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.

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[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).

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

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.

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

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

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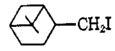
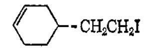
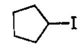
(1) J. R. Johnson, H. R. Snyder, and M. G. VanCampen, Jr., *J. Am. Chem. Soc.*, **60**, 115 (1938).

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

Table I. Conversion of Terminal Olefins into Primary Iodides *via* Hydroboration–Iodination

Olefin	Organoboranes (10 mmol)	I_2, mmol	NaOH–CH_3OH, mmol	Product	Yield, %[a]
1-Butene	R_3B	10	10	$CH_3(CH_2)_2CH_2I$	33
	R_3B	20	20		65
	R_3B	30	30		65
1-Hexene	$(Sia)_2BR$	11	11	$CH_3(CH_2)_4CH_2I$	95
1-Decene	R_3B	22	22	$CH_3(CH_2)_8CH_2I$	65
	$(Sia)_2BR$	11	11	$CH_3(CH_2)_8CH_2I$	95
Isobutylene	R_3B	22	22	$(CH_3)_2CHCH_2I$	63
2,4,4-Trimethyl-1-pentene	R_3B	22	22	$(CH_3)_3CCH_2CH(CH_3)CH_2I$	63 (54)
	$(Sia)_2BR$	11	11	$(CH_3)_3CCH_2CH(CH_3)CH_2I$	92
α-Methylstyrene	R_3B	22	22	$C_6H_5CH(CH_3)CH_2I$	63 (50)
β-Pinene	R_3B	22	22		60 (40)
4-Vinylcyclohexene	$(Sia)_2BR$	11	11		66 (60)
Cyclopentene	R_3B	22	22		33
2-Butene	R_3B	22	22	$CH_3CH_2CH(CH_3)I$	30

[a] Glpc yields, isolated yields in parentheses. The yields are based in the amount of starting olefin.

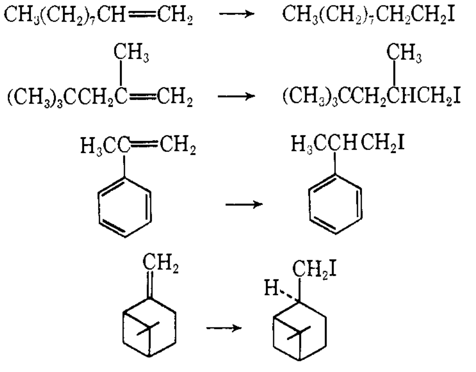
Secondary alkyl groups, such as 2-butyl and cyclopentyl, react more sluggishly, and under these mild conditions only one of the three groups reacts. The greater sluggishness of secondary alkyl groups in this reaction is also indicated by the purity of 99% *n*-butyl iodide obtained from the usual organoborane prepared *via* hydroboration from 1-butene, containing approximately 6% *sec*-butylboron groups.[3]

The failure to utilize the third group in organoboranes prepared from terminal olefins restricts the yield of iodide from a particular terminal olefin to a maximum of 66.7%. Fortunately, the use of disiamylborane[4] circumvents this difficulty, since the primary group reacts in preference to the secondary siamyl groups (4).

$$RCH{=}CH_2 + (Sia)_2BH \longrightarrow RCH_2CH_2B(Sia)_2$$

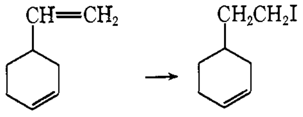
$$RCH_2CH_2B(Sia)_2 + I_2 + NaOH \longrightarrow RCH_2CH_2I + (Sia)_2BOH + NaI \quad (4)$$

The reaction appears to be generally applicable, as shown by the following representative transformations (5)



(5)

It is evident that many functional groups may be accommodated in this reaction. Some indication of its versatility is provided by the ready conversion of 4-vinylcyclohexene to the unsaturated primary iodide (6).



(6)

If a yield of approximately 65% is adequate, the simpler hydroboration with diborane can be utilized. However, if yields approaching 100% are desired, or if the structure requires a more selective hydroboration, then the procedure utilizing disiamylborane is preferable.

The experimental results are summarized in Table I. A representative procedure is that utilized for the conversion of β-pinene to *cis*-myrtanyl iodide. A dry 500-ml flask equipped with septum inlet, thermometer well, pressure-equalizing dropping funnel, and magnetic stirrer was flushed with nitrogen and then maintained under a static pressure of the gas. The flask was charged with 75 ml of tetrahydrofuran and 23.4 ml (150 mmol) of β-pinene and placed in a water bath at 25°. Conversion to the trialkylborane was achieved by dropwise addition of 25.8 ml of a 2.00 *M* solution of borane (155 mmol of hydride) in tetrahydrofuran. The solution was stirred for 1 hr at 25°, then 1 ml of methanol was added to destroy excess hydride. Iodine (28.0 g, 110 mmol) was added all at once, followed by dropwise addition of a solution of sodium hydroxide in methanol (37 ml of a 3 *M* solution, 110 mmol) over a period of 5 min. Glpc analysis of the reaction mixture with *n*-octane for internal standard indicated a 60% yield of *cis*-myrtanyl iodide. The reaction mixture was poured into 150 ml of water containing 3 g of sodium thiosulfate to remove excess iodine and the aqueous layer was extracted with two 100-ml portions of pentane. The combined pentane layers were dried with anhydrous sodium sulfate and distilled under vacuum.[5] There was obtained 16.0 g (40% yield) of *cis*-myrtanyl iodide, bp 85° (0.8 mm), $n^{20}D$ 1.5467.

This development suggests the possibility that the reaction of many other reagents with organoboranes

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[3] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

[4] H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

[5] Isolation of the iodides obtained from disiamylalkylorganoboranes was facilitated by the oxidation of residual boron compounds with alkaline hydrogen peroxide prior to distillation.

may be strongly catalyzed by sodium hydroxide, and we are exploring this possibility.

(6) National Science Foundation Postdoctorate Fellow at Purdue University, 1967–1968.

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The Electronic Structure and Reactivity of Small-Ring Compounds. III. Mechanistic Studies of the Bicyclobutane–Benzyne Reaction[1]

Sir:

We recently reported that the reaction of bicyclobutane with benzyne[1] gives 3-phenylcyclobutene and benzobicyclo[2.1.1]hex-2-ene. We wish now to report some studies on the mechanism of these reactions.

2-Deuteriobicyclobutane (I) was prepared by the method of Friedman and Wiberg[2] by the thermal decomposition of cyclopropanecarboxaldehyde *p*-tosylhydrazone in ethylene glycol-O,O-d_2 containing 0.9 equiv of the conjugate base of the solvent. The bicyclobutane I was shown by nmr spectroscopy to contain 0.83 deuterium per molecule, with 81% *endo* and 19% *exo*. That is, I had 0.67 deuterium *endo* and 0.16 deuterium *exo* at the 2 position.[3]

When I was allowed to react with benzyne, from the thermal (45°) decomposition of *o*-benzenediazoniumcarboxylate in ethylene dichloride, and the products were separated by vlpc,[4] it was determined by nmr analysis that the cycloadduct II had all of the deuterium in the *endo* position.[6,7] In addition, the "ene" synthesis product, deuterated 3-phenylcyclobutene (III), had half of the original deuterium at the 4 position *cis* to the phenyl ring.[6] The other half of the deuterium was attached to the phenyl ring, as a result of "ene" synthesis with abstraction of the deuteron. Thus, if there is an isotope effect in this reaction it must be very small (see Table I for a summary of the data).

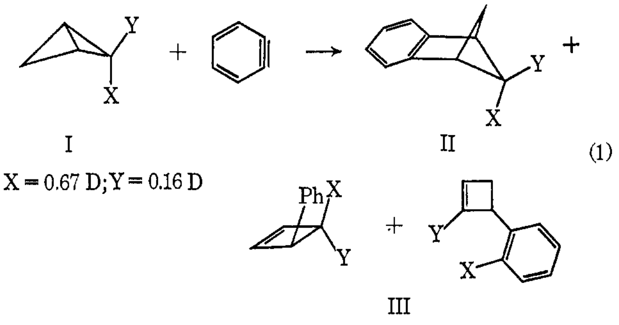
The conclusion, therefore, is that both the "ene" synthesis and cycloaddition reaction occur by bottomside attack of benzyne on bicyclobutane (eq 1). We use the term bottomside to refer to the *endo* direction. The cycloaddition reaction thus results in double inversion at the bridgeheads, whereas the "ene" synthesis gives a single inversion.

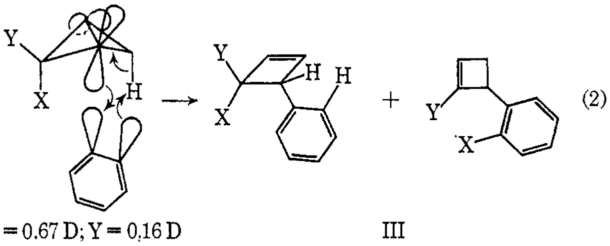
Table I

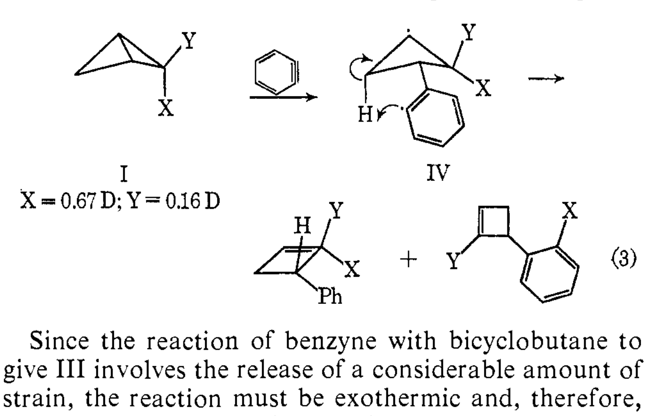
Compound	Hydrogen	Obsd nmr hydrogen ratio	Calcd ratio for bottomside attack
Bicyclobutane (I)	Bridgehead	2.00	
	exo-2	1.84	
	endo-2	1.33	
Benzobicyclo-[2.1.1]hex-2-ene (II)	Aromatic	*a*	4.00
	Bridgehead	2.00	2.00
	exo-5	1.84	1.84
	endo-5	1.34	1.33
3-Phenylcyclobutene (III)	Aromatic	4.66	4.66[b]
	Vinyl	1.90	1.92[b]
	Benzylic-3	1.00	1.00[b]
	trans-4	0.94	0.92[b]
	cis-4	0.67	0.66[b]

[a] Not obtained. [b] Calculated assuming no isotope effect.

One mechanistic possibility for the formation of III is a concerted reaction as indicated in eq 2. The p orbitals which are utilized[8] are in the proper orientation for such a reaction. The "ene" synthesis employing olefins has usually been assumed to be concerted,[9] but has recently, in the case of bicyclo[2.1.0]pentane, been questioned.[10] The alternative possibility in the present case would involve a diradical (IV) as pictured in eq 3.







Since the reaction of benzyne with bicyclobutane to give III involves the release of a considerable amount of strain, the reaction must be exothermic and, therefore, according to Hammond's postulate, the transition state occurs early along the reaction coordinate. A small

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(1) Part II: M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).

(2) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966); J. H. Bayless, Jr., Ph.D. Thesis, Case Institute of Technology, Cleveland, Ohio, 1967; K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 365, 5272 (1966).

(3) To simplify the discussion this bicyclobutane will be referred to as *endo*-2-deuteriobicyclobutane.

(4) Pure II was obtained directly by vlpc; III, however, was collected with a small amount of II as contaminant. The nmr spectrum of III was obtained with an internal standard present; the solution was then heated in order to remove III by rearrangement to 1-phenyl-1,3-butadiene,[5] and finally another nmr spectrum was obtained. In this way the integrated spectrum of III was analyzed by difference.

(5) M. Pomerantz and P. M. Hartman, *Tetrahedron Letters*, 991 (1968).

(6) By "all of the deuterium" we mean all that was originally present in the *endo* position in the bicyclobutane. (The small amount of deuterium in the *exo* position was, therefore, found in the *exo* position of II and distributed between the vinyl positions and the 4 position *trans* to the phenyl group in III.)

(7) See ref 1 for nmr peak assignments.

(8) M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966).

(9) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966).

(10) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968).