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

		Percentages in product gas mixture					
Solvent	Salt	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.

Acknowledgment. The mass spectral data were obtained by Mr. Robert Pfost.

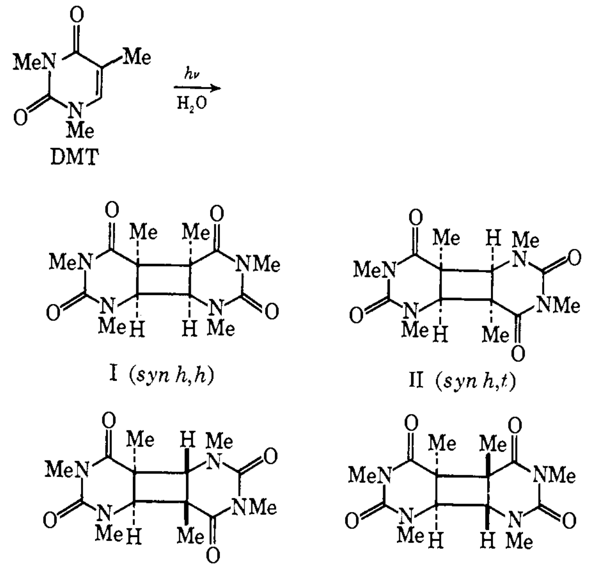
J. C. Crano, E. K. Fleming, G. M. Trenta
Pittsburgh Plate Glass Industries, Chemical Division
Barberton, Ohio 44203

Received July 25, 1968

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.



DMT

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	*syn h,t*	*syn h,h*	*anti h,t*	*anti h,h*	Rate[a]
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.

---

(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.

Table II. Quenching of DMT Photodimerization by *cis*-Piperylene[a]

Solvent	% *syn* *h,t*	*syn* *h,h*	*anti* *h,t*	*anti* *h,h*	Over-all
Methanol					0
Acetonitrile	−6	−18	−5	−27	−12
Benzene	−27	−61	−16	−100	−33

[a] Solutions 0.1 *M* in DMT and 0.1 *M* in *cis*-piperylene.

If it is assumed that total quenching of triplets is occurring in each solvent, *the data require that the percentage of triplet contribution to dimerization is appreciably solvent sensitive. In addition, the same assumption requires that the observed product distribution (with quencher present) be brought about by the DMT singlet state in these three solvents, and that the "quenched product" distribution be derived from the DMT triplet state.* Although the basic assumption of total quenching would seem valid,[8] it is one which can be readily tested. Photosensitized dimerization of DMT with benzophenone in a given solvent should lead to a distribution of dimers characteristic of the DMT triplet in that solvent, and these data should then correspond to the "quenched product" distribution. Both sets of data are displayed in Table III.

Table III. DMT Dimer Distribution upon Photosensitization with Benzophenone

Solvent	% *syn h,t*	*syn h,h*	*anti h,t*	*anti h,h*
Benzene				
Obsd	51	30	13	6
Predicted[a]	50	30	14	6
Acetonitrile				
Obsd	16	74	4	6
Predicted	18	70	4	7
Methanol				
Obsd	22	71	2	5
Predicted[b]				

[a] Using the quenching data of Table II; see text. [b] Unavailable since quenching was not observed (see Table II).

The compatibility of the data supports the assumption of complete triplet quenching by piperylene; furthermore, the product distributions from the triplet state in the two polar solvents are quite similar, but differ from the nonpolar solvent benzene in that the latter leads mainly to head-to-tail dimers.

Just as the dimer distributions from the triplet state are displayed in Table III, distributions from the singlet state in benzene, acetonitrile, and methanol are listed in Table IV. The data are those actually observed upon photolysis in the presence of the quencher. Once again, the apparent difference between the two polar solvents is diminished (compare Table I); the three solvents now favor head-to-tail dimerization.

Table IV. Solvent Dependence of DMT Dimerization from the Singlet State

Solvent	% *syn h,t*	*syn h,h*	*anti h,t*	*anti h,h*
Benzene	63	11	25	0
Acetonitrile	40	44	12	3
Methanol	42	37	18	3

In summary, dimerization of DMT in liquid solutions has been shown to (*a*) *proceed from both singlet and triplet states, with the percentage contribution of each apparently a function of solvent, and* (*b*) *yield a mixture of four dimers from either excited state, with the product composition a function of both the excited-state precursor as well as solvent.* Studies designed to ascertain the source (s) of these solvent effects are presently in progress.

Harry Morrison, Robert Kleopfer
Chemistry Department, Purdue University
Lafayette, Indiana 47907
Received May 17, 1968

---

[8] The same percentage of quenching is observed in acetonitrile with 0.01 and 0.05 *M* solutions of *cis*-piperylene.

A Fast Reaction of Organoboranes with Iodine under the Influence of Base. A Convenient Procedure for the Conversion of Terminal Olefins into Primary Iodides *via* Hydroboration–Iodination

Sir:

The reaction of organoboranes with halogens is surprisingly sluggish.[1,2] However, we have observed that organoboranes undergo a very rapid reaction with iodine under the influence of sodium hydroxide, the reaction being essentially complete in less than 5 min at 25°. This makes possible a simple procedure for the conversion of terminal olefins into primary iodides (1).

$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{HB}} \mathrm{RCH_2CH_2B}{<} \longrightarrow \mathrm{RCH_2CH_2I} \qquad (1)$$

It has long been evident that the simple conversion of organoboranes to the corresponding halides would open up new synthetic possibilities for these versatile boron intermediates. However, information in the literature indicated that simple treatment of the organoboranes would not be satisfactory. Thus bromine reacts only with difficulty with tri-*n*-butylboron to convert only one of the three alkyl groups to *n*-butyl bromide,[1] and a temperature of 150° was utilized for the reaction of iodine with tri-*n*-propylboron, again converting only one group.[2]

We have confirmed that the reaction of iodine with simple trialkylboranes, such as tri-*n*-butylborane, is indeed slow under ordinary conditions. However, the addition of 1 equiv of sodium hydroxide in methanol to a mixture of 1 mol of the organoborane and 1 mol of iodine brings about an almost instantaneous reaction with an essentially quantitative formation of 1 mol of alkyl iodide (2). A second mole of iodine and base reacts similarly (3). However, the third alkyl group resists reaction under these mild conditions.

$$\mathrm{(RCH_2CH_2)_3B + I_2 + NaOH \longrightarrow RCH_2CH_2I + NaI + (RCH_2CH_2)_2BOH} \qquad (2)$$

$$\mathrm{(RCH_2CH_2)_3B + 2I_2 + 2NaOH \longrightarrow 2RCH_2CH_2I + 2NaI + RCH_2CH_2B(OH)_2} \qquad (3)$$

---

(1) J. R. Johnson, H. R. Snyder, and M. G. VanCampen, Jr., *J. Am. Chem. Soc.*, 60, 115 (1938).

(2) L. H. Long and D. Dollimore, *J. Chem. Soc.*, 3902, 3906 (1953).