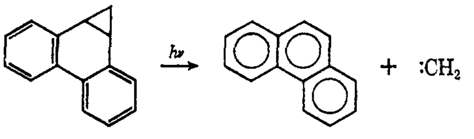
# Fragmentation and Rearrangement Pathways in Benzonorcaradiene Photochemistry

*Sir:*

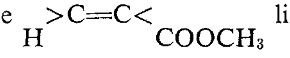
Dibenzonorcaradiene (I) undergoes photolysis to give phenanthrene (II) and methylene in greater than 90% yield.[1a] Likewise, the only reported products from benzonorcaradiene irradiation were naphthalene



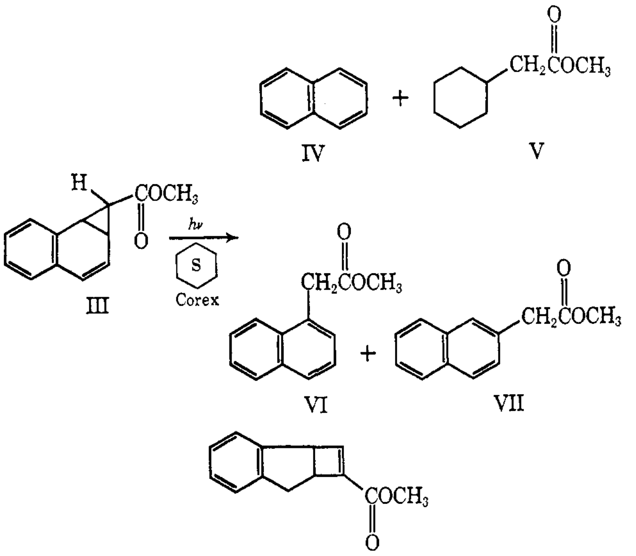
I II

and bismethanonaphthalene.[1b] We wish to report radically different behavior for the carbomethoxy-substituted benzonorcaradiene (III)[2] on irradiation. Whereas I follows a single reaction pathway, III shows a complex spectrum of products. One of these photoisomers arises *via* a sequence without apparent analogy in these systems.

When the photolysis of III in cyclohexane was monitored by vpc (5% PDEAS on 60–80 Chrom W) there was observed the formation of five major products. In a typical irradiation 0.63 g of III in 150 cc of cyclohexane was irradiated for 5 hr to give the following volatile products:[3] recovered III (12%); naphthalene, IV (13%); methyl cyclohexylacetate, V (10%); methyl 1- and 2-naphthylacetates, VI (14%) and VII (4%); and VIII (11%). Products IV, V, VI, and VII were separated by preparative vpc and assigned structures by ir and nmr comparison with authentic compounds.

The remaining product was isolated and purified by vpc. The mass spectrum (70 eV) showed a parent ion at *m/e* 200 as well as predominant peaks at 169, 141, 116, and 115. The ir (neat) absorptions at 5.79, 6.19, and 6.23 μ suggested the presence of a conjugated ester. This was confirmed by the nmr spectrum ($CCl_4$) which showed the aromatic protons as a singlet at τ 2.90 (4 H), a low-field vinyl absorption at τ 3.07 (1 H), two broad absorptions centered at τ 5.82 (1 H) and about 6.16 (1 H), a methoxy resonance at τ 6.34 (3 H), and a doublet with fine structure centered at τ 6.93 (2 H). The appearance of the two absorptions centered at τ 5.82 and 6.16 together with the deshielded olefinic proton resonance at τ 3.07 suggested a tricyclic ring system having two bridgehead hydrogens and incorporating the  $\underset{H}{>C}{=}\underset{COOCH_3}{C<}$ linkage.

Two structures for the photoester in agreement with the spectroscopic data would be VIII and IX. The availability of the known nitriles XIa and XIb[4,5]



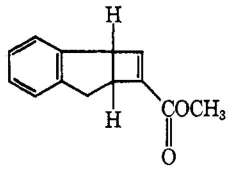
IV V

III

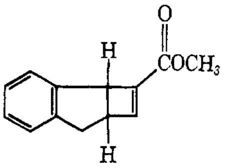
VI VII

VIII

allowed a direct test for IX by comparison of the hydrogenated photoacid with the hydrolysis products of the nitriles. Preparation of X, XIa, and XIb *via* the sequence outlined below and comparison of their ir and



VIII



IX

nmr spectra showed them to be three different compounds. Thus, the photolysis product does not correspond to IX.

Since no facile synthesis of X was apparent, it was degraded *via* the perester to the hydrocarbon XIII (49% yield);[6] mass spectrum (70 eV): 144 (parent, 3% of base peak), 116 (base peak); exact mass calculated, 144.0936; found, 144.0928. Decarboxylation of XIIa in a similar fashion led to isolation of the identical hydrocarbon XIII as established by a comparison of vpc retention times and of ir and nmr spectra. The identification of the ring structure coupled with the nonidentity of the hydrogenated photoacid X with either

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[1] (a) D. B. Richardson, L. R. Durrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretsky, *J. Am. Chem. Soc.*, **87**, 2763 (1965); (b) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6798 (1967); **89**, 6799 (1967).

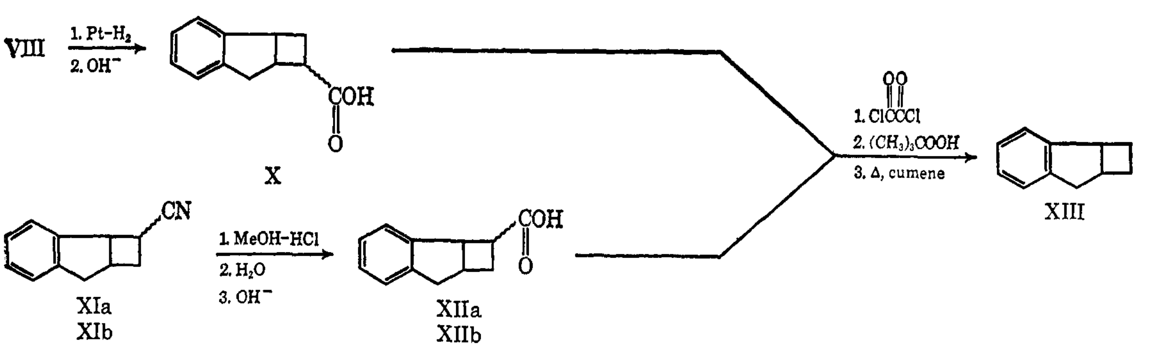
[2] Ciganek has reported that the carboethoxy derivative of III yields naphthalene and ethyl cyclohexylacetate upon irradiation: E. Ciganek, *ibid.*, **89**, 1458 (1967).

[3] All photolyses were carried out with a 450-W medium-pressure source in an atmosphere of purified nitrogen. Yields of VI were dependent upon irradiation and work-up conditions. Prolonged irradiation, irradiation through Vycor, or prolonged heating of the reaction mixture led to reduced yields of VIII. Vpc yields were determined using added diphenyl ether as internal standard. The nonvolatile products are currently under investigation and will be reported in a full account of this work.

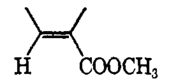
[4] J. J. McCullough and C. W. Huang, *Chem. Commun.*, 815 (1967). A full discussion of this work is accepted for publication in *Can. J. Chem.* We wish to thank these authors for a generous gift of nitriles XIa and XIb.

[5] The configuration of the epimeric nitriles is unknown. Here they will be distinguished by melting point. Nitrile XIa, mp 67–69°, was converted to acid XIIa, mp 141–143°. Nitrile XIb, mp 48–50°, was converted to acid XIIb, mp 85–87°. X had mp 101–104°. Satisfactory analyses were obtained for X, XIIa, and XIIb.

[6] J. Meinwald, P. G. Gassman, and J. J. Hurst, *J. Am. Chem. Soc.*, **84**, 3722 (1962). We thank Professor Gassman for suggesting this procedure.

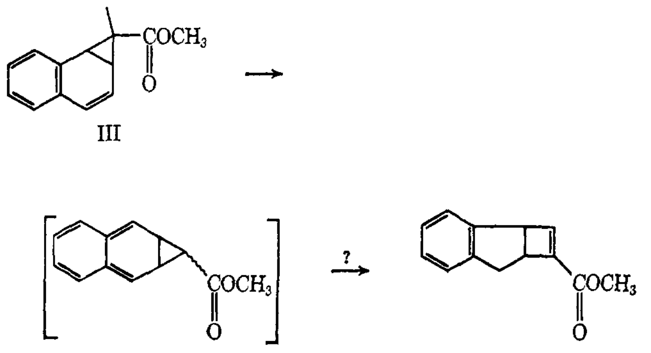


XIIa or XIIb and the requirement of the



linkage establishes the photoisomer as VIII.

The photofragmentation of I to naphthalene and carbomethoxycarbene has much analogy in earlier work.[1,2] Although processes analogous to the formation of esters VI and VII have not been reported,[1,2] they are easily understood by breakage of the external bond of the cyclopropane ring followed by a 1,2-hydrogen shift.[7] The intriguing transformation of III → VIII appears to be without precedent in these systems. Most mechanisms which can be written involve stable ground-state precursors which have not been detected in our studies. It is apparent that either carbomethoxy migration has occurred or else an intermediate having the symmetry of XIV is involved in this rearrangement. We are pursuing experiments aimed at establishing the mechanism of this interesting and unusual transformation.



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(7) D. I. Schuster and I. S. Krull, *J. Am. Chem. Soc.*, **88**, 3456 (1966).

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## Enthalpies of Transfer of SN2 and SNAr Transition States from a Protic to a Dipolar Aprotic Solvent

*Sir:*

The much faster rates and lower activation enthalpies of SN2 and SNAr reactions in dipolar aprotic solvents relative to polar protic solvents have been the subject of much recent study and speculation.[1] This effect can be attributed to enhanced solvation of the nucleophiles in the protic solvent or to greater solvation of the transition states in the dipolar aprotic solvent. Recently we were able to show[2] that the effect on the enthalpy of activation in the case of an SN2 reaction involving an *uncharged nucleophile* (pyridine) was caused entirely by increased solvation of the transition state in the dipolar aprotic solvent (dimethylformamide) and not by increased solvation of the reactants in the protic solvent (methanol). We now present data showing that a similar conclusion holds for a representative sample of SN2 and SNAr reactions involving *charged nucleophiles.*

The enthalpy of transfer of a transition state from one solvent to another, $\delta H^{t}$, is obtained from the relation: $\delta H^{t} = \delta\Delta H_{s} + \delta\Delta H^{\ddagger}$, where $\delta\Delta H_{s}$ is the enthalpy of transfer of the reactants from one solvent to the other and $\delta\Delta H^{\ddagger}$ is the difference in the enthalpies of activation of the reaction in the two solvents. Table I shows the results of our calorimetric measurements of the heats of solution, $\Delta H_{s}$, in methanol and DMF of a number of reagents of interest. Making the assumption that tetrabutylammonium ion and tetrabutylboride ion have the same enthalpies of transfer[3] we can then calculate the single ion enthalpies of transfer for the nucleophiles of interest listed in Table II.

Table III compares the $\delta\Delta H_{s}$ values for the reactants in three SN2 reactions and four SNAr reactions with their respective $\delta\Delta H^{\ddagger}$ values, from which are calculated the $\delta H^{t}$ values for these reactions. As can be seen, in all cases the enthalpy of transfer of the transition state from methanol to DMF is exothermic. In all but one case, the enthalpies of transfer of the reactants are also exothermic!

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(1) For a recent discussion and references see R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968).

(2) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginzberg, and P. Steinhertz, *Chem. Commun.*, 194 (1968).

(3) Similar assumptions had been made by E. M. Arnett and D. R. McKelvie, *J. Amer. Chem. Soc.*, **88**, 2598 (1966); O. Popovych, *Anal. Chem.*, **38**, 558 (1966).