electrophilic substitution.[8] In addition, similar interactions are believed to be responsible for the catalysis of the acetolysis of fluorenyl tosylates by phenanthrene.[9] All the evidence suggests that there is some binding of the cation with the aromatic π system rather than a chance encounter, and the ability of phenols to stabilize R^+ is greater than that of simple univalent electrolytes (Figure 1 and ref 2 and 10). Neighboring group participation by aryl substituents is often interpreted in terms of intermediate phenonium ions,[11] but interactions between the π system and the forming carbocation may be important.

Despite their low basicities, phenoxide and thiophenoxide ions[12] are excellent nucleophiles toward triarylmethyl cations, and interactions between the cation and the aromatic π system of the nucleophile may be important, although formally, one could also regard this high reactivity of phenoxide ion as an α effect, which is the high nucleophilicity observed when an atom having unshared electrons is adjacent to the reaction center. However, the reactions of thiophenoxide ion were with stable triarylmethyl dye cations, where the importance of nucleophile–cation ion pairing and general base catalysis has been postulated.[13] Slow proton transfers do not appear to be of great importance in reactions of the tri-*p*-anisylmethyl cation.[1,2,13]

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(13) E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 2565 (1968).

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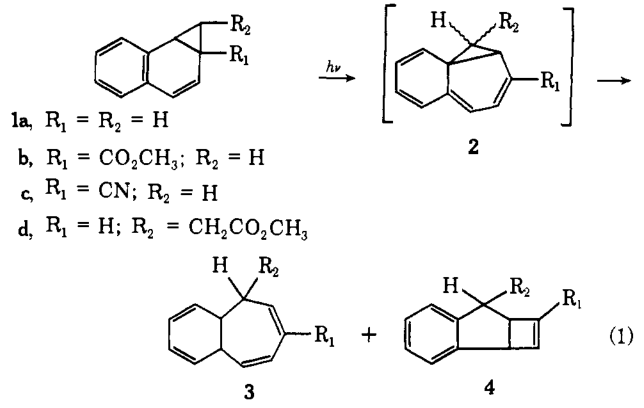
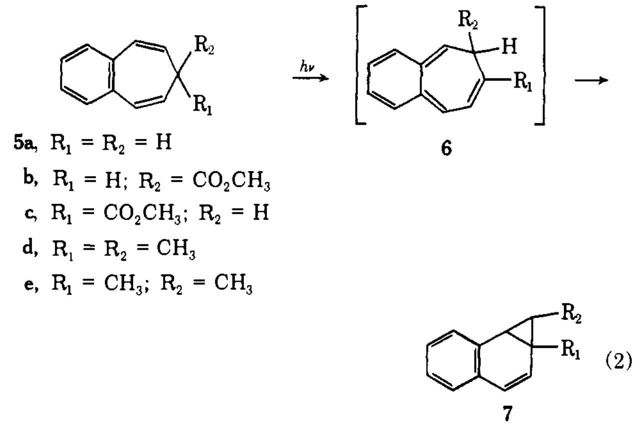
Selectivity in the Excited State Rearrangements of Homobenzotropilidenes

Sir:

The photochemistry of benzonorcaradienes[1a-f] and benzotropilidenes[1d-g,2] has been of general interest in recent years. A major process in benzonorcaradiene photochemistry involves a formal 1,5-sigmatropic shift with eventual production of either a 1,2-benzotropilidene[1c,e] or a 2,3-benzobicyclo[3.2.0]hepta-2,6-diene (eq 1),[1c,f,3] while the photochemistry of benzotropilidenes is dominated by 1,7-group migration (eq 2).[4]



1a, $R_1 = R_2 = H$
b, $R_1 = CO_2CH_3$; $R_2 = H$
c, $R_1 = CN$; $R_2 = H$
d, $R_1 = H$; $R_2 = CH_2CO_2CH_3$



5a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CO_2CH_3$
c, $R_1 = CO_2CH_3$; $R_2 = H$
d, $R_1 = R_2 = CH_3$
e, $R_1 = CH_3$; $R_2 = CH_3$

Aside from the intrinsic interest in the photochemistry of homo systems,[5] there existed rearrangement possibilities in 1,2-homo-3,4-benzotropilidenes which are formally analogous to high efficiency processes in both benzonorcaradienes and benzotropilidenes.[6] We wish to report here the highly selective, facile photoisomerization of homobenzotropilidenes **8a** and **8b** to the corresponding 4,5-benzobicyclo[4.2.0]octa-2,4-dienes **9a** and **9b**.

Irradiation of **8a** in cyclohexane at 300–330 nm through Pyrex led to rapid formation of a single product at low conversion (10–15%). Extended irradiation produced naphthalene and several uncharacterized compounds in addition to this initially formed material. The major product was isolated by vpc and its structure established as **9** by comparison of its nmr spectrum with that of 4,5-benzobicyclo[4.2.0]octa-2,4-diene (**9a**).[7,7a] To obtain additional evidence on the

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(1) (a) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967); (b) J. S. Swenton and A. J. Krubsack, *ibid.*, **91**, 786 (1969); (c) G. W. Gruber and M. Pomerantz, *ibid.*, **92**, 4004 (1970); (d) D. M. Madigan and J. S. Swenton, *ibid.*, **92**, 7515 (1970); *Tetrahedron*, **28**, 2703 (1972); (e) D. M. Madigan and J. S. Swenton, *J. Amer. Chem. Soc.*, **93**, 6316 (1971); (f) M. Kato, M. Kawamura, Y. Okamoto, and T. Muva, *Tetrahedron Lett.*, 1171 (1972); (g) H. Dürr and H. Kober, *ibid.*, 1255 (1972).

(2) (a) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **89**, 6798, 6799 (1967); **93**, 6615 (1971); (b) K. A. Burdett, D. H. Yates, and J. S. Swenton, *Tetrahedron Lett.*, in press.

(3) Whether 1,2-benzotropilidenes or benzobicyclo[3.2.0]hepta-2,6-dienes are produced is dependent upon the particular system. For a discussion, see ref 1e.

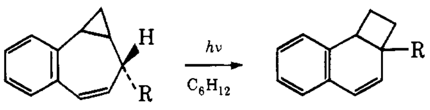
(4) Recently, it has been noted that a 1,3-hydrogen shift in the parent 3,4-benzotropilidene competes with the more common 1,7 process to the extent of ~10%.[2b]

(5) For an interesting series of papers in homofulvene photochemistry, see: (a) T. Tabata and H. Hart, *Tetrahedron Lett.*, 4929 (1969); (b) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **92**, 3474 (1970); (c) N. K. Hamer and M. Stubbs, *Chem. Commun.*, 1013 (1970), and references cited therein.

(6) The quantum efficiency of the **1b** → **3b** reaction is 0.45–0.35, while we have observed that the efficiencies of 1,7 shifts in five different 3,4-benzotropilidenes are always >0.5.

(7) A. M. Braun, *J. Org. Chem.*, **35**, 1208 (1970).

(7a) NOTE ADDED IN PROOF. Recently [P. Crews and J. Beard, *J. Org. Chem.*, **38**, 522 (1973)] 7,8-benzobicyclo[4.2.0]-2,7-octadiene (i) has been isolated instead of **9a** from the benzyne–cyclohexadiene reaction. This compound was presumably thermally converted to **9a** in the previous study. To exclude this thermal rearrangment in our work, we have examined the crude nmr spectrum of the irradiation of **8a** and find no evidence for i in our reaction.

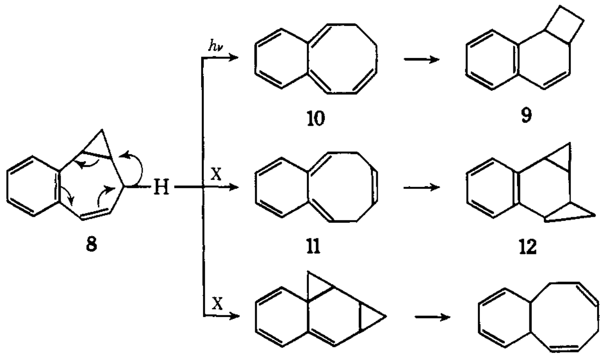


8a, R = H
b, R = CH_3

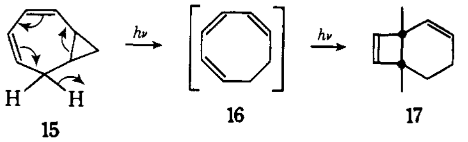
9

course of this isomerization, the methyl derivative **9b** was studied. Irradiation of **9b** under similar conditions as the parent compound yielded one major product as detected by vpc. The mass spectrum indicated that the product was isomeric with **8b**, and the base peak of 142 (P − 28) was strongly suggestive that a simple cyclobutane ring was present. The 100-MHz nmr (CCl_4) spectrum showed: τ 3.12 (m, 4 H), 3.78 (d, J = 10 Hz, 1 H), 4.46 (d, J = 10 Hz, 1 H), 6.84 (br t, 1 H), 7.98 (m, 4 H), and 8.86 (s, 3 H). The appearance of the two vinyl protons as a simple AB quartet and the methyl group as a sharp singlet indicates that both the vinyl and methyl groups are bonded to tertiary centers. This, together with the mass spectral evidence, establishes the photoproduct as **9b**.

The formation of **9a** from **8a** is explained by a homo-1,7 shift in excited **8a** yielding **10** which undergoes valence tautomerization to **9a**. Neither **12**, which would have been expected from hydrogen shift of **1a** in the opposite sense, nor **14**, which would have been formed *via* the homo-1,5-sigmatropic shift route, could be detected in these studies. The exclusive formation of the hydrogen-migrated product **9b** from **8b** is in accord with the much greater migratory aptitude of hydrogen *vs.* methyl in the benzotropilidene system.[8] While qualitative observations from preparative irradiation suggested a moderately efficient process, quantum yields were measured to directly compare this reaction with hydrogen migration in the parent 3,4-benzotropilidene. The quantum yields for disappearance of **8a** and appearance of **9a** were 0.24 and 0.20, respectively, indicating a process of good efficiency. Since the quantum yield for hydrogen migration in 3,4-benzotropilidene is 0.87,[2b] the analogous shift in the homosystem is four–five times less efficient.



The present results demonstrate the unique photochemical behavior of 1,2-homo-3,4-benzotropilidenes. Previous studies on homotropone[9] and homoazepin[10] derivatives showed that the major products were those expected from the individual chromophores without specific involvement of the total homo-π system. The previous reported irradiation of the homotropilidene **15** to afford **17**, which was noted without comment concerning mechanism,[11] may also proceed *via* a homo-1,7-hydrogen shift. The observed product **17** would necessarily have arisen by secondary irradiation of initially formed **16**. The present results, together with the inferences drawn for the literature, indicate the unique involvement of the cyclopropane ring of homotropilidenes and homobenzotropilidenes in the highly selective and moderately efficient homo-1,7 shifts. Full synthetic details and mechanistic discussion will be presented in our full paper.[12]



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[8] Photolysis of 7-methyl-3,4-benzotropilidene proceeds with a quantum efficiency of 0.93 and yields solely 5-methylbenzonorcaradiene. The migration ratio of hydrogen *vs.* methyl is at least 1000 : 1.

[9] L. A. Paquette and R. J. Haluska, *J. Org. Chem.*, **35**, 132 (1970).

[10] L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).

[11] (a) W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965). (b) Interestingly, labeling studies used to support a 1,5-hydrogen shift mechanism in the photochemistry of 1,3,6-cyclooctatriene are equally consistent with the sequence

$$\text{1,3,6-cyclooctatriene} \xrightarrow{h\nu} \mathbf{15} \xrightarrow{h\nu} \mathbf{16} \xrightarrow{h\nu} \mathbf{17}$$

[12] All new compounds gave acceptable combustion analyses. The general route to the homobenzotropilidenes involves Simmons–Smith reaction with the corresponding 3,4-benzocyclohepta-1,3-diene, followed by NBS bromination and dehydrobromination with $CaHPO_3$ in DMF (D. J. Bertelli and C. C. Ong, *J. Amer. Chem. Soc.*, **87**, 3719 (1965)). Direct Simmons–Smith reaction with 3,4-benzotropilidenes gives complex mixtures of products.

[13] Alfred P. Sloan Fellow (1970–1972); Camille and Henry Dreyfus Teacher–Scholar Awardee, 1971–1976.

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Nybomycin. VI. Incorporation of Acetate-^{13}C, Acetate-^{14}C, and Methionine-^{14}C[1]

Sir:

The structure **1** assigned[2] to the antibiotic nybomycin by its spectral and chemical properties has been confirmed by the total synthesis[1] of nybomycin. The unusual structure of nybomycin involves a ring system thus far unique in nature (except for the naturally occurring deoxynybomycin)[3,4] and it stimulates speculation on its origin.[5] We present evidence here, including studies with a ^{13}C label, which clearly and unequivocally defines acetate as the source of the exterior carbons of the pyridone rings but rules out acetate as the primary source of the carbons of the central ring. We also present evidence which defines

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[1] Paper V: R. M. Forbis and K. L. Rinehart, Jr., *J. Antibiot.*, **24**, 326 (1971).

[2] K. L. Rinehart, Jr., G. Leadbetter, R. A. Larson, and R. M. Forbis, *J. Amer. Chem. Soc.*, **92**, 6994 (1970).

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[4] R. M. Forbis and K. L. Rinehart, Jr., *J. Amer. Chem. Soc.*, **92**, 6995 (1970).

[5] (a) K. L. Rinehart, Jr., 17th National Organic Chemistry Symposium, Bloomington, Ind., June 25–29, 1961; (b) K. L. Rinehart, Jr., R. A. Larson, R. M. Forbis, and G. Leadbetter, Abstracts, 5th International Symposium on the Chemistry of Natural Products, IUPAC, London, July 1968, p 79; (c) R. A. Larson, Ph.D. Thesis, University of Illinois, Urbana, 1968.