

chemical shift difference (exchange lifetime $\ll 3 \times 10^{-3}$ sec). The latter possibility is more likely (*vide infra*).

Within an uncertainty of *ca.* 0.5 Hz no solvent-dependent differences in vicinal coupling constants (or in line widths of unresolved multiplets) were detected for any resolved peaks including those for the backbone protons of C10, C11, and C13 or those for the cyclic ether ring protons on C14 and C19. Thus large conformational changes in much of the backbone or in the rings do not occur although the data do not exclude minor adjustments ($\lesssim 10^\circ$) of the dihedral angles. Furthermore, the coupling constants in CDCl_3 and in acetone are all within ~ 1 Hz of those estimated¹⁰ on the basis of the torsion angles found in crystal modification I.

In contrast to the lack of variation of coupling constants with solvent, marked changes in the chemical shifts occur. Of particular interest are changes in peaks due to the methyl protons on the ethyl side chains since these resonances should be relatively insensitive to the changes in solvent *per se* or to changes in electron density around possible ligands to metal ions. In fact, one of the methyl triplets changes from δ 0.58 in CDCl_3 to δ 0.83 in acetone-*d*₆, a difference of 0.25 ppm, while the triplets at δ 0.80 and δ 0.98 in CDCl_3 are found in acetone at δ 0.84 and δ 0.90, respectively. Data for the free acid of Br-X-537A are useful for an interpretation of these effects. (This derivative has yielded only one crystalline form from several solvents and contains a "head" to "head" dimer.⁴) In CDCl_3 the three methyl triplets are found at δ 0.81, 0.83, and 0.94 ppm, and in acetone at δ 0.84, 0.84, and 0.87 ppm. None of the resonances of the free acid changes by more than 0.07 ppm between solvents so it is unlikely that the 0.25 ppm change seen for one peak in the sodium salt is a direct result of solvent interactions. Anisotropy due to an aromatic ring current is the most probable cause of the large upfield shift observed in the less polar solvent.

A conformational change within the monomeric unit is one possibility for the difference in going from acetone to CDCl_3 . However, placing any one of the ethyl group methyls above the aromatic ring and close enough to give a 0.25 ppm shift requires a fairly substantial rearrangement. Such a conformation would probably not bind sodium and would probably be manifest in significant changes for vicinal coupling constants for backbone resonances, changes which are not observed. The crystal structure data offer another, more plausible, explanation for the ring current-induced shift.

In the molecular structure (Figure 1) obtained from crystals grown in CCl_4 (modification I) none of the methyl groups would experience any appreciable upfield shift due to the aromatic ring of their own chain. However, the protons of methyl C37 would be shifted upfield ~ 0.7 ppm¹¹ due to the aromatic ring of its partner in the head-to-tail dimer. We have tentatively assigned the triplet at δ 0.58 ppm in CDCl_3 to C37.¹² Osmotic pressure data on the Na^+ salt of 5-Br-X-537A

(10) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969.

(11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965.

are consistent with dimer formation in chloroform, whereas in 1:1 CHCl_3 -isopropyl alcohol, monomer is suggested.¹³

The nmr data strongly suggest the presence in non-polar solvents of a dimeric form of Na^+ salt of 5-Br-X-537A similar (but not quite identical) to that found in the X-ray study on the crystals obtained from CCl_4 . The progression of the C37 chemical shift to lower field as the solvent polarity increases is probably due to a facile equilibrium between a head-to-tail dimer and either a dimeric species of quite different orientation or else a monomeric species. In any case the backbone conformation is not appreciably perturbed by the solvent change. It is significant to note that a dimeric structure has been found in all six crystal structures of derivatives of X-537A and their salts (present work and ref 4-7). Furthermore the torsion angles in the backbone chain for the 12 independent X-537A molecules or anions do not vary by more than $\pm 8^\circ$.

We believe that our work emphasizes the great importance of dimeric structures for X-537A in nonpolar solvents and also the need to recognize a high degree of conformational integrity in this system, factors which apparently have not always been given due attention.³

Acknowledgment. This work was supported by NIH Grants GM 19336 (I. C. P.) and GM 18038 (P. G. S.). We thank Dr. J. W. Westley of Hoffmann-La Roche, Inc., for provision of samples and helpful discussion.

(12) Exact agreement with the predicted shift change is not expected because of the great sensitivity of ring current-induced shifts to orientational factors, especially in the case of an ethyl group having several degrees of possible internal rotational freedom.

(13) J. W. Westley and V. Toome, private communication.

Paul G. Schmidt,* Andrew H.-J. Wang, Iain C. Paul*
W. A. Noyes Chemical Laboratory, University of Illinois
Urbana, Illinois 61801
Received June 19, 1974

Effect of Pressure on the Competing [2 + 2] and [2 + 2 + 2] Cycloadditions of Tetrachlorobenzene and Norbornadiene¹

Sir:

It is a well-known fact that liquid phase reactions characterized by bond formation are greatly facilitated by the application of hydrostatic pressure and, conversely, that bond cleavage is strongly impeded.² In recent years we obtained indications that processes involving multiple bond changes are proportionately more sensitive.³ Since then a number of applications have been reported; thus, Eckert has shown by means of high pressure experiments that the Diels-Alder reaction is a concerted one and that it is subject to attractive secondary orbital interactions when these are possible.⁴ Stewart⁵ has applied the criterion to the

(1) Paper XXXII in the series: "Kinetics of Reactions in Solutions under Pressure."

(2) For a recent review, see R. C. Neuman, *Accounts Chem. Res.*, **5**, 381 (1972).

(3) (a) W. J. le Noble, R. Goitien, and A. Shurpik, *Tetrahedron Lett.*, 895 (1969); (b) I. Fleming and C. R. Owen, *J. Chem. Soc. B*, 1293 (1971).

(4) (a) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 2918, 7149 (1970); (b) C. A. Eckert, *Accounts Chem. Res.*, in press; (c) C. Brun and G. Jenner, *Tetrahedron*, **28**, 3113 (1972); C. Brun, G. Jenner, and A. Deluzarche, *Bull. Soc. Chim. Fr.*, 2332 (1972); (d) K. Seguchi, A. Sera, and K. Maruyama, *Tetrahedron Lett.*, 1585 (1973); (e) W. G. Dauben and A. P. Kozikowski, *J. Amer. Chem. Soc.*, **96**, 3664 (1974).

(5) C. A. Stewart, *J. Amer. Chem. Soc.*, **94**, 636 (1972).

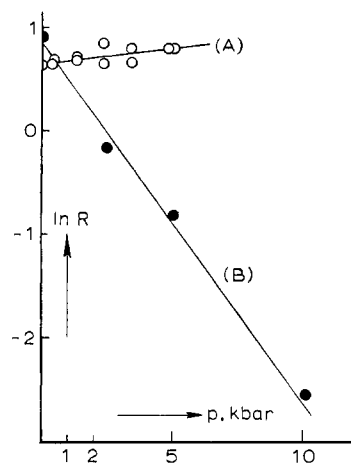
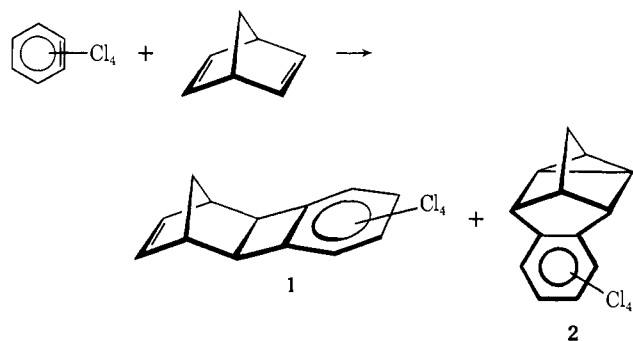


Figure 1. The effect of pressure on the ratio of cycloaddition products: (A) $R = 1/2$; (B) $R = 3/4$.

dimerization of chloroprene and found that the [2 + 4] adducts become greatly favored at high pressure over the competing [2 + 2] products—presumably because the latter are formed by a pathway in which only one bond is developing in the main transition state.

It is also known² that the solvation of ionic sites causes large volume decreases (electrostriction), and it seemed to us that this effect might well mask the indication of a moderate activation volume for a stepwise cycloaddition; in fact, it seemed possible that pressure might favor this process over a concerted one if the intermediate is a full-blown zwitterion. In our search for examples, we have found that the cycloaddition of tetrachlorobenzene to norbornadiene, a reaction first studied by Heaney,⁶ is a case in which solvation indeed compensates for a lag in bonding. The benzyne can be generated either by diazotation of tetrachloroanthranilic acid or by the reaction of butyllithium with hexachlorobenzene; the product ratio is virtually independent of the method of generation. Since the decomposition of pentachlorophenyllithium proceeds at a convenient rate at room temperature in ether, we employed this technique to generate the benzyne. The ratio 1/2 was

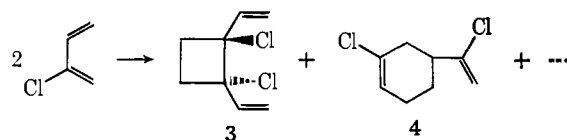


measured as a function of pressure by means of vpc; we showed that the several minor side products visible in the gas chromatograms derive from pentachlorophenyllithium alone, and that 1 and 2 are stable to our conditions. At high pressure these side reactions quickly become dominant, and it was not possible to

(6) H. Heaney, J. M. Jablonski, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc. C*, 3129 (1971).

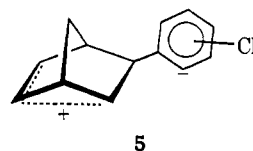
make measurements above 5 kbar. The results are shown in Figure 1.

For comparison we show Stewart's data for the ratio of 3/4 in the dimerization of chloroprene. It is clear



from this plot that the advantage bestowed upon the concerted cycloaddition by the application of pressure in Stewart's case is not present in ours; in fact, the [2 + 2] reaction is slightly favored. The $\Delta\Delta V^\ddagger$ values are +8.4, and -0.7 cm³/mol, respectively.

We ascribe the disappearance of this advantage to solvation of a zwitterionic intermediate, 5, and note



that this is in agreement with solvent effects on the product ratio noted by Heaney.⁷ We conclude that inferences regarding the degree of concertedness drawn from the pressure effect in pericyclic reactions are safe only if definite information is available to judge the degree of diradical *vs.* zwitterionic character of any intermediates that might be intervening.⁸

Acknowledgment. Professor Heaney kindly sent us samples of his products for comparison. The National Science Foundation generously supported this work.

(7) H. Heaney and J. M. Jablonski, *Tetrahedron Lett.*, 2733 (1967).

(8) A similar problem has been encountered by Neuman² in the presumably concerted perester decomposition; electrostriction around the radicals due to partial charge development reduces the value of the activation volume in that case also.

W. J. le Noble,* R. Mukhtar

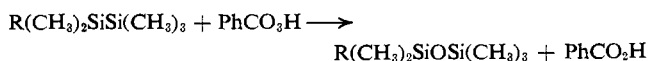
Department of Chemistry, State University of New York
Stony Brook, New York 11794

Received July 6, 1974

Charge-Transfer Spectra and Peracid Oxidation of 1,2-Disilacycloalkanes. A Rate-Charge-Transfer Relationship in the Electrophilic Reaction at σ -Bonds

Sir:

In 1965 we reported an oxidation reaction of organo-disilanes with perbenzoic acid involving direct insertion of an oxygen atom into the silicon-silicon σ -bond.¹



This reaction, with obvious indications by kinetic results,¹ can be considered as a typical example of electrophilic reactions taking place at the σ -bond.² Recently,

(1) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *J. Amer. Chem. Soc.*, **87**, 4001 (1965).

(2) M. Kira, Ph.D. Thesis, Tohoku University, Sendai, Japan, 1973.