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A SOLVENT EFFECT IN REACTIONS OF SINGLET METHYLENE

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Summary: The effect of several solvents on the selectivity of singlet methylene (^{1}:CH$_2$) was investigated. It was found that product ratios from reactions in pentane, ethyl ether and cyclohexene solutions were identical; however, product ratios from reactions carried out in benzene were slightly different.

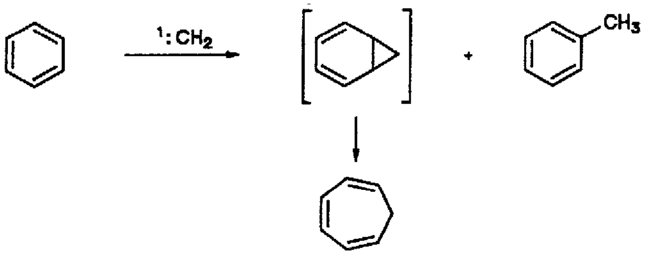
It has been suggested that, in some situations, reaction of a carbene with an electron pair donor might produce a loosely bound carbene complex. This has found some support in theoretical studies,[1] and carbene complexes have often been proposed as reaction intermediates.[2,3] The formation of such a complex between a carbene and a solvent molecule might influence the reactivity of the carbene towards a solute molecule. The study of solvent effects on reactions involving carbenes may therefore be a way to study carbene-molecule complexes, if they do indeed exist, or other carbene-molecule interactions.

Reported here are results of experiments in which the effect of solvent on the selectivity of singlet methylene (^{1}:CH$_2$) was investigated. The results of these experiments extend the earlier findings of Russell and Hendry, who reported a difference in the distribution of products from the reaction of benzene with singlet methylene in aromatic solvents versus aliphatic solvents.[4] The reaction of 2,3-dimethylbutane with the carbene was also examined in the earlier study, but within experimental error, no solvent effect was seen. The present experiments employed the reaction of singlet methylene with two solutes, benzene and 2,5-dimethylhexane. Pentane, benzene, ethyl ether (an n-donor)[5] and cyclohexene (a pi-donor)[6] were used as solvents.

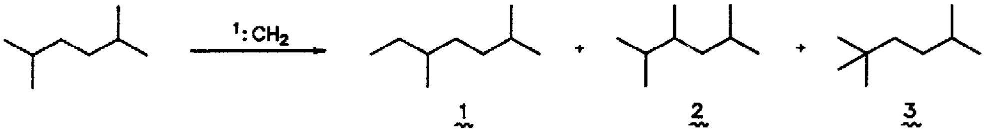
Because of the great reactivity and notoriously low selectivity of methylene, only small changes in selectivity were expected in these experiments. Offsetting this disadvantage was the fact that methylene can be reliably produced in the singlet state, in a wide variety of solvents, by the photolysis of diazomethane. Also, reaction of singlet methylene with hydrocarbons occurs faster than intersystem crossing to the more stable triplet state, simplifying the interpretation of the experimental results.[7]

Diazomethane was generated by the addition of a solution of N-methyl-N-nitroso-*p*-toluenesulfonamide in 2-ethoxyethyl ether to 50% aq. KOH at 85°. The diazomethane was swept from this mixture by a stream of nitrogen and trapped in decahydronaphthalene. The resulting decahydronaphthalene solution was dried over KOH and purged with nitrogen. The diazomethane was then transferred in a stream of nitrogen from the decahydronaphthalene solution to a 10% solution of the solute in the solvent being studied. The resulting solutions were photolyzed at room temperature under N_2 using a medium pressure 450 W Hg lamp with a pyrex filter.

The carbene reacted with both the solute and the solvent and in all cases the reactions led to the anticipated products. In a typical reaction 3-5% of the solute reacted with methylene. Toluene and cycloheptatriene, the products of the reaction of methylene with benzene (eq 1), were identified by comparison of GC retention times and mass spectra with those of authentic samples. Products of the reaction of methylene with 2,5-dimethylhexane (eq 2) were isolated by preparative gas chromatography and identified through ^{1}H NMR, ^{13}C NMR, and mass spectrometry. The product distributions were determined by gas chromatography and are shown in Table 1. GC (FID) response factors were not determined, but were assumed to be equal for isomeric compounds.



(1)



(2)

There was no significant difference between the ratio of cycloheptatriene to toluene produced when the reaction was run in pentane (3.86:1) and the product ratio produced in either ether or cyclohexene solution. In contrast, there was a small but significant difference between this product ratio and that produced in benzene (4.14:1). The product ratios found in pentane and in benzene agree reasonably well with those reported by Russell and Hendry (see Table 1).

In the reaction of methylene with 2,5-dimethylhexane, the choice of solvent was again found to have an effect on the product distribution. Product ratios are identical (within experimental error) in pentane, ethyl ether and cyclohexene solutions, while the ratio of **1** to **3** is significantly different when the reaction is run in benzene. It should be noted that in this reaction the usual gas phase order of C-H bond reactivity, $3^{o}>2^{o}>1^{o}$, was not observed. Instead, per bond C-H selectivities of 1.2:0.6:1.0 (3^{o}:2^{o}:1^{o}) were seen in pentane solution. It has been suggested that steric factors, as well as bond energies, may be important in controlling

Table 1. Distribution of products from the reaction of ^{1}:CH$_2$ with benzene and the reaction of ^{1}:CH$_2$ with 2,5-dimethylhexane in four different solvents.

	benzene + ^{1}:CH$_2$ [a]		2,5-dimethylhexane + ^{1}:CH$_2$ [b]		
solvent	cyclo-heptatriene	toluene	1	2	3
pentane	3.86 ± 0.02	1.00	5.18 ± 0.04	1.44 ± 0.01	1.00
	3.8 ± 0.2 [c]	1.0			
ethyl ether	3.87 ± 0.01	1.00	5.22 ± 0.02	1.43 ± 0.01	1.00
cyclohexene	3.87 ± 0.05	1.00	5.19 ± 0.03	1.46 ± 0.01	1.00
benzene	4.14 ± 0.02	1.00	5.38 ± 0.01	1.48 ± 0.01	1.00
	4.8 ± 0.4 [d]	1.0			

[a] Product concentrations are expressed relative to that of toluene. Errors are reported as the standard deviation for three experiments. [b] Product concentrations are expressed relative to that of 3. Errors are reported as the standard deviation for three experiments. [c] Value reported in ref 4 for reaction run in 2,3-dimethylbutane. [d] Value reported in ref 4.

the rate of singlet methylene reaction with C-H bonds.[8] The decreased preference for attack on the 2° C-H bonds of 2,5-dimethylhexane, which are both alpha and beta to isopropyl groups, may be due to steric hindrance.

The consistency of the product ratios from reactions run in pentane, cyclohexene and ethyl ether is in keeping with the very low selectivity of singlet methylene and with reaction rates approaching the diffusion limit.[7] Any interaction of methylene with the pi-bond in cyclohexene or the oxygen atom in ether must lead directly to products or to species which do not react with the solute to give the anticipated products.[9]

The small change in methylene selectivity in benzene solution stands out against this background, with the results obtained with 2,5-dimethylhexane suggesting that this solvent effect may be more general than was realized previously. In the earlier study,[4] Russell and Hendry suggested that the difference in selectivity that they observed between reactions run in aromatic and aliphatic solvents was due to the formation of a complex between the carbene and the pi-system of the aromatic solvent molecules. While the results of the experiments reported here are consistent with this explanation, the observation of a solvent effect only requires a change in the relative free energies of the transition states involved and does not necessarily indicate the presence of a stable carbene-solvent complex. We also point out that although the product ratios are different in benzene than in the other solvents, methylene is not necessarily *more* selective in benzene.

In summary, it was found, in the reaction of singlet methylene with benzene and with an alkane, that the selectivity of the carbene was identical in pentane, ethyl ether and cyclohexene. The selectivity was found to be altered slightly in reactions run in benzene solution and this is ascribed to an interaction of the carbene with the solvent. The reaction of methylene with additional solutes is being examined to confirm the generality of this solvent effect. Other solvents, in particular aromatic solvents, are also being examined, as well as other less reactive carbenes.

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References and Notes

(1)(a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2250. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (c) Eades, R. A.; Gassman, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 1066. (d) Gleiter, R.; Hoffmann, R. *Tet.* **1968**, *34*, 5899.

(2)(a) Moss, R. A.; Lawrynowicz, W.; Turro, N. J.; Gould, I. R.;Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028. See, however, (b) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tet.* **1985**, *41*, 1555. (c) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919.

(3)(a) Lambert, J. B.; Larson, E. G.; Bosch, R. J. *Tet. Lett.* **1983**, 3799. (b) Dehmlow, E. V.; Kramer, R. *Ang. Chem. Int. Ed. Engl.* **1984**, *23*, 706. (c) Liu, M. T. H.; Soundarajan, N.; Paike, N.; Subramanian, R. *J. Org. Chem.* **1987**, *52*, 4223. (d) Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 2101.

(4) Russell, G. A.; Hendry, D. G. *J. Org. Chem.* **1963**, *28*, 1933.

(5) Ether solvents have been reported to effect the selectivity of arylcarbenes. See Tomioka, H.; Ozaki, Y.; Izawa, Y. *Tet.* **1985**, *41*, 4987.

(6) It has been suggested that carbene-molecule complexes are intermediates in the addition of halocarbenes to alkenes. See ref 2.

(7) (a) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (b) Jones, M.; Moss, R. A. *Carbenes*; Wiley: New York; vol. 1, 1972; vol. 2, 1975.

(8) Halberstadt, M. L.; Crump, J. *J. Photochem.* **1972/73**, *1*, 295.

(9) The carbene may react with ethyl ether to give an oxonium ylide. See Kirmse, W.; Kund, K. *J. Am. Chem. Soc.* **1989**, *111*, 1465 and references cited therein.

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