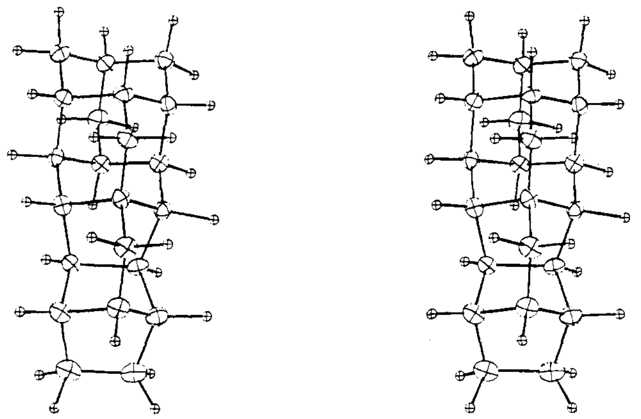

Figure 2. Stereopair representation of nonacyclo[11.7.1.$1^{2,18}$.$0^{3,16}$.$0^{4,13}$.$0^{5,10}$.$0^{6,14}$.$0^{7,11}$.$0^{15,20}$]docosane (VI).

bornane, noradamantane,[11] bicyclo[3.2.1.]octane, and diamantane units are all interconnected. In effect, the two carbon atoms shown by heavy dots in II have been moved to the extreme upper left in VIa to make an ethylene bridge (C_8 and C_9) of the norbornane moiety.

I, II, and III must be considerably more stable than VI. Despite this, none of the regular tetramantanes are formed, at least from V. We have also heated VI with the catalyst at 150° but, besides loss of material,[7] no further isomerization could be observed. This result shows that, at least in the higher members of the series, the usual thermodynamic considerations[3-5,7,11,12] do not alone control the nature of the product obtained. Not only diamondoid molecules but also polycyclic cage systems of irregular structure can be prepared by the rearrangement route.

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(11) Noradamantane can also be prepared by rearrangement: P. von R. Schleyer and E. Wiskott, *Tetrahedron Letters*, 2845 (1967).

(12) A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, 31, 1617 (1966).

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Reactions of Olefins and Palladium Chloride in the Presence of Fluoride Salts

Sir:

The dimerization of ethylene to an isomeric mixture of butenes catalyzed by palladium salts in organic solvents has been reported.[1,2] We have discovered an unusual effect of fluoride salts, most notably sodium fluoride, on the course of this reaction. For example, the reaction of ethylene, palladium chloride, and sodium fluoride in benzonitrile at 160° resulted in the formation of propylene as the major hydrocarbon product.

In a typical experiment, a mixture of 0.010 mol of palladium chloride, 0.10 mol of sodium fluoride, and 40 ml of benzonitrile was heated under vacuum to 160° in a shaking autoclave with a capacity of 75 ml. Ethylene was then added to a pressure of 20 psig. After 4 hr (11 psig) the gas was transferred to an evacuated sample bulb and then examined with gas chromatography using a supported dibutyl maleate column at 45° and a silica gel column programmed from 50 to 200°. The gas sample had the following analysis: ethylene (56.6%), propylene (15.1%), 1-butene (0.98%), *trans*-2-butene (2.7%), *cis*-2-butene (0.96%), methane (2.9%), ethane (1.6%), vinyl fluoride (0.21%), acetaldehyde (1.4%), carbon monoxide (1.0%), and carbon dioxide (21.5%).[3] In the absence of sodium fluoride, there occurred a similar pressure drop, but in this case the product gas mixture contained very little propylene (<0.3%). The addition of potassium fluoride resulted in a slight increase in the amount of propylene formed, whereas lithium fluoride and cesium fluoride inhibited propylene formation. The results of the experiments performed in benzonitrile are summarized in Table I.[4]

Table I. The Reaction of Ethylene and Palladium Chloride in Benzonitrile[a]

Salt	Percentages in product gas mixture C_2H_4	C_3H_6	C_4H_8[b]	CH_4	C_2H_6	C_2H_3F
NaF	56.6	15.1	3.7	2.9	1.6	0.21
None	68.0	0.28	1.2	0.57	20.8	*c*
KF	85.0	0.66	1.1	0.70	0.81	0.12
LiF	85.6	0.047	0.30	0.13	13.7	
CsF	96.3	0.062	0.13	0.28	2.5	0.29
NaF[d]	99.9					

[a] 40 ml of solvent, 0.010 mol of $PdCl_2$, 0.10 mol of salt, 160° for 4 hr. [b] Mixture of isomers. [c] 0.61% C_2H_3Cl found. [d] No $PdCl_2$ present.

Similar results were obtained with adiponitrile and nitrobenzene as solvents (Table II). Again, the addition of sodium fluoride catalyzed the formation of propylene from ethylene. However, in nitrobenzene this effect is not as pronounced as in the nitrilic solvents. Using adiponitrile as the solvent, sodium chloride was shown to cause a slight increase in the amount of propylene.

All of the reactions are complicated by a concurrent reaction of solvent with palladium chloride which resulted in formation of palladium metal. The organic products of these reactions have not been investigated thoroughly. It has been determined, however, that

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(1) A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).

(2) J. T. Van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964).

(3) All products were identified by comparisons of gas chromatographic retention times and mass spectra with those of authentic samples.

(4) The amounts of acetaldehyde, carbon monoxide, and carbon dioxide formed in these reactions were not reproducible and are not given in the tables. The formation of these products is probably due to small amounts of water and oxygen in the reaction system.

Table II. The Reaction of Ethylene and Palladium Chloride in Adiponitrile (ADN) and Nitrobenzene (NB)[a]

Solvent	Salt	Percentages in product gas mixture					
		C_2H_4	C_3H_6	C_4H_8[b]	CH_4	C_2H_6	C_2H_3F
ADN	NaF	68.5	8.4	0.95	1.2	12.0	0.1
	None	69.5	0.05	1.03	0.70	21.0	c
	NaCl	82.2	0.22	0.34	0.29	14.1	d
NB	NaF	83.0	0.77	4.8	0.14	0.18	0.80[e]
	None	67.0	0.30	1.8	1.4	13.4	f

[a] 40 ml of solvent, 0.010 mol of $PdCl_2$, 0.10 mol of salt, 175° for 4 hr. [b] Mixture of isomers. [c] 0.40% C_2H_3Cl found. [d] 0.19% C_2H_3Cl found. [e] 6.9% 1,3-butadiene found. [f] 1.4% C_2H_3Cl found.

one of the products in the adiponitrile–$PdCl_2$ reaction is acrylonitrile. These side reactions have not permitted us to determine if palladium metal is also produced in the propylene-forming reaction.

The unusual nature of this formation of propylene prompted us to study the reactions of olefins other than ethylene with palladium chloride in the presence of sodium fluoride. Therefore, propylene and vinyl fluoride were allowed to react with palladium chloride and sodium fluoride in adiponitrile at 175°. With propylene, no evidence for the formation of any higher molecular weight hydrocarbon products were obtained. Detected in the product gas mixture were propylene, propane, carbon dioxide, 2-fluoropropylene, and 3-fluoropropylene.

With vinyl fluoride, the reaction resulted in a very complex mixture of gases. This mixture was carefully examined and found not to contain any fluorinated propylenes or propanes. The major constituents in the product gas mixture were identified as vinyl fluoride, ethyl fluoride, propylene, vinyl chloride, acetyl fluoride, and carbon dioxide. Traces of ethane, methane, ethylene, methyl chloride, trifluorochloromethane, and propane were also detected.

Any speculation on the mechanism of the propylene formation from ethylene would obviously be premature. We hope the work now in progress will yield results which have mechanistic implications.

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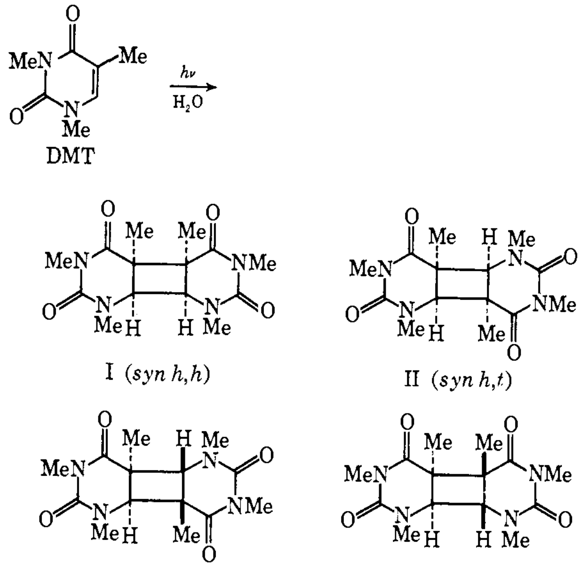
Solvent Effects on the Liquid-Phase Photodimerization of Dimethylthymine[1-3]

Sir:

Recently we reported[1] that photolysis of dimethylthymine (DMT) in aqueous solution (0.1 *M*) yields four dimers (I–IV) with an over-all quantum efficiency of 0.05. We now present data which indicate that *at least* three of the photochemical and photophysical processes in this system are solvent sensitive,[4] *e.g.*, dimerization from the singlet state, degree of intersystem crossing, and dimerization from the triplet state. Furthermore, these data will be shown to be quite useful as a means of ascertaining the contributions of singlet- and triplet-state intermediates to the over-all reaction.



I (*syn h,h*)

II (*syn h,t*)

III (*anti h,t*)

IV (*anti h,h*)

Table I displays the product distribution upon photodimerization of DMT in six different solvents.[5] As can be seen from these data, the solvents can be grouped as nonpolar, polar protic, and polar aprotic, with each such grouping found to give similar dimer distributions. The possibility that such solvent effects are being brought about by varying degrees of intersystem crossing[6] always warrants the experimental test, and the results of appropriate quenching experiments with *cis*-piperylene are presented in Table II.[7]

Table I. Photodimerization of DMT in Different Solvents

Solvent	%				Rate[a]
	syn *h,t*	*syn* *h,h*	*anti* *h,t*	*anti* *h,h*	
Benzene	59	17	21	3	1.2
Dioxane	61	12	26	1	1.3
Water	37	39	18	6	16.4
Methanol	42	37	17	4	1.9
Acetonitrile	36	49	11	4	1.0
Dimethylformamide	33	53	10	4	1.7

[a] Rates relative to acetonitrile; the rate data can be readily converted to quantum yields by using a value of 0.05 for water.[1] All solutions 0.1 *M* in DMT.

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(1) Organic Photochemistry. VIII. For part VII, see H. Morrison and R. Kleopfer, *Chem. Commun.*, 358 (1968).

(2) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. P-85.

(3) Support of this research by the National Cancer Institute of the Public Health Service (CA 10733-01) is gratefully acknowledged.

(4) For a recent review of solvent effects on photodimerization, *cf.* O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Record Chem. Progr.*, 28, 167 (1967).

(5) All solvents were dried and distilled.

(6) For an example of such an effect, see: A. R. Horrocks, T. Medinger, and F. Wilkinson, *Photochem. Photobiol.*, 6, 21 (1967). An effect by heavy-atom solvents has been reported: D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, 89, 3068 (1967).

(7) The value cited for benzene was obtained using Fisher Spectrograde solvent distilled from calcium hydride. This number has been found to vary with the source of the benzene and its method of purification. We have chosen this value because it is the lowest thus far obtained and correlates well with a value of 31% observed for toluene. Similar variations have been obtained in these laboratories for benzene in the coumarin system (R. Hoffman, unpublished data), and the origin of these effects is presently being sought.