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COMPETITIVE HYDROGEN AND CARBOMETHOXY MIGRATION IN THE PHOTOCHEMISTRY OF 7-CARBOMETHOXY-3,4-BENZOTROPILIDENE

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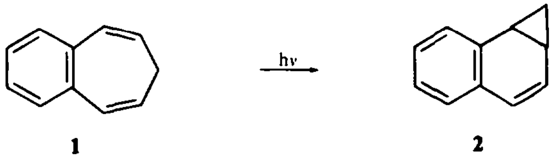
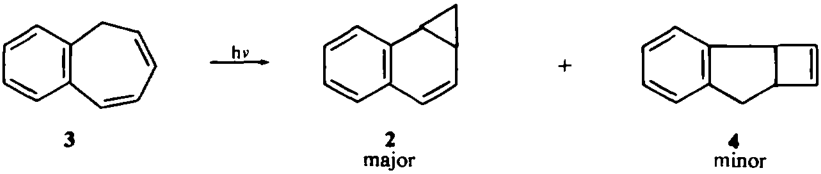
Abstract—The preparative photolysis of 7-carbomethoxy-3,4-benzotropilidene (**7**) in cyclohexane at 300–380 nm yields 6-carbomethoxy-2,3-benzonorcaradiene (**11**) 51%; 7-carbomethoxy-2,3-benzonorcaradiene (**5**) 35%; and 6-carbomethoxy-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**6**) 14%; as photoproducts. Deuterium labeling has established that the major product (**11**) arises from a formal 1,7-hydrogen shift, while **5** is formed by a formal 1,7-carbomethoxy migration. A substantial isotope effect was noted in the photolysis of the 7-deutereo-7-carbomethoxy-3,4-benzotropilidene. Mechanisms are discussed for the direct production of **6** from **7**. Multiplicity studies indicate that these reactions of **7** occur from the excited singlet state and quantum yield determinations demonstrate that the overall reactive process is highly efficient.

INTRODUCTION

IN RECENT years the photochemical transformations of olefinic substrates have been of both synthetic and mechanistic interest. The 1,7-sigmatropic shifts in cycloheptatrienes have been one area of special relevance in relation to Woodward–Hoffmann selection rules.[2] More recently a study of the benzoanalogs of the heptatrienes has been initiated,[3] and deuterium labeling studies have established that formal 1,7 shifts likewise occur in these systems. Thus, irradiation of either 3,4-benzotropilidene[3a] (**1**) or 1,2-benzotropilidene[3b] (**3**) yielded benzonorcaradiene (**2**) as major product. Interestingly, photochemical electrocyclic ring closure of **3** to yield **4** was observed as a very minor process.





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* Alfred P. Sloan Foundation Fellow.

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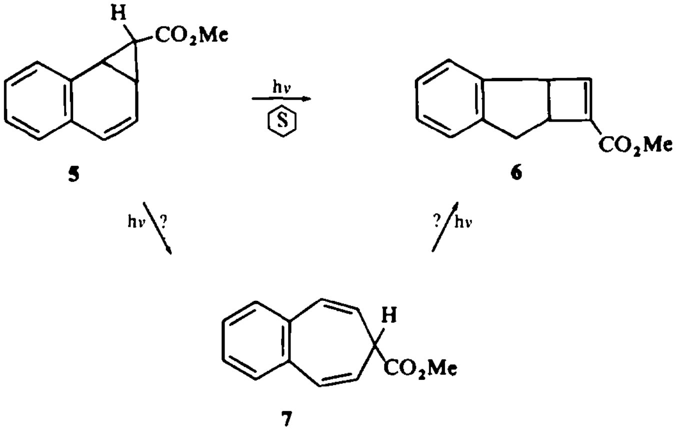
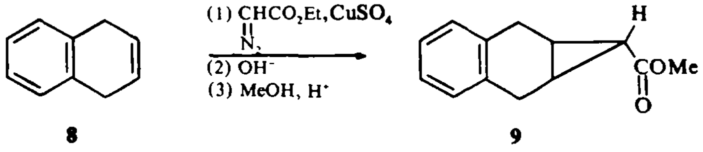
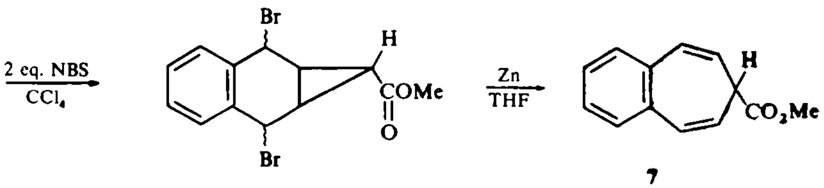
Our interest in the photochemistry of benzotropilidene emanated from earlier work in which we showed that the photolysis of 7-carbomethoxy-2,3-benzonorcaradiene (**5**) yielded cyclobutene (**6**) in addition to fragmentation and hydrogen-shift products.[4] Since a possible route from **5** and **6** involved the formation of 7-carbomethoxy-3,4-benzotropilidene (**7**) we initiated a study of the photochemistry of this compound. Here we deal in detail with the photochemistry of 7-carbomethoxy-3,4-benzotropilidene, and in future papers we will explore the interrelations of 3,4-benzotropilidenes in the photochemistry of benzonorcaradienes.



Synthesis of 7-carbomethoxy-3,4-benzotropilidene

Upon initiating this work, we found the literature records no general high-yield route to the 7-substituted-3,4-benzotropilidenes. The synthesis of 3,4-benzotropilidene *via* reaction of di-Wittig reagents with *o*-phthalaldehyde had met with only limited success.[3d] Furthermore, any reaction scheme employing basic conditions, acidic conditions, or prolonged heating during the formation of the 3,4-benzotropilidene nucleus, would result in rearrangement of the 3,4-benzotropilidene compound to its thermodynamically more stable 1,2-isomer. Thus, we sought a general route to the ring system under mild conditions in essentially neutral media. Our route began with the copper sulfate catalyzed addition of ethyl diazoacetate to 1,4-dihydronapthalene followed by saponification of the mixture and isolation of the carboxylic acid by crystallization. Esterification of the resulting acid yielded the ester (**9**) which was subsequently dibromated with N-bromosuccinimide to yield the dibromo ester (**10**). While the dibromo ester was somewhat inert to zinc in ether, smooth debromination to the 3,4-benzotropilidene (**7**) occurred in THF at 50° in *ca.* 0·5 hr. The resulting tropilidene (**7**) was produced in high yield as a crystalline solid with no contamination from the 1,2-isomer.





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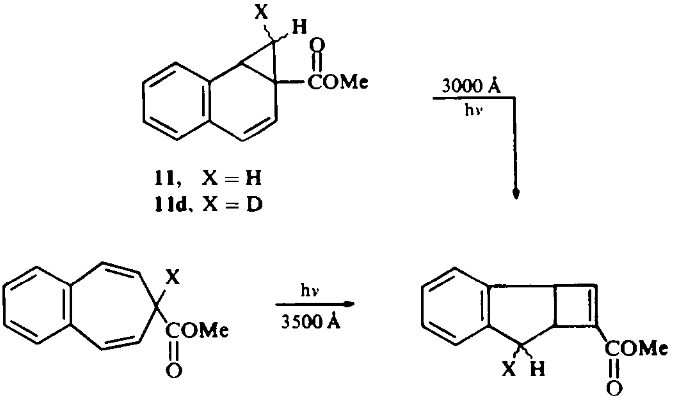
7

Preparative photolysis

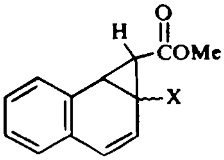
Photolysis of the ester (**7**) in cyclohexane with *ca.* 3500 Å light proceeded rapidly and yielded a mixture of three products in a ratio of 14 : 51 : 35. Isolation of the materials by prep VPC lead to the ready identification of two of these as the norcaradiene (**5**) (35%) and the cyclobutene (**6**) (14%) by comparison of the IR and NMR spectra with authentic materials. The structure of the major photoproduct has been assigned as **11** on the basis of its further photochemical transformations and its spectroscopic properties, the most conclusive being the NMR spectrum: aromatic hydrogens τ 2·5–2·9 (m, 4 H); vinyl hydrogens, AB quartet centered at τ 3·5 ($J = 9{\cdot}5$ Hz, 2 H); OMe resonance at τ 6·3 (s, 3 H), benzylic cyclopropyl hydrogen, quartet centered at τ 7·0 ($J = 6{\cdot}5$, 10 Hz, 1 H); *exo*-cyclopropyl hydrogen, quartet centered at τ 7·9 ($J = 10$, 3 Hz, 1 H); and the *endo*-cyclopropyl hydrogen, quartet centered at τ 9·8 ($J = 6{\cdot}5$, 3 Hz, 1 H).



11, X = H
11d, X = D

7, X = H
7d, X = D

6, X = H
6d, X = D



5, X = H
5d, X = D

Because of the complex photochemical interconversions noted in similar systems, we first sought to establish the primary products from the photolysis of **7**. Careful monitoring of the photolysis products by VPC indicated that the ratio of **5** : **6** : **11** was nearly invariant within experimental error from 10% to 95% conversion (Fig. 1).

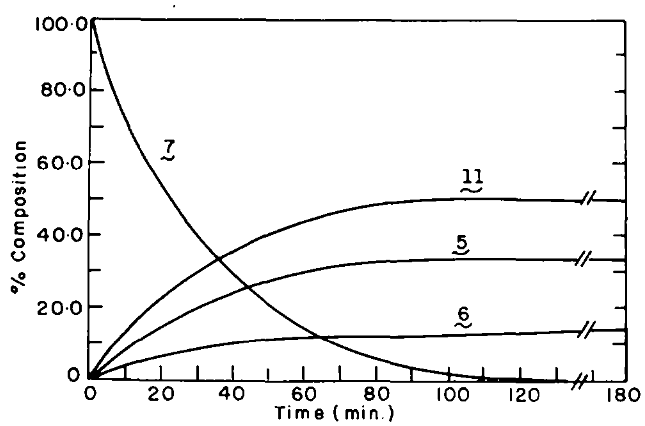
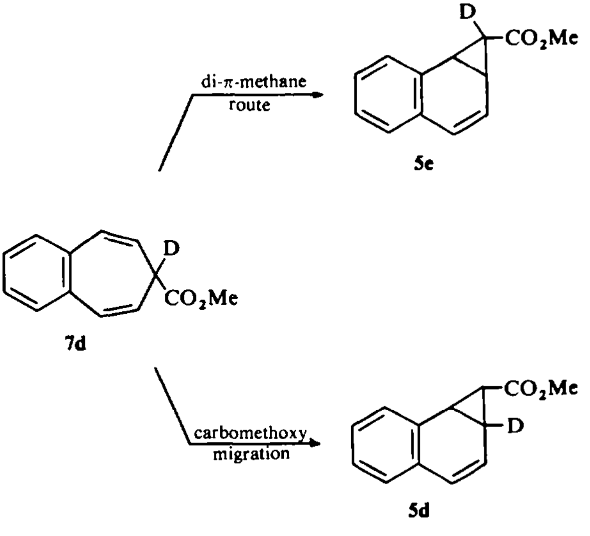


FIG 1. Dependence of product yields of 7-carbomethoxy-3,4-benzotropilidene on time.

Furthermore, both **5** and **11** were photochemically stable at 3500 Å, conditions under which ester **7** was rapidly transformed to products. However, photolysis of **11** at shorter wavelength, *ca.* 3000 Å, does produce the cyclobutene (**6**) in high yield. To further confirm that **6** from photolysis of **7** is not formed *via* initial production of **11** followed by secondary photolysis of **11** to **6**, the rate of **6** formation measured from simultaneous photolysis of **7** and **11** at 3500 Å showed that under conditions where **7** was nearly completely (> 99%) converted to products, **11** had reacted only to the extent of < 1%. While these data indicate that both **5** and **11** are primary products from **7** and that **6** in the **7** photolysis is not formed from further photolysis of **11**, an undetected intermediate photoproduct for the direct product of **6** from **7** cannot be excluded (*vide infra*).

Having established the nature of the products, we next focused our attention on the



mode of production of the two major products, **5** and **11**. While the formation of **11** would arise by the hydrogen-shift mechanism of Pomerantz and Gruber,[3a] the production of **5** could involve either of two routes. One of these is the now rather commonplace di-π-methane-vinylcyclopropane reaction,[5] while the other involves a rather rare carbomethoxy migration.[6] To affirm the hydrogen-shift mechanism for production of **11** and to distinguish between the two alternative mechanisms for formation of **5**, the deuterated compound, **7d**, was studied. Photolysis of the deuterated derivative (**7d**) likewise produced a mixture of three compounds; however, the proportion of the materials differs markedly from that noted for its hydrogen analog, **7** (Table 1). Isolation and purification of the individual components of the photolysis mixture showed that **5d**, **6d** and **11d** were produced in a ratio of 67 : 5 : 27. Compound **11d** showed by NMR integration that the deuterium was equally distributed in the *endo* and *exo* positions of the cyclopropane ring, thus confirming the hydrogen-shift mechanism for its production from **7d**. Interestingly, the NMR analysis of **5d** showed the deuterium label exclusively at the cyclopropyl allylic position, establishing that carbomethoxy migration was followed in exclusive preference to the di-π-methane reaction.

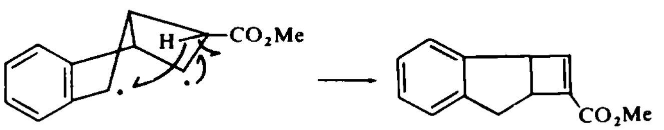
TABLE 1. PHOTOLYSES OF **7**, **7d**, **11d**

Starting Material (% d_1)	Composition % (d_1)[a]			% Yield
	5	**11**	**6**	
7	35	51	14	98
7d(78)	64 (81)	31 (74)	6	—
7d (94)	67 (96)	27 (87)	5 (72)	92
11d (87)			90 (87)[b]	90

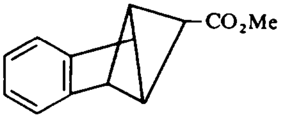
[a] The deuterium content was determined by NMR.

[b] The yield reported is that for the undeuterated material.

The deuterium labeling studies on **7** also afforded some information on the mechanism for formation of the cyclobutene compound, **6**. Isolation by VPC of the **6d** produced from **7d** photolysis and NMR assay for deuterium showed the deuterium to be located at the secondary-benzylic position. Unfortunately, this deuterium distribution is consistent with two general mechanisms which can be envisioned for direct conversion of **7** to the cyclobutene (**6**.) One of these involves disproportionation of diradical **12** formed either *via* 1,5-bonding in excited **7** or thermolysis of the strained hydrocarbon **13**. While some analogy can be found for either of these routes to yield **12**,[7, 8] no definitive statement can



12 **6**



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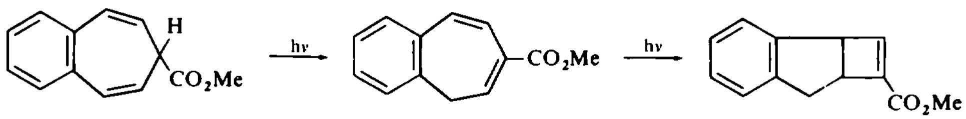
be made. A fundamentally different mechanism would involve 1,3-hydrogen shift in excited **7** to yield the 1,2-benzotropilidene (**14**) which would undergo photocyclization in a second step to yield **6**. This possibility is strengthened by an independent study[9] of



7 **14** **6**

the photochemistry of **14** which has shown that a major process is ring closure to yield **6**. While we tend to favor the 1,3-shift mechanism, since both overall processes have identical labelling consequences, they are indistinguishable from our present data.

Quantum yields

While preparative studies had suggested that the photochemistry of **7** was of high efficiency, we desired more exact information on both the quantum yield of **7** and the effect of deuterium substitution on the photochemistry of **7d**. Thus, quantum yields for the disappearance of **7** and the appearance of **5**, **6**, and **11** were measured with 330 nm light from a Bausch and Lomb monochrometer. The values reported in Table 2 support our earlier[1] supposition that the excited state chemistry of **11** was a process of high efficiency.[10]

TABLE 2. QUANTUM YIELDS FOR PHOTOLYSIS OF 7-CARBOMETHOXY-3,4-BENZOTROPILIDENE, 11, AT 3300 Å

	Quantum yields			
Run	**7**	**11**	**5**	**6**
1	0·57	0·38	0·20	0·03
2	0·57	0·38	0·21	0·03
3	0·72	0·42	0·22	0·02

Of considerable mechanistic interest was the quantum yield of the deuterated material, **7d**. Since quantum yields in organic systems are seldom more than 10% in accuracy, we have measured the relative quantum efficiencies of **7** vs. **7d** (Table 3). Significantly,

TABLE 3. RELATIVE QUANTUM YIELDS OF 7-PROTIUM VS. 7-DEUTERIUM-7-CARBOMETHOXY-3,4-BENZOTROPILIDENE

Compound	Wavelength	Φ_{11}	Φ_5	Φ_6	$\frac{\Sigma\Phi_7}{\Sigma\Phi_{7d}}$
7	3300Å	0·38	0·20	0·03	
7d	3300 Å	0·21	0·40	0·008	1·00
7	3500 Å				
7d	3500 Å				1·08

the total efficiency of the product formation from **7d** is nearly identical with that of **7**. The deuterium then does not markedly alter the overall efficiency of reactive excited state, but only changes the product distribution.

Multiplicity studies

Several studies in cycloheptatriene systems have established that 1,7-hydrogen shifts arise from the excited singlet state.[11] While it seemed reasonable that the hydrogen shift compound **11** was a singlet state product, no precedent was available to suggest the multiplicity of the excited state responsible for carbomethoxy migration. Thus, to rigorously establish the multiplicity of the state(s) responsible for product formation, sensitization and quenching studies were carried out on **7**. Since sensitizations are generally more reliable in establishing the multiplicity of reactant state than quenching studies,* we first investigated results from triplet energy transfer to **7**.

The triplet energy of **7** is unknown; however, a reasonable upper limit would be 59–62 kcal/mol.† To insure adequate exothermicity in the triplet transfer and to remove any possibility of singlet energy transfer,‡ acetophenone was chosen as sensitizer. The results of these acetophenone sensitizations of **7** in both cyclohexane and benzene as solvent are shown in Table 4. The results indicate that the sensitization quantum yields for the products are only about 2–3% of those recorded for the direct irradiation of **7**. Although there was noticeable disappearance of starting material in these sensitizations,

TABLE 4. ACETOPHENONE SENSITIZATION OF 1-CARBOMETHOXY-3,4-BENZOTROPILIDENE (**7**) AT 330 nm

			Quantum yields			
Run	Solvent	Conversion of **7**	**7**	**11**	**5**	**6**
1	Cyclohexane[a,b]	16%	0·26	0·08	0·04	0·008
2	Cyclohexane[a,c]	4%	0·24	0·01	0·01	—
3	Benzene[c,b]	6%	0·15[d]	0·02[d]	0·03[d]	0·003

[a] Solution was 0·13 M in acetophenone.

[b] Solution was $1{\cdot}6 \times 10^{-2}$ M in **7**.

[c] Solution was 0·56 M in acetophenone.

[d] The relative quantum yields in benzene are approximate, since the quantum yields for the unsensitized reaction were assumed to be those measured in cyclohexane.

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* It may be readily established that the triplet state of a substrate molecule is produced provided a sufficiently high energy sensitizer is used and the concentration of substrate is adjusted so that singlet energy transfer from the sensitizer is of low efficiency. On the other hand, bimolecular quenching of rapid unimolecular photochemical transformations may be difficult at even high quencher concentrations.[12a] Furthermore, at high quencher concentrations, deactivation of the substrate singlet state and/or chemical reaction of the quencher with the substrate[12b] may occur.

† The triplet energy of β-methylstyrene is 61·8 kcal/mol[13a] while that for indene is 59 kcal/mol.[13b]

‡ For a rate constant for diffusion in benzene of 5×10^9/l/mol sec,[14a] a concentration of **7** of 10^{-2} M, and the decay of excited singlet acetophenone of $> 10^{10}$ sec^{-1},[14b] the efficiency of diffusion controlled singlet energy transfer from acetophenone is less than 0·001. However, since the decay rate for acetophenone triplet in benzene at room temperature is about 10^5 sec^{-1},[14b] under these same conditions diffusion controlled triplet transfer is *ca.* 99% efficient.

no new volatile products were apparent by VPC.* To insure that the low product quantum yields in these sensitizations were not due to products being destroyed by the sensitizer, the photostability of **5**, **6**, and **11** under sensitization conditions was examined. It was found that **5**, **6**, and **11** are totally stable under our sensitization conditions. Thus, the sensitization studies establish the lowest triplet state of **7** is not an important state for the production of **5**, **6**, or **11**, and further imply the excited singlet state of **7** as responsible for the observed products.

To provide further evidence on the multiplicity of the reactant state in the photochemistry of **7**, quenching studies were undertaken. Unfortunately, without an exact value for the triplet state energy of **7** the proper selection of a quencher was made difficult. For convenience we first examined the effect of piperylene at high concentration on the efficiency of the **7** reaction. The results of these studies are shown in Table 5 (runs 1 and 2). The effect of piperylene was to slightly lower the quantum efficiency for production of both **5** (0·21 to 0·15)† and **11** (0·38–0·31)† without alternation of quantum yield for the disappearance of **7**. In view of the small decrease in quantum yields for product formation at these high quencher concentrations, we studied the effect of a lower energy quencher, 1,3-cyclohexadiene (E_T = 54 kcal/mole)[15] on the photolysis of **7** (runs 3 and 4, Table 5). Here again, the only result was a slight decrease in the product forming quantum efficiencies. While the results from the quenching studies are not as clean as would be desired, the lack of significant quenching at the high quencher concentration supports the intermediacy of an excited singlet state as the reactant.

TABLE 5. QUENCHING REACTIONS OF 7-CARBOMETHOXY-3,4-BENZOTROPILIDENE,(7)

Run	Quencher (conc. M)	Conversion of 7	6	11	5	7
1	Piperylene (2·1 M)	10%	0·03	0·31	0·15	0·57
2	Piperylene (2·8 M)	40%	0·02	0·31	0·14	0·59
3	1,3-Cyclohexadiene (1·2 M)	10%	0·03	0·35	0·17	0·60
4	1,3-Cyclohexadiene (2·3 M)	10%	0·03	0·33	0·17	0·59

DISCUSSION

The photochemistry of 7-carbomethoxy-3,4-benzotropilidene (**7**) is characterized by three major processes. Furthermore, the excited state of **7** shows only inefficient deactivation processes, since the overall efficiency of the processes is about 0·60. While quenching and sensitization studies indicate that the excited singlet state is the important intermediate for these reactions, the molecular details of the rearrangements have not

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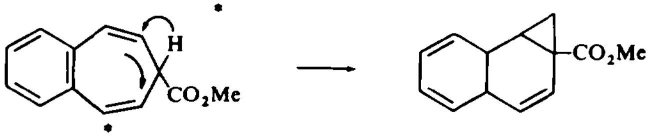
* The loss of starting material may be due to dimerization processes or reaction of the triplet **7** with sensitizer. The non-volatile products from the sensitizations were not studied.

† (a) While the quantum yields for production of **5** and **11** are lowered in the quenching irradiations, the quantum yield for **7** is unchanged. The lower product yields may result from the known chemical reaction of excited aromatic hydrocarbon singlets with ground state diene (for leading references see [11b]); (b) In both the piperylene and cyclohexadiene quenching irradiations, the quantum yield for **5** is decreased more than for **11**. This would result if a small portion of the carbomethoxy migrated product arises from the triplet state. Note also the sensitization results (Table 4).

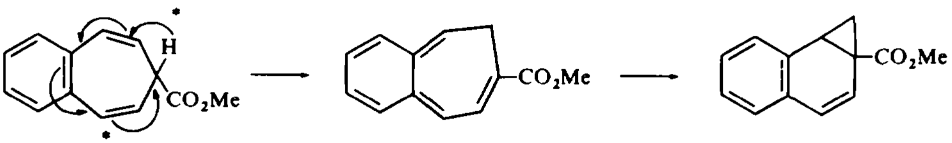
been completely established. As has been noted,[3a] two general types of mechanism can be envisioned. One of these involves migration being concerted with cyclopropane ring formation (Scheme 1), while the second involves a 1,7-migration followed by valence tautomerization to a benzonorcaradiene (Scheme 2). While we favor the 1,7-shift mechanism, either process accommodates the formation of **11** from **7**.

SCHEME 1. Concerted migration and ring formation



7 **11**

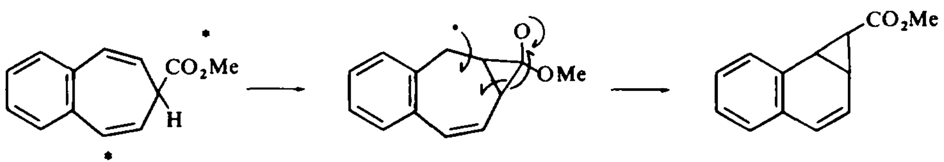
SCHEME 2. The 1,7-shift mechanism



7 **12** **11**

Likewise, the molecular details of the carbomethoxy migration have not been established. In addition to the two general mechanisms noted for hydrogen migration (*vide supra*), a third reaction pathway is available for carbomethoxy migration. This process, which may be viewed as a variant of the oxa-di-π-methane reaction,[*] is outlined in Scheme 3. While reports of photochemical carbomethoxy migration are rare, the high efficiency for the migration observed here suggests that possibility of ester migration in suitable photochemical systems should not readily be dismissed.

SCHEME 3. The oxa-di-π-methane process



7 **13** **5**

The complete absence of the carbo-di-π-methane process in 3,4-benzotropilidenes initially seemed unusual in view of the generality of the process.[17] However, a recent rationale for the inefficient vinyl-vinyl di-π-methane process in 1-methylene-4,4-dimethylcyclohexadiene may also be applicable to the 3,4-benzotropilidene system. Zimmerman[18] suggested the low reactivity in his di-vinylmethane system was a result of its *cisoid*-like geometry. While the origin of this effect is unclear, the 3,4-

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[*] Reactions emanating from carbonyl–vinyl bridging [16a,b] have been recognized as general processes and termed the oxa di-π-methane rearrangement.[16c]

benzotropilidene system does fit the requirements of a *cisoid*-like 1,4-diene system.

The final aspect of the discussion centers on the deuterium isotope effect in the photolysis of **7d**. The substitution of deuterium for hydrogen may exert a marked effect on certain decay processes in the excited state.[19]* In addition to the effect on radiationless processes in the excited state, deuterium substitution may also alter photochemical results in the more usual fashion involving breakage of the C—D bond.

In this study, the isotope effect as reflected by the change in product ratio from the parent tropilidene (**7**) and its 7-deutereo-analog (**7d**) is quite large. The validity of a precise number for the isotope effect of hydrogen vs. deuterium migration is somewhat questionable, since the corresponding rates of the reactions are unknown. However, if the rate of carbomethoxy migration is assumed to be equal† in **7** and **7d**, the k_H/k_D value for hydrogen migration is ~3·4.‡ Of special relevance is that the product distribution is markedly altered by deuterium distribution, while the overall efficiency of product formation in **7** and **7d** is nearly identical. Thus, deuterium substitution here is not markedly effecting the amount of radiationless decay vs. reactivity from the reacting excited state. The absence of an appreciable effect on overall product efficiency suggests that the isotope effect here arises from the breaking of the C—H vs. C—D bond in the transition state for migration.

In conclusion we wish to point out that many of the properties of the 3,4-benzotropilidene system fulfil requirements for meaningful photochemical migratory aptitude studies. These studies are in progress and will be reported at a later date.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer Infracord Model 137 spectrometer. UV spectra were determined with a Cary 14 recording spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer. NMR spectra were measured at 60 Mc using TMS as internal standard. All elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All photolyses were carried out in an atmosphere of purified nitrogen.

exo-3,4-*Benzobicyclo*[4.1.0]*heptane-7-carboxylic acid.* A mixture of 33·3 g (0·26 m) of 1,4-dihydronaphthalene[22] and 40·0 g (0·35 m) of ethyl diazoacetate was added dropwise over a period of 5 hr to a stirred mixture of 42·2 g (0·32 m) of 1,4-dihydronaphthalene and 2·5 g of anhyd $CuSO_4$ at 90–100°. After evolution of N_2 ceased, the dark brown mixture was diluted with 100 ml of ether and filtered. The ether was distilled from the filtrate and the residue refluxed for 48 hr with methanolic KOH [60 ml MeOH, 200 ml of water, and 30 g (0·83 m) KOH]. The cooled hydrolysis mixture was extracted with ether (3 × 200 ml), the aqueous phase acidified to pH = 2 with conc. HCl, and the liberated acid extracted with ether (3 × 200 ml). The combined ether extracts were washed with water (100 ml) and dried over Dricrite. Removal of the ether *in vacuo* yielded the acid as a brown solid. Three recrystallizations yielded 22·1 g of slightly yellow acid, m.p. 164–170°. Chromatography of the dark brown mother liquor on silicic acid (2·3 × 20 cm column) with $CHCl_3$ as eluent yielded an additional 8·9 g, m.p. 167–170°, of the acid for an overall crude yield of 31·0 g (47%). The analytical sample recrystallized from hexane–EtOAc showed: m.p. 170·5–173·5°; § NMR ($CDCl_3$) 2·85 (m, 4 H), 6·87 (s, 4 H), 7·95 (m, 2 H), and 8·51 (t, $J = 4$ Hz, 1 H) τ. (Calc. for $C_{12}H_{12}O_2$: C, 76·59; H, 6·38. Found: C, 76·47; H, 6·42%).

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* One of the largest such effects is the effect of deuterium on the lifetime of naphthalene triplet[20] (i.e., $C_{10}H_8$, $\tau = 2{\cdot}1$ sec; $C_{10}D_8$, $\tau = 16{\cdot}9$ sec).

† While a reasonable estimate for a secondary isotope effect in this system appears to be lacking, recorded secondary isotope effects in photochemical olefin isomerizations appear to be small.[21]

‡ Interestingly, the change in product ratio for production of cyclobutene, **6**, from **7** and **7d** corresponds to an isotope effect of about 3.

§ This compound was previously reported[23] to have m.p. 126–127°. The discrepancy between the value reported earlier and our results remains unexplained.

exo-7-*Carbomethoxy*-3,4-*benzobicyclo*[4.1.0]*Heptane* (**9**). A mixture of 20·0 g (0·11 m) of *exo*-3,4-benzobicyclo[4.1.0]heptane-7-carboxylic acid, 12·4 g (0·12 m) of 2,2-dimethoxypropane, 70 ml of absolute MeOH, and 0·1 ml of conc HCl was stirred and refluxed for 12 hr. After solvent removal *in vacuo*, the residual oil was dissolved in 150 ml ether and extracted with saturated NaCl aq (100 ml), 5% $NaHCO_3$ (50 ml), and saturated NaCl aq (50 ml). Removal of solvent from the dried ($CaSO_4$) ether layer yielded an oil which was crystallized from hexane to yield 18·2 g (82%) of white crystalline solid, m.p. 50–52°. Recrystallization from ether–hexane yielded the analytical sample: m.p. 50·5–52·0°; IR (KBr) 3·20–3·43 (w), 5·84 (s), 6·97 (s), 7·42 (s), 7·71 (m), 7·91 (s), 8·28 (m), 8·38 (s), 8·51 (s), 9·67 (m), 10·14 (s), 10·86 (m), 12·20 (m), 13·34 (s), 13·93 (m), and 14·16 (m) μ; NMR ($CDCl_3$) 2·94 (d, 4 H), 6·37 (s, 3 H), 6·95 (s, 4 H), 8·05 (mult., 2 H), and 8·52 (t, 1 H) τ. (Calc. for $C_{13}H_{14}O_2$: C, 77·20; H, 6·98. Found: C, 77·21; H, 7·00%).

exo-7-*Carbomethoxy*-2,5-*dibromo*-3,4-*benzobicyclo*[4.1.0]*heptane* (**10**). A mixture of 9·0 g (51 mm) of NBS, 5·0 g (25 mm) of **9**, 0·15 g of dibenzoyl peroxide, and 125 ml of CCl_4 was refluxed. The reaction was judged complete when the NBS at the bottom of the flask had disappeared and the succinimide floated (*ca.* 1 hr). The succinimide was filtered whilst hot and the solvent removed from the filtrate *in vacuo*, yielding a yellow oil. Trituration of the oil with ether yielded a nearly white crystalline solid: 4·7 g, m.p. 168–172° (decomp.). The mother liquors upon standing yielded an additional 0·9 g of material, total yield 65%. Initial attempts to further purify this material were unsuccessful. Since this crude dibromide afforded good yields in the debromination step, the crystalline material was utilized without further purification. The dibromide showed: IR (KBr) 5·82 (s), 6·95 (s), 7·67 (s), 7·82 (s), 8·38 (s), 8·55 (s), 8·66 (s), 10·32 (m), 12·83 (m), and 13·65 (m) μ; NMR ($CDCl_3$) 2·63 (s, 4 H), 4·27 (m, 2 H), 6·26 (s, 3 H), 7·19 (m, 2 H), and 8·49 (t, $J = 4$ Hz, 1 H) τ.

7-*Carbomethoxy*-3,4-*benzotropilidene* (**7**). To a solution of 5·0 g (13·9 mm) of dibromide **10** in 80 ml THF was added 0·92 g (14·5 mm) of Zn dust and 0·1 ml of glacial AcOH. The mixture was refluxed and stirred under N_2 for 0·5 hr (prolonged heating leads to polymerization) during which the cloudy dark grey mixture changed to cloudy off-white. After removal of solvent *in vacuo*, the oily residue was chromatographed on silica gel (2·3 x 100 cm column—slurry packed in 4% ether–hexane). Elution proceeded as follows: 4% ether–hexane, 1·5 l, nil; 4% ether–hexane, 1·5 l, 2·3 g (83%) of white crystalline solid (m.p. 57–59°). Recrystallization of this material from MeOH yielded the analytical sample, m.p. 60–61°: NMR (CCl_4) 2·82 (s, 4 H), 3·45 (doublet split into doublet, $J = 10$ Hz, $J = 1·5$ Hz, 2 H), 4·10 (quartet, $J = 10$ Hz, $J = 5$ Hz, 2 H), 6·29 (s, 3 H), and 6·95 (m, 1 H) τ. (Calc. for $C_{13}H_{12}O_2$: C, 78·00; H, 6·00. Found: C, 78·00; H, 6·00%).

Preparation of deuterated ethyl diazoacetate. A heterogeneous mixture of 20 g of ethyl diazoacetate and 15 g D_2O was vigorously stirred in the dark at RT for 72 hr. The aqueous layer was separated and procedure repeated with 20 g D_2O (96 hr reaction time). Then 30 ml of ether was added to the mixture, the aqueous layer separated, and the ethereal solution filtered and dried ($CaSO_4$). After evaporation of the ether in N_2, the deuterium assay by NMR integration showed 88% monodeuteration. To this 88% deuterated material, 6 g of 93% deuterated ethyl diazoacetate (from a previous run) was added and the material stirred for 48 hr with 16 ml of D_2O. This mixture was worked up as described above to yield 11·9 g of 97% deuterated ethyl diazoacetate. This material was used as obtained for the reaction with 1,4-dihydronaphthalene.*

7-*Deutereo*-3,4-*benzobicyclo*[4.1.0]*heptene*-exo-7-*carboxylic acid.* A mixture of 42·2 g (0·32 m) of 1,4-dihydronaphthalene and 11·9 g (a max. of 0·10 m) of 97% monodeuterated ethyl diazoacetate was added over 4 hr to a stirred mixture of 49·4 g (0·38 m) of 1,4-dihydronaphthalene and 2·5 g anhyd $CuSO_4$ at 98–105°. The cooled mixture was worked up as described for the undeuterated compound, refluxed for 15 hr with methanolic KOH (15 g KOH, 100 ml of water, 100 ml MeOH). The hydrolysis mixture was worked up as previously described to yield 3·7 g of the deuterated acid.

Preparation of exo-(7-*carbomethoxy*)-7-d-3,4-*benzobicyclo*[4.1.0]*heptane* (**9d**) *and* exo-(7-*carbomethoxy*)-7-d-2,5-*dibromo*-3,4-*benzobicyclo*[4.1.0]*heptane* (**10d**). A mixture of 3·7 g (0·02 m) of the deuterated acid, 4·0 g (0·04 m) of 2,2-dimethoxy propane, 0·1 ml of conc HCl, and 60 ml of absolute MeOH was stirred and refluxed for 12 hr. Removal of solvent *in vacuo* yielded 3·8 g (97%) of crude ester as a colorless oil. Reaction of this material with 8·0 g (0·04 m) of NBS, 0·30 g of dibenzoyl peroxide in 100 ml CCl_4 as described for the hydrogen compound yielded 2·8 g of dibromoester (41% overall yield from acid).

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* Noticeable decomposition accompanies the exchange reaction and the final material is undoubtedly contaminated with other products. While these impurities result in apparent lower yields in the next step, they do not create any purification problems.

Preparation of 7-deutereo-7-carbomethoxy-3,4-benzotropilidene (**7d**). In a manner analogous to that of the hydrogen compound, 2·8 g (7·6 mm) of the deuterated dibromoester, 0·60 g (9·2 mm) of Zn dust, and 0·1 ml of dibromoethane in 80 ml THF were reacted to yield 0·93 g (61%) of **7d**, m.p. 58·0–60·0°. Analysis for deuterium by NMR integration* showed 94% deuterium in the 7-position: NMR (CCl_4) 2·76 (s, 4 H), 3·73 (AB quartet, $J = 10$ Hz, 4 H), 6·28 (s, 3 H) τ.

Quantum yields for reaction of 7-carbomethoxy-3,4-benzotropilidene (**7**). The quantum yields for appearance and disappearance of products were determined with 330 nm light from a Bausch and Lomb high intensity grating monochromator (front and back slits at 5 mm). The cylindrical photolysis cell contained two identical compartments, each 4·5 cm in diameter with a 5 cm optical path. The cell was constructed from 4·5 cm Pyrex tubing and had optical quartz faces and a quartz spacer which separated the two compartments. In addition, each cell compartment was equipped with a 14/20₸ male joint and a 7/25₸ female joint for a thermometer.

Quantum yield determinations consisted of two irradiations. The first irradiation was carried out with potassium ferrioxalate in both compartments and the total light output determined. Typical values of light intensity were on the order of 5×10^{-3}mE/(min) (65 ml). The second irradiation was performed with the sample in the first cell and a fresh solution of potassium ferrioxalate in the back cell. In a typical determination, a stock solution was formed from 0·26279 g of **7** and 0·02783 g of nonadecane in 70 ml of purified cyclohexane. After irradiation of 65 ml of the magnetically stirred, N_2-purged photolysis solution, the assay for starting material and products was made by VPC [12′ × ⅛″, 5% PDEAS on 60/80 Chrm. W-column temp. 155°]. For each run the VPC was calibrated immediately prior to analysis with known mixtures of **5**, **7**, **11** and nonadecane, and the peak areas in the quantum yield measurements corrected for compound sensitivity using the relationship

$$\frac{\text{Wt. Compound}}{\text{Wt. Standard}} = F\,\frac{\text{(Area Compound)}}{\text{(Area Standard)}}$$

Since **6** was not available in sufficient quantity, its sensitivity factor was taken equal to that of **11**. The results of the quantum yield determinations are given in Table 6.

TABLE 6. QUANTUM YIELDS FOR 7-CARBOMETHOXY-3,4-BENZOTROPILIDENE (7)

Conc. $\dot{M} \times 10^{-3}$	Time (min)	Total light Intensity (mE/65 ml)	Light Transmitted (mE/65 ml)	Light Absorbed (mE/65 ml)	**7** mm × 10^{-3} (Φ)	**11** mm × 10^{-3} (Φ)	**5** mm × 10^{-3} (Φ)	**6** mm × 10^{-3} (Φ)
19·2	60	291	15	276	155 (0·56$_6$)	106 (0·38$_4$)	55·2 (0·20$_1$)	7·6 (0·02$_8$)
18·8	60	295	20	275	155 (0·56$_6$)	103 (0·37$_8$)	58·7 (0·21$_4$)	8·5 (0·03$_1$)
18·9	60	313	23	290	210 (0·72$_5$)	122 (0·42$_2$)	64·0 (0·22$_1$)	10·0 (0·03$_4$)

Determination of relative quantum yields of 7-carbomethoxy-3,4-benzotropilidene (**7**) *and its 7-deutereo-analog with* RPR-3500 Å *source*. In a typical determination, a stock solution of 0·0320 g of **7** and 0·01122 g of nonadecane in 25 ml of cyclohexane was prepared. Twenty milliliters of the above solution was placed in a Pyrex test tube, purged with purified N_2, and sealed. This material was irradiated with a similarly prepared solution of the deutereo compound in a merry-go-round apparatus with emission from eight RPR-3500 Å lamps for 11·00 min. The resulting photolysis mixture was then analyzed by VPC using the appropriate calibration solutions to correct for compound sensitivity (see quantum yield measurements for

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* In view of the small amount of hydrogen in the 7-position, the NMR assay was carried out by integrating the multiplet at 6·95 τ relative to the nearby C_{13} satellite peak of the OMe singlet. Since each peak of the C_{13} satellite was 0·5% of the area of three protons, the total area represents 0·015 hydrogen. Using this relationship and the integration results, the proton content of the 7-position was found to be 5·8%.

details). The sensitivity factors for the deuterated products were assumed to be the same as those for the corresponding hydrogen products. These results are tabulated in Table 7.

Determination of relative quantum yields of 7-carbomethoxy-3,4-benzotropilidene (7) and its 7-deutereo-analog at 3300 Å. Identical cyclohexane solutions of the hydrogen compound and its deuterated derivative with eicosane as internal standard were prepared and irradiated for 76 min using 3300 Å light as described for the quantum yields. The resulting photolysis mixtures were then analyzed by VPC using appropriate calibration solutions. The sensitivity factors for the deuterated products were assumed to be the same as the corresponding hydrogen analogs. The results are tabulated in Table 8.

TABLE 7. RELATIVE QUANTUM EFFICIENCIES OF 7-PROTIUM VS. 7-DEUTERIUM-7-CARBOMETHOXY-3,4-BENZOTROPILIDENE WITH RPR-3500 Å SOURCE

Isotope	Compound (mg)	Standard (mg)	Disappearance of **7** (mg)	Formation of products **11** (mg)	**5** (mg)	**6** (mg)
H	83·20	11·22	—[a]	4·85	3·23	0·28
D	83·32	11·30	7·9	2·24	5·50	—[b]
H	82·25	11·37	8·1	5·40	3·49	—[a]
D	82·26	11·41	—[a]	2·36	5·18	—[b]

[a] Value not determined.

[b] Product not formed in measureable amounts.

TABLE 8. RELATIVE QUANTUM EFFICIENCIES OF 7-PROTIUM VS. 7-DEUTERIUM-7-CARBOMETHOXY-3,4-BENZOTROPILIDENE WITH 3300 Å LIGHT

Isotope	Compound (mg)	Standard (mg)	Formation of products **11** (mg)	**5** (mg)	**6** (mg)
H	266·34	30·59	20·8	12·6	0·8
D	265·23	30·24	11·7	25·2	

Acetophenone sensitization of **7**. The following is typical of the sensitization runs. A stock solution of **7** was prepared from 0·16586 g of **7** and 1 ml of an eicosane standard (0·75644 g of eicosane in 25 ml of cyclohexane) diluted to 50 ml with cyclohexane. A 10 ml aliquot of the above solution in a Pyrex test tube was degassed with purified N_2, sealed, and the stirred solution irradiated for 0·5 hr with 330 nm light from a Bausch and Lomb monochromator (200-watt super pressure lamp). Then a second 10 ml aliquot was irradiated under identical conditions with 0·6727 g of acetophenone added. The two photolyses and the stock solution were immediately analyzed by VPC and the quantum yields calculated on the basis of the known values for the direct irradiation at this wavelength. The results are recorded in Table 4 of the text.

Stability of the photoproducts to acetophenone sensitization conditions. A 10 ml aliquot of the stock photolysis solution was irradiated for 0·5 hr in an identical manner to that utilized in the sensitization experiments. The composition of the solution was as shown below (Run 1). To this photolyzed solution was added 0·20950 g of acetophenone; the solution was degassed, sealed, and irradiated for 0·5 hr under identical conditions to the first irradiation. Analysis of the resulting photolysis solution showed no product instability under the sensitization conditions (Run 2).

	6	**11**	**5**	**7**
Run 1	1·5%	11·2%	6·1%	81%
Run 2	1·7%	13·0%	6·9%	68%

Quenching photolyses of 7. The following is typical of several runs. A stock solution of 0·16586 g of 7 and 1 ml of eicosane solution (0·75644 g of eicosane in 25 ml of cyclohexane) in 50 ml of purified cyclohexane was prepared. A 10 ml aliquot of the above solution in a Pyrex test tube was degassed with purified N_2, sealed, and the stirred solution irradiated for 0·5 hr with 330 nm light from a Bausch and Lomb monochromator (200-watt super pressure lamp). A second solution was prepared by concentrating a 10 ml aliquot of the stock solution, addition of 1·419 g of piperylene, and dilution to 10 ml with cyclohexane. This solution was irradiated under identical conditions to the first photolysis. Analysis of the zero time solution and the two photolyses yielded the results shown in Table 5 of the text.

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