaking carbon–nitrogen bond, as in the acyclic molecules, or is held in the correct position, as in homocubylidene, it participates in nitrogen loss. When a bond is not properly aligned, as in bicy-clo[2.2.2]octylidene, carbene chemistry is observed. Nitrogenous precursors should be avoided when possible in all cases in which neighboring groups can position themselves to assist nitrogen loss.



^a Average of several runs. All runs within ± 5%

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