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(23) Data for **2**: ir ($CDCl_3$) 1725, 1680, 1620, 1260 cm^{-1}; pmr ($CDCl_3$, 100 MHz) δ 9.51 (1 H, d), 6.50 (2 H, m), 4.90 (2 H, m), 3.64 (1 H, m); uv (CH_3CN) λ_{max} 246 (ϵ 590), 310 nm (ϵ 110); mass spectrum (70 eV) *m/e* parent 110, base 81. Exact mass of *p*-nitrophenylhydrazone calcd for $C_{12}H_{11}N_3O_3$, 245.0800; found, 245.0797.

(24) Yield based on **9** after isolation by preparative glc.

(25) Compared by glc coinjection (Carbowax 20M and SE-30) and by mixture melting point of phenylurethane derivatives.

(26) Compared by ir, pmr, and mass spectrum. Exact mass of **10** prepared *via* **1**: calcd for $C_6H_{12}O_2$, 116.0837; found, 116.0840. Exact mass of **11** prepared *via* **2**: calcd for $C_6H_{12}O_2$, 116.0837; found, 116.0840.

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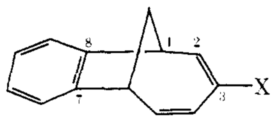
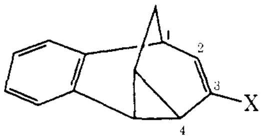
Substituent and Multiplicity Effects on Rearrangements of Some Benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes[1]

Sir:

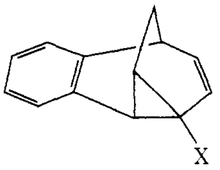
Compounds which can *a priori* react by more than one photochemical pathway can be good substrates for delineating structural effects on photochemical reactivity. Substituted benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes (BBNT's) such as **2–4** are "four-way threats" in this respect, capable of undergoing either of two di-π-methane (DPM) rearrangements[2] to benzobarbaralanes or either of two disrotatory ring closures to exo or endo cyclobutenes. The parent triene (**1**) has only three options, since the DPM products are enantiomers. We report here some preliminary results of a systematic study of substituent effects on BBNT photochemistry. These include the rare ability of 3-MeBBNT (**4**) and parent **1** to undergo both singlet and triplet DPM rearrangement, the surprising *inability* of 3-Cl- and 3-BrBBNT (**2** and **3**) to undergo either singlet or triplet DPM rearrangement, and pronounced substituent and multiplicity effects on exo-endo cyclobutene ratios.



1, X = H
2, X = Cl
3, X = Br
4, X = CH$_3$

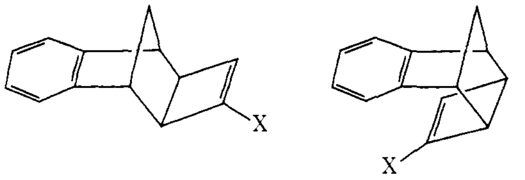


5, X = H
6, X = CH$_3$



exo cyclobutenes

7. X = CH$_3$



endo cyclobutenes

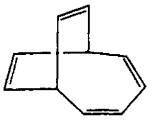
Syntheses of **1** and **2** were reported elsewhere;[3] **3** was prepared in analogous fashion, and **4** was made by reaction of **2** or **3** with lithium dimethylcuprate.[4] Direct or sensitized irradiation of "trienes" **1–4** gave rapid conversion to photoproducts (summarized in Table I),[5] which were isolated by preparative vpc or high-pressure liquid chromatography and characterized spectroscopically.[6]

Regarding first the hydrocarbons **1** and **4** in Table I, one can see that sensitized irradiation affords only DPM products, presumed to arise from triplet excited states, whereas direct irradiation gives DPM products and cyclobutenes. The latter, then, must arise only from singlet excited states, while the multiplicity responsible for DPM products from direct irradiation of **1** and **4** was uncertain. Formation of a photodimer of **1** on sensitization (triplet assumed) but not on direct irradiation suggested minimal formation of the triplet state of **1** on direct irradiation.[9] Thus it appeared that **1** has the ability, rare among bicyclic systems, to undergo DPM rearrangement *via* either the singlet or triplet excited state. The presence of three photoproducts (a fingerprint) from direct irradiation of **1** encouraged attempts to quench formation of **5**. These attempts, using up to 5 *M* piperylene or 1 *M* cyclooctatetraene, produced no detectable change in the photoproduct distribution,[10] and strengthened our conclusion that the direct irradiation **1** → **5** DPM reaction is essentially completely a singlet excited state process.

Positive "fingerprint" evidence (Table I) points also to the ability of 3-MeBBNT (**4**) to undergo either singlet or triplet DPM rearrangement. This evidence is the altered regioselectivity in formation of DPM products; the triplet excited state strongly favors formation of 3-methylbenzobarbaralane (**6**), while the singlet favors the 4-methyl isomer.[11] Clearly, the same excited state does not give rise to two different isomer distributions; again, the direct irradiation DPM reactions appear to be predominantly singlet processes.

The above gives strongly suggestive evidence that all products of irradiation of **1** and **4** come from singlet excited states. Within the singlet manifold, it is noted further that the competitive balance shown by **1** (0.67:1 ratio of cyclobutenes *vs.* DPM product) is strongly skewed in favor of cyclobutene formation (9.0:1) by introduction of the 3-methyl substituent in **4**. This high sensitivity of certain bicyclic systems to structural changes is further demonstrated by the following comparisons with literature work. Direct irradiation of trienes **8**[12a] and **9**[12b] gives only the DPM products bullvalene and benzobullvalene. In contrast, direct irradiation of **11** reportedly affords only cyclobutenes,[8a] while **10** is reported[8c,13] to parallel **1** in yielding significant amounts of DPM product as well as cyclobutenes.

The complete preference of the excited triplets of **1** and **4** for DPM rearrangement over cyclobutene ring closure parallels the behavior of **10**[8c] and **11**;[8a] a similar total DPM preference can be assumed for the triplets of **8** and **9**. By comparison with these six trienes, the sensitized photochem-



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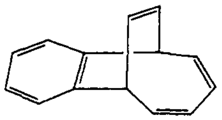

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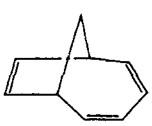

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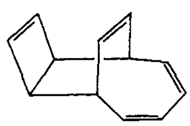
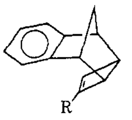
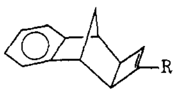
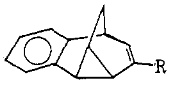
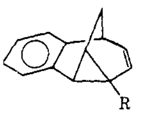


11

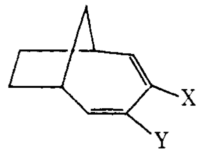
Table I. Product Distributions from Irradiations of 3-Substituted Benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes

Triene	Irradiation mode	Products (%)			
					
1	Direct[a]	23	17	60	
(R = H)	Sensitized[b]	0	0	100[c]	
2	Direct[a]	48	52	~0	~0
(R = Cl)	Sensitized[b]	68	32	0	0
3	Direct[a]	64	36	~0	~0
(R = Br)	Sensitized[b]	61	39	0	0
4	Direct[a]	70	20	7.8	~2.2
(R = CH_3)	Sensitized[b]	0	0	21	79

[a] Corex filter, *ca.* 5 × 10^{-3} *M* solution in pentane or ether. [b] Acetone or Michler's ketone. [c] Some dimer was isolated, but no other monomers.

istry of 3-Cl- and 3-BrBBNT (**2** and **3**; Table I) is striking; essentially *no* DPM products are formed. Thus, introduction of a chloro or bromo substituent into the 3-position of **1** suffices to completely suppress the triplet DPM rearrangement. A similar "halogen squelch" of the DPM reaction occurs on direct irradiation; this is superficially similar to the reduction in singlet DPM reaction caused by the 3-methyl substituent. However, the triplet behavior of **2** and **3** is unique among presently discussed systems; the halogen effect, therefore, appears to be fundamentally different from that of a methyl group.

Finally, attention is called to results in Table I which add a new dimension to the problem of explaining exo-endo cyclobutene ratios from diastereogenic dienes (*e.g.*, **13–15**).[14] The exo-endo ratios from photocyclization of **13–15** (30:70, 53:47, and 60:40, respectively) led Jefford and Delay to suggest that the two-carbon bridge of **13** offers less hindrance than the one-carbon bridge to the cyclobutene "nascent double bond." The ratios observed for **1** and **10** (42:58 and 27:73[8c,11]) support this analysis, and further indicate that an unsaturated two-carbon bridge creates about the same steric effect as a saturated two-carbon bridge. In this context, the decrease in the ratio for 3-MeBBNT (**4**) (22:78) is not unexpected.



13, X = Y = H

14, X = Cl; Y = H

15, X = Y = Cl

However, the behavior of the chlorotrienes (**2**, **14**, and **15**) is anomalous; enhanced exo formation occurs. Jefford and Delay ascribed this to attraction between polarizable chlorine(s) and the methylene bridge. Yet this second factor still is insufficient; sensitization of chlorotriene **2** causes a remarkable change in the cyclobutene ratio in favor of the endo isomer (32:68). We conclude that steric, polar, and multiplicity effects all must be among the factors considered. In this light, it is pertinent to note the *small* change in exo-endo ratio on direct *vs.* sensitized irradiation of 3-BrBBNT (**3**). This is consistent with a heavy-atom effect;[15] *i.e.*, the bromine may so facilitate $S_1 \rightarrow T_1$ intersystem crossing that reaction of **3** occurs almost completely from T_1, regardless of the identity of the initial excited state.

Further study of these highly reactive compounds and related structures is in progress.

References and Notes

(1) Portions of this work were presented at the 5th Northeast Regional Meeting of the American Chemical Society, Rochester, N.Y., Oct 15–17, 1973.

(2) *Cf.* S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973), and references therein.

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(4) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).

(5) Prolonged irradiation caused slower formation of secondary photoproducts which also are under study.

(6) Ir and pmr spectra of **5** were identical with those of independently prepared benzobarbaralane.[7] Cyclobutene isomers were identified *via* pmr spectra; the vinyl signal appears at characteristically[8] lower field for the exo than for the endo isomer.

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(8) *Cf.* (a) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969); (b) I. Murata, Y. Sugihara, and N. Ueda, *ibid.*, 1183 (1973); (c) H. Tsuruta, T. Kumagai, and T. Mukai, *Chem. Lett.*, 933 (1973).

(9) The photodimer has mp 203–205°; mass spec (70 eV) *m/e* 336 ($M\cdot^+$, 0.23% of base; mol wt calcd for $C_{26}H_{24}$ = 336), 337 (M + 1, ~30% of M; M + 1 caicd for $C_{26}H_{24}$ = 28% of M), 168 (base peak), pattern at lower *m/e* values very similar to mass spectra of **1**; pmr ($CDCl_3$) τ 6.02 (2 H, dd, *J* = 10, 9 Hz, vinyl H's) and 6.70 (2 H, dd, *J* = 10, 4 Hz, vinyl H's). Presence of only two types of vinyl protons indicates a [2 + 2] adduct; discussion of stereoisomeric possibilitles and reasons for the apparently high stereoselectivity is deferred to our full paper.

(10) At the quencher concentrations cited, both singlet and triplet quenching almost certainly occur. However, for the product distribution to remain unchanged, both quenching modes would have to be equally efficient for both quenchers. We regard this as unlikely.

(11) The triplet selectivity of 4 is attributable to formation of the more stable of two possible triplet diradicals *via* 2,8-bridging; rationalization of the reversed singlet selectivity is more elusive.

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(13) H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970); we thank Professor Brown for additional experimental details.

(14) C. W. Jefford and F. Delay, *J. Amer. Chem. Soc.*, **94**, 4794 (1972), and references therein.

(15) *Cf.* G. Kavarnos, T. Cole, P. Scribe, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 1032 (1971), and references therein.

(16) National Science Foundation Trainee, 1973.

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Polar Effects in Radical Reactions. IV. Nucleophilic Character of the 3-Heptyl Radical[1]

Sir:

Hammett σρ correlations for hydrogen abstraction from the side chain of ring-substituted toluenes (eq 1) have been reported for a number of radicals.[2] Polar effects arguments

$$R\cdot + CH_3C_6H_4X \xrightarrow{k_H} RH + \cdot CH_2C_6H_4X \qquad (1)$$