triethylcarboxide gave an 85% yield. The yields quoted were realized with reaction mixtures containing 1 molar equiv each of tri-*n*-butylborane and chloroform, and 2 molar equiv of the alkoxide. Use of 1 molar equiv of base resulted in lower yields.

The 85% yield realized with lithium triethylcarboxide appeared promising. Accordingly, the latter conditions were adopted for a study of the relative effectiveness of related trisubstituted methanes. The results are summarized in Table I.

Table I. Reaction of Tri-*n*-butylborane with Representative Trisubstituted Methanes under the Influence of Lithium Triethylcarboxide[a]

Reagent	Oxidation products, %[b] *n*-Bu_3COH	 *n*-Bu_2CO
Chloroform	85	5
Dichlorofluoromethane	79	20
Chlorodifluoromethane	98	Trace
Fluoroform	0	0
1,1-Dichlorodimethyl ether[c]	80	0.5
Trimethyl orthoformate	0	0

[a] The reaction mixture containing 10 mmol each of the organoborane and the reagent, and 20 mmol of the base heated under reflux in THF–*n*-hexane for 1 hr. [b] Glpc analysis. [c] Only 1 molar equiv of base was required and used.

The remarkably high yield realized with chlorodifluoromethane was especially interesting and led to a more detailed study of this reagent. The results are summarized in Table II.

Table II. Reaction of Tri-*n*-butylborane with Chlorodifluoromethane under Various Conditions

Base	Equiv of base	Temp, °C	Time, hr	Oxidation products, % *n*-Bu_3-COH	 *n*-Bu_2-CO	 *n*-BuOH
tert-BuOK	1	25	20	53	0	25
tert-BuOK	2	25	20	75	0	14
Et_3COK	2	0	1	57	0	23
Et_3COLi	1	25	20	43	0	37
Et_3COLi	2	25	1	88	0	
Et_3COLi	2	25	3	93	0	
Et_3COLi	2	25	20	97	0	1.5
Et_3COLi	2	65	1	98	0	1.5

Consequently, it appears that the reaction of chlorodifluoromethane with tri-*n*-butylborane under the influence of lithium triethylcarboxide proceeds satisfactorily even at 25°, so that this reaction provides the desired convenient room-temperature route from organoboranes to the corresponding trialkylcarbinols.

The following procedure is representative of those followed in this study. Into the usual dry reaction flask maintained under nitrogen was placed 20 ml of THF and 1.82 g of tri-*n*-butylborane (10.0 mmol). The flask was cooled to 0° and 11.5 ml of a 1.75 *M* solution of lithium triethylcarboxide (20.0 mmol) in hexane (prepared from *n*-butyllithium and triethylcarbinol) was added, followed by addition of the chlorodifluoromethane introduced as a gas. The reaction mixture was brought to reflux temperature and maintained there for 1 hr. The mixture was cooled, 5 ml each of 3 *M* sodium acetate and 30% hydrogen peroxide were added, and oxidation was completed by refluxing for 1 hr. Solid potassium carbonate was added, the organic phase was separated, undecane was added to serve as an internal standard, and the product was determined by glpc analysis on a 6-ft column (10% Carbowax). There was found 98% tri-*n*-butylcarbinol, trace amounts of di-*n*-butyl ketone, and 1.5% 1-butanol.

The procedure utilizing chloroform is somewhat more convenient. In cases where the slightly lower yield, 85%, is not serious, the reaction with chloroform may be preferred.

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(10) Graduate research assistant on Grant No. GP 6492 X supported by the National Science Foundation.

(11) On leave from the University of Adelaide, South Australia.

(12) Postdoctorate research associate on Grant No. GM 10937 supported by the National Institutes of Health.

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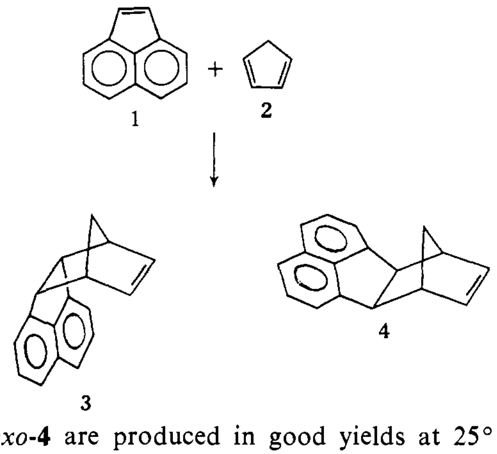
Received November 25, 1970

Heavy-Atom Solvent Effect on the Photoaddition of Acenaphthylene and Cyclopentadiene

Sir:

Considerable interest has been evinced in the photochemical heavy-atom solvent effect. The photochemical dimerization of acenaphthylene (**1**) was shown to involve a legitimate heavy-atom solvent effect on interstate crossing efficiency.[1] There is a heavy-atom effect on the cross cycloaddition of **1** with acrylonitrile,[2] and recently the heavy-atom effect was utilized to cross-cycloadd **1** to maleic anhydride to form a product which ultimately led to the synthesis of pleiadiene.[3] All of these reactions are [2 + 2] cycloadditions. We report here the first known example of the heavy-atom solvent effect on a [4 + 2] photochemical cycloaddition.

The ground-state Diels–Alder reaction between **1** and cyclopentadiene (**2**) occurs in a sealed tube at 175° to produce the endo and exo isomers of 7,10-methano[6b,7,10,10a]tetrahydrofluoranthene in a ratio of about 3:1, respectively.[4] We have found that *endo*-**3** and *exo*-**4** are produced in good yields at 25° by irradiating dilute mixtures of **1** in an excess of **2** in a heavy-atom solvent with 3660-Å light. Using a benzophenone-sensitized isomerization of *trans*-stilbene as



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(1) (a) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); (b) *J. Amer. Chem. Soc.*, **89**, 3068 (1967); (c) *ibid.*, **92**, 6281 (1970).

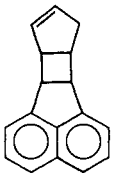
(2) B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970).

(3) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, **92**, 7604 (1970).

(4) R. Baker and T. J. Mason, *J. Chem. Soc.*, 596 (1970).

an actinometer in a merry-go-round apparatus, we have measured the quantum yield of the overall cycloaddition.[5] We find that heavy-atom solvents increase the quantum yield, change the ratio of *endo*-**3** to *exo*-**4** from that of the ground-state reaction, and increase the proportion of [2 + 2] cycloadducts **5**.

Compound **5** crystallizes from MeOH with a mp of 90–91°, has a correct elemental analysis, and has an nmr spectrum ($CDCl_3$) consistent with its structure: δ 2.6 (perturbed doublet, 3 H, allylic), 3.2 (broad singlet, 1 H), 3.8 (m, 2 H, benzylic), 6.0 (multiplet, 2 H, vinylic), and 7.4 ppm (multiplet, 6H , aromatic). Although its stereochemistry is unproven, we believe it to be anti.[7] The separation of **5** from **3** and **4** was achieved by selective reaction of the [4 + 2] adducts with chlorosulfonyl isocyanate followed by aluminum oxide chromatography.[8]



5

The data in Table I verify the heavy-atom effect.[9] The increasing proportion of **5** in the heavy-atom solvents is indicative of a photochemically induced process, because no **5** can be found in the thermal Diels–Alder reaction between **1** and **2**.[10] The fact that **5** increases from 18% of the total products in cyclohexane to 38% of the total products in 1,2-dibromoethane suggests that we may be observing cycloaddition from competing excited states. In the non-heavy-atom solvents, some of the [4 + 2] product may arise either from (a) a singlet excited state or (b) a photochemically induced vibrationally excited ground state.[11,12]

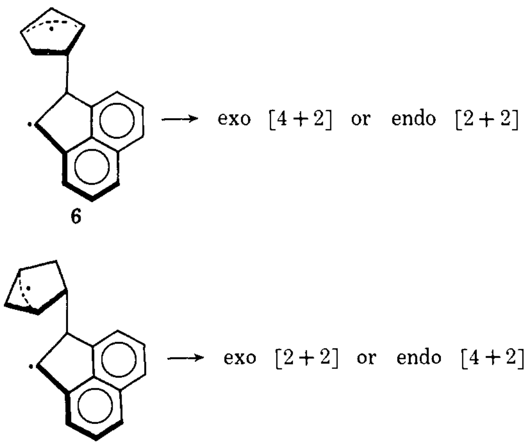
Table I

		Product ratio[a]			
	Quantum	[4 + 2]			
Solvent	yield, Φ	Endo	Exo	[2 + 2]	Φ_{rel}[b,c]
1,2-Dibromoethane	0.20	0.44	1.2	1.00	25
Bromobenzene	0.15	0.44	1.3	1.00	19
Bromoethane	0.12	0.54	1.5	1.00	15
Acetonitrile	0.013	2.9	2.8	1.00	2
Cyclohexane	0.008	2.6	2.1	1.00	1

[a] Normalized to the [2 + 2] photoadduct for each run. [b] Quantum yield relative to cyclohexane. [c] Low conversions of acenaphthylene (7–20%) were used.

Consideration of two possible geometries of the biradical intermediates that might arise in a two-step mechanism (Chart I) from the attack of triplet **1** upon **2** leads to the conclusion that intermediate **6** can produce by a least-motion process either an exo [4 + 2] adduct or an endo [2 + 2] adduct. Intermediate **7** can produce by a least-motion process the endo [4 + 2] adduct or the exo [2 + 2] product. Further mechanistic interpretations of the data must await more detailed studies.

Chart I



Bartlett[14] has shown that the thermal cycloaddition of *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene to **2** produces a [2 + 2] adduct by a biradical pathway and a [4 + 2] adduct by a concerted pathway. This evidence in conjuction with Cowan's[1] studies suggests that similar mechanisms may be operative in the reaction of **1** with **2**.

The results cited here offer further support for the usefulness of the heavy-atom effect in mechanistic and synthetic photochemistry.[15] Subsequent papers dealing with the limitations of this effect will be published.

Acknowledgment. We gratefully acknowledge the support of the Robert A. Welch Foundation.

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(5) A Hanovia 450-W medium-pressure mercury lamp with circulating copper nitrate solution effectively removed all light below 3660 Å.[6] A Rayonet apparatus MGR-500 was used to achieve uniform radiation of all samples. Each sample was degassed with three freeze–thaw cycles before the irradiation.

(6) The apparatus and conditions used in this study are similar to those used in previous studies of stilbene isomerizations: G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 319 (1964).

(7) In *endo*-**3** the vinylic resonance at 5.3 ppm shows an upfield shift of about 0.8 ppm from the *exo*-**4** due to the diamagnetic anisotropy of the naphthalene moiety. Because the vinylic resonance of **5** does not show a similar shielding effect the assignment of anti stereochemistry to **5** seems justified.

(8) The selective reaction of chlorosulfonyl isocyanate with norbornene systems was recently reported: E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968). This reaction upon compounds **3** and **4** will be reported in subsequent papers.

(9) All product analyses were performed on a Varian Hy-Fl 1200 under the following conditions: 6 ft × 0.125 in. SS 304 OV-17 column; He = 35 ml/min at 60 psig; column, 155°; injector, 250°; and detector, 270°. Peak areas were approximated by triangulation and the following retention times (min) were found: **3**, 17; **4**, 18.4; **5**, 22.0.

(10) We have verified that tbe thermal reaction of **1** with **2** produces no detectable [2 + 2] product as measured by glc.

(11) During the same time interval we have determined that the ground-state Diels–Alder reaction (dark reaction) contributes very little to product formation.

(12) A referee has commented that because the Diels–Alder reaction is "forbidden" as a concerted process from any excited state, it must be that the Diels–Alder reaction pathway observed in the non-heavy-atom solvents is arising solely by reaction of a vibrationally excited ground state that is "hot" enough to do at room temperature what will happen thermally only at 175°. However, Cowan[13] has proposed that some acenaphthylene photodimerization occurs through a singlet excimer. Thus, it seems plausible that some of the photochemical reaction of **1** with **2** in non-heavy-atom solvents could occur through a singlet exciplex formed between **1** and **2**. We therefore do not feel that a choice of mechanism for non-heavy-atom solvents can be made at this time.

(13) D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **92**, 6286 (1970).

(14) R. W. Wheland and P. D. Bartlett, *ibid.*, **92**, 3822 (1970), and references therein.

(15) NOTE ADDED IN PROOF. A recent report concerning heavy-atom effects is pertinent: N. J. Turro, J. C. Dalton, G. Kavarnos, T. Cole, and P. Scribe, *ibid.*, **93**, 1032 (1971).

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Received January 28, 1971