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A PHOTOCHEMICAL SOURCE OF DIBROMO- AND DICHLOROCARBENE[1,2]

A CAUTIONARY TALE REGARDING THE STEREOCHEMISTRY OF DIBROMOCARBENE ADDITION REACTIONS

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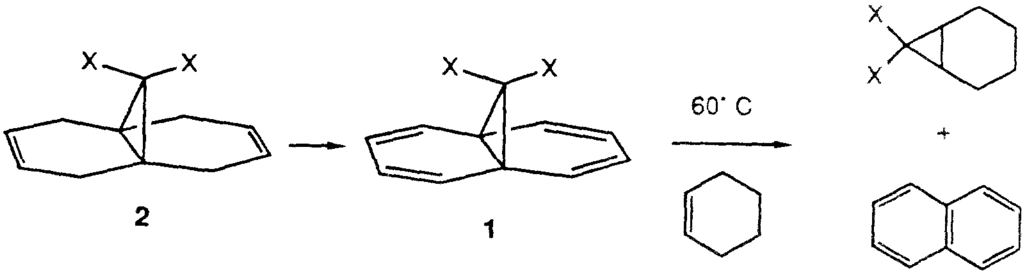
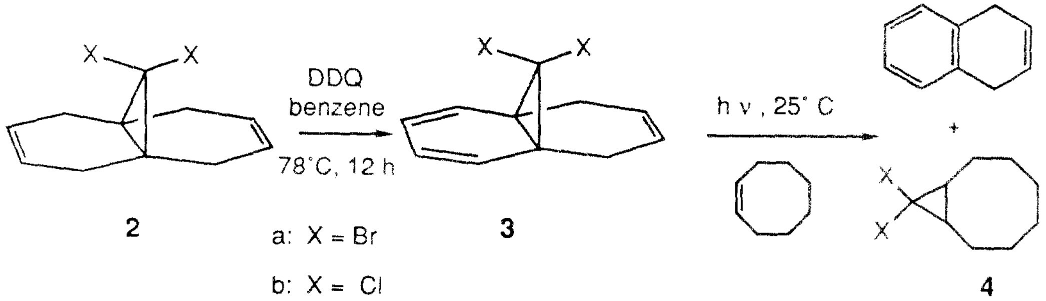
Abstract:: Photolysis of triene **3a** or **3b** yields dibromo- and dichlorocarbene which can be transferred to olefins in good yield. A warning is offered regarding the data recently interpreted as being "only consistent" with the formation of an intermediate in the addition of dibromocarbene to *trans*-cyclooctene.

DIHALOCARBENES, or their organometallic "carbenoid" equivalents, are so simple to make and use that there has been little interest in preparatively significant photochemical sources of these intermediates. An early examination of the halogenation of diazomethane yielded only extraordinarily unstable monohalogenated intermediates and has not been followed up.[3] The photochemical extrusion of dichlorocarbene from 1,1-dichloro-2-phenylcyclopropane, discovered by one of us 20 years ago,[4] gives the carbene only in low yield and has found neither a useful synthetic niche nor mechanistic application. Moreover it suffers from a serious lack of generality: neither the difluoro nor dibromo analogue undergoes the extrusion reaction.[5] We report here a new, photochemical precursor for dibromo- and dichlorocarbene which gives carbene products in high yield and promises generality. We also comment upon a recent report of the formation of a dibromocarbene-olefin complex with *trans*-cyclooctene.[6]

It has been known for some years[7] that tetraene **1** produced naphthalene at temperatures as low as 60°C. However, formation of **1** from its precursor **2** proceeds in only 2-6% yield, even in very capable hands.



Accordingly we settled upon the trienes **3a** and **3b** as potential photochemical sources of dichloro- and dibromocarbene.[7] Partial dehydrogenation of **2a** and **2b**[7b] with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) led to **3a** and **3b** in 50% yield. Irradiation of 10 mg **3a** in 0.2 mL *cis*-cyclooctene with a 450 watt Hanovia medium pressure mercury arc in a Pyrex vessel led to **4a** in ca. 80% yield as determined gas chromatographically using an internal standard. Dichlorocarbene could be transferred in similar yield to give **4b**.



Dibromocarbene produced from bromoform and potassium *tert*-butoxide is minimally affected by carbenoid involvement, at least as judged by the similarity of the :CBr_2 selectivities measured for alkene additions in the presence and absence of 18-crown-6.[8] The table compares the selectivities of dibromocarbene formed from bromoform and potassium alkoxide[8] in the presence of 18-crown-6 with that from photolysis of **3a**.

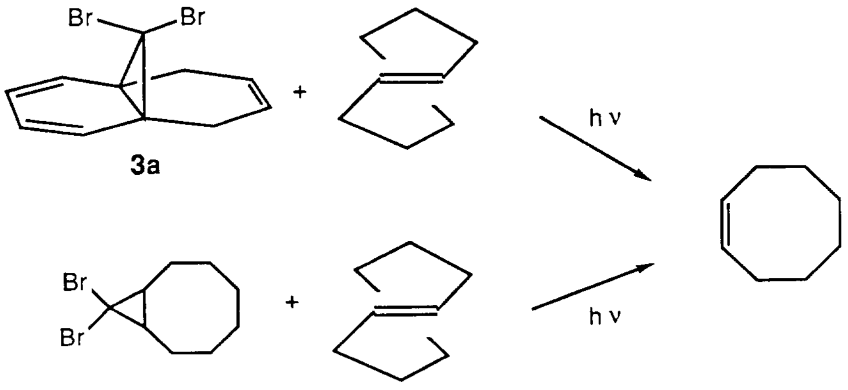
Table. Relative reactivities of olefins towards dibromocarbene.

olefin	reactivity relative to isobutene from **3a**	 from bromoform/base/crown
tetramethylethylene	3.03 3.05 (a)	4.0
trimethylethylene	1.69	2.6
trans-2-butene	0.35	0.35

(a) in the presence of 18-crown-6

These data yield selectivity indices[9] of $m = 0.55$ for dibromocarbene from **3a**. In contrast, $m = 0.65$ for dibromocarbene generated from bromoform in the presence of 18-crown-6. To the extent that the difference is significant, the carbene from **3a** is slightly less selective than that from bromoform. We doubt that a different electronic state of $:CBr_2$ is involved in the photolysis of **3a**; the selectivity differences are not large enough to reflect the great energy difference that would be involved in such a circumstance. Perhaps the carbene generated from **3a** is "solvated" by dihydronaphthalene.

We had originally hoped to use **3a** to test the extraordinary results of Dehmlow and Kramer[6] who, elaborating on earlier work of Cope,[10] found that "dibromocarbene" generated by phase-transfer mediated alcoholysis of bromoform reacted with *trans*-cyclooctene to give a somewhat non-stereospecific addition (trans/cis = 92/8, 77/23 at 30-40% and 80-90% conversion) and largely isomerized starting olefin (trans/cis = 8/9 and 1/9 at 30-40% and 80-90% conversion). Dehmlow and Kramer explained these startling data by invoking a carbene-olefin complex, which (by inference) was able to isomerize olefin but not to form cyclopropane efficiently. Dichlorocarbene behaved in the traditonal manner: neither non-stereospecific addition nor isomerized starting olefin was found. Although we have reproduced the data of Dehmlow and Kramer *exactly,* in performing control experiments we have also revealed the exceptional sensitivity of this system. Not only is *trans*-cyclooctene substantially isomerised to the cis isomer when a solution of **3a** is irradiated, but even photolysis of a simple geminate dibromocyclopropane such as **4a** serves to induce the isomerization! We suspect the active ingredient is a small number of bromine atoms, and have verified that photolysis of 36 mg NBS in .1 mL *trans*-cyclooctene and 2 mL CCl_4 also completely isomerizes the olefin to the more stable cis isomer with little other evident reaction.



3a

4a

Thus our reproduction of the earlier[6] results is illusory and has no relevance to the question at hand. Therefore we do not (indeed, cannot) cast any direct light on the findings of Dehmlow and Kramer, but we can attest to the sensitivity of the olefin and suggest that very close attention be given to the possibility of isomerization of starting olefin by organometallic, radical (or other) agents.

These isomerizations may be general. We have found that a similar conversion, this time cis to trans, occurs when **3a** is used to transfer dibromocarbene to *cis*-4,4-dimethyl-2-pentene, as long as the concentration of the olefin is kept relatively low. If the usual immense excess of olefin is used, no isomerization of the solvent can be noticed.

References and Notes:

1. We are grateful to the National Science Foundation for support of this work through grants CHE 83 18345 (Princeton) and CHE 85 11822 (Rutgers). We thank David R. Myers for helpful comments.

2. Much of this work is taken from the Thesis of JFH submitted in partial fulfillment of the requirements of the B.A. degree, Princeton University, 1986.

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