

at such a rate that the temperature did not exceed -20°C . After an additional 3 h at -20°C , the reaction mixture was allowed to warm to 0°C and then treated with 30 mL of saturated NH_4Cl solution. After being allowed to stand overnight at room temperature, the mixture was concentrated in vacuo and then treated with 200 mL of CH_2Cl_2 and 100 mL of H_2O . The CH_2Cl_2 was separated, washed with H_2O , dried with anhydrous MgSO_4 , filtered, and concentrated to give a solid that was recrystallized from the appropriate solvent given in Table I.

6-(*p*-Chlorobenzoyl)-5-(*p*-chlorophenyl)-2,3-dihydroimidazo[2,1-*a*]isoquinoline (10). A stirred solution of 8.0 g (0.05 mol) of 2-(*o*-methylphenyl)imidazoline in 100 mL of THF maintained under a N_2 atmosphere was treated dropwise with 105 mL (0.15 mol of *n*-BuLi) of 1.6 M *n*-BuLi in hexane and then heated at 35°C for ca. 4 h. The mixture was then treated dropwise with a solution of 17.2 g (0.10 mol) of methyl *p*-chlorobenzoate in 50 mL of THF, heated at 50°C for ca. 5 h, and then allowed to stand overnight at room temperature. The cooled mixture was treated with 30 mL of saturated NH_4Cl and stirred for ca. 2 h at room temperature. The organic layer was separated, dried with MgSO_4 , filtered, and concentrated in vacuo to an oil (6.5 g). Chromatography on 200 g of silica gel with $\text{CHCl}_3/\text{CH}_3\text{OH}$ (90:10) as the eluant gave 2.7 g of 10: mp $210\text{--}212^{\circ}\text{C}$ ($\text{CH}_2\text{Cl}_2/\text{pentane}$); R_f 0.3 ($\text{CHCl}_3\text{--CH}_3\text{OH}$, 90:10); IR (CHCl_3) 6.05 ($\text{C}=\text{N}$), 6.15 ($\text{C}=\text{O}$) μm ; ^1H NMR (CDCl_3) δ 3.90 (4 H, octet, $\text{NCH}_2\text{CH}_2\text{N}$), 7.08–7.88 (11 H, m, aromatic), 8.23 (1 H, m, H-10); ^{13}C NMR (CDCl_3) δ 49.6 and 52.8 ($\text{NCH}_2\text{CH}_2\text{N}$), 156.8 ($\text{C}=\text{N}$), 194.9 ($\text{C}=\text{O}$); mass spectrum, m/e 419 (M^+), 308 ($\text{M}^+\text{C}_6\text{H}_4\text{Cl}$), 280 ($\text{M}^+\text{OCC}_6\text{H}_4\text{Cl}$). Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}$: C, 68.7; H, 3.8; Cl, 16.9; N, 6.7. Found: C, 68.5; H, 3.8; Cl, 16.9; N, 7.0.

5-Phenyl-2,3,5,6-tetrahydroimidazo[2,1-*a*]isoquinolin-5-ol (9e) from 3-(Dimethylamino)-1-phenyl-2-propen-1-one and 18. The lithium reagent from 4.0 g (0.025 mol) of 2-(*o*-methylphenyl)imidazoline, 150 mL of THF, and 53 mL (0.075 mol) of 1.6 M *n*-BuLi in hexane was cooled to -20°C and treated with 8.6 g (0.050 mol) of 18 in 100 mL of THF. After an additional 3 h at -20°C , the mixture was treated with 15 mL of saturated NH_4Cl solution and allowed to stand overnight at room temperature. The mixture was evaporated in vacuo to a paste and treated with CH_2Cl_2 and H_2O . The CH_2Cl_2 was separated, dried with anhydrous MgSO_4 , filtered, and concentrated to give 2.2 g (33%) of 9e: mp $186\text{--}188^{\circ}\text{C}$ dec (CH_2Cl_2); R_f 0.40 ($\text{CHCl}_3\text{--CH}_3\text{OH}$, 1:1); NMR ($\text{Me}_2\text{SO}-d_6$) δ 2.75–3.80 (6 H, m, CH_2 , $\text{NCH}_2\text{CH}_2\text{N}$), 6.05 (1 H, s, OH), 6.95–7.62 (8 H, m, aromatic), 7.86 (1 H, m, H-10); mass spectrum, m/e 264 (M^+), 246 ($\text{M}^+\text{--H}_2\text{O}$). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}$: C, 77.2; H, 6.1; N, 10.6. Found: C, 77.5; H, 6.4; N, 10.4.

2-[2-[(Phenylsulfonyl)methyl]phenyl]-4,5-dihydro-1H-imidazole (17). The lithium reagent from 16.0 g (0.10 mol) of 2-(*o*-methylphenyl)imidazoline, 250 mL of THF, and 210 mL (0.30 mol) of *n*-BuLi of 1.6 M *n*-BuLi was cooled to -20°C and treated dropwise with 19 g (0.12 mol) of benzenesulfonyl fluoride in 100 mL of THF. After an additional 3 h at -20°C , the mixture was treated with 60 mL of saturated NH_4Cl solution. The resulting solid was filtered off and crystallized from CH_2Cl_2 –petroleum ether to give 6.1 g (28%) of 17: R_f 0.1 ($\text{CHCl}_3\text{--CH}_3\text{OH}$, 98:2); mp $193\text{--}195^{\circ}\text{C}$; NMR ($\text{Me}_2\text{SO}-d_6$) δ 3.65 (4 H, m, CH_2CH_2), 5.53 (2 H, s, CH_2S), 6.42 (1 H, br, NH), 7.23–7.75 (9 H, m, C_6H_5 , C_6H_4). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: C, 64.0; H, 5.4; N, 9.3; S, 10.7. Found: C, 64.1; H, 5.7; N, 9.4; S, 10.4.

2-(4,5-Dihydro-1H-imidazol-2-yl)- α,α -diphenylbenzene-ethanol (16). The lithium reagent from 3.2 g (0.02 mol) of 2-(*o*-methylphenyl)imidazoline, 50 mL of THF, and 42 mL (0.06 mol) of *n*-BuLi of 1.6 M *n*-BuLi in hexane was treated at room temperature with a solution of 8.4 g (0.046 mol) of benzophenone in 50 mL of THF. The mixture was held at 35°C for 3 h, allowed to stand overnight at room temperature, cooled in an ice bath, and treated with 10.8 mL of saturated NH_4Cl solution. The two-phase system was separated, and the THF was treated with anhydrous MgSO_4 and activated charcoal and filtered through Celite. The filtrate was concentrated and the residue crystallized from Et_2O –pentane to give 4.5 g (66%) of 16: mp $148\text{--}150^{\circ}\text{C}$; R_f 0.10 ($\text{CHCl}_3\text{--CH}_3\text{OH}$, 95:5); NMR ($\text{Me}_2\text{SO}-d_6$) δ 3.70 (4 H, s, CH_2CH_2), 3.85 (2 H, s, CH_2), 6.25 (1 H, dd, $J = 8\text{ Hz}$, $J' = 2\text{ Hz}$, HC), 6.80–7.60 (14 H, m, 12 aromatic, NH, OH); ^{13}C NMR ($\text{Me}_2\text{SO}-d_6$) 44.13 (NCCN) 76.70 ($\text{C}=\text{O}$), 165.81 ($\text{C}=\text{N}$); mass spectrum, m/e 342 (M^+), 324 ($\text{M}^+\text{--H}_2\text{O}$), 314 ($\text{M}^+\text{CH}_2\text{CH}_2$). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}$: C, 80.7; H, 6.5; N, 8.2. Found: C, 80.5; H, 6.8; N, 8.3.

Acknowledgment. We are grateful to W. Bonkoski and his associates for microanalyses, S. DiCataldo and A. Kahle for NMR spectra, and B. Owens for mass spectral measurements.

Registry No. 3a, 936-49-2; 3b, 57327-93-2; 4a, 38385-75-0; 4b, 83633-99-2; 5a, 22232-71-9; 5b, 83634-00-8; 5c, 83634-01-9; 7, 83634-02-0; 8, 83634-03-1; 9a, 56882-42-9; 9b, 56882-51-0; 9c, 83634-04-2; 9d, 83634-05-3; 9e, 56882-45-2; 10, 83634-06-4; 16, 83634-07-5; 17, 83634-08-6; 18, 1201-93-0; methyl *p*-chlorobenzoate, 1126-46-1; dibenzosuberone, 1210-35-1; benzenesulfonyl fluoride, 368-43-4; methyl 2,4-dichlorobenzoate, 35112-28-8; methyl phenylacetate, 101-41-7; benzophenone, 119-61-9; methyl mandelate, 771-90-4; methyl 2-furoate, 611-13-2; methyl pivalate, 598-98-1.

Naphthoannelated Cycloheptatrienyliene and Cycloheptatetraene: Generation and Properties

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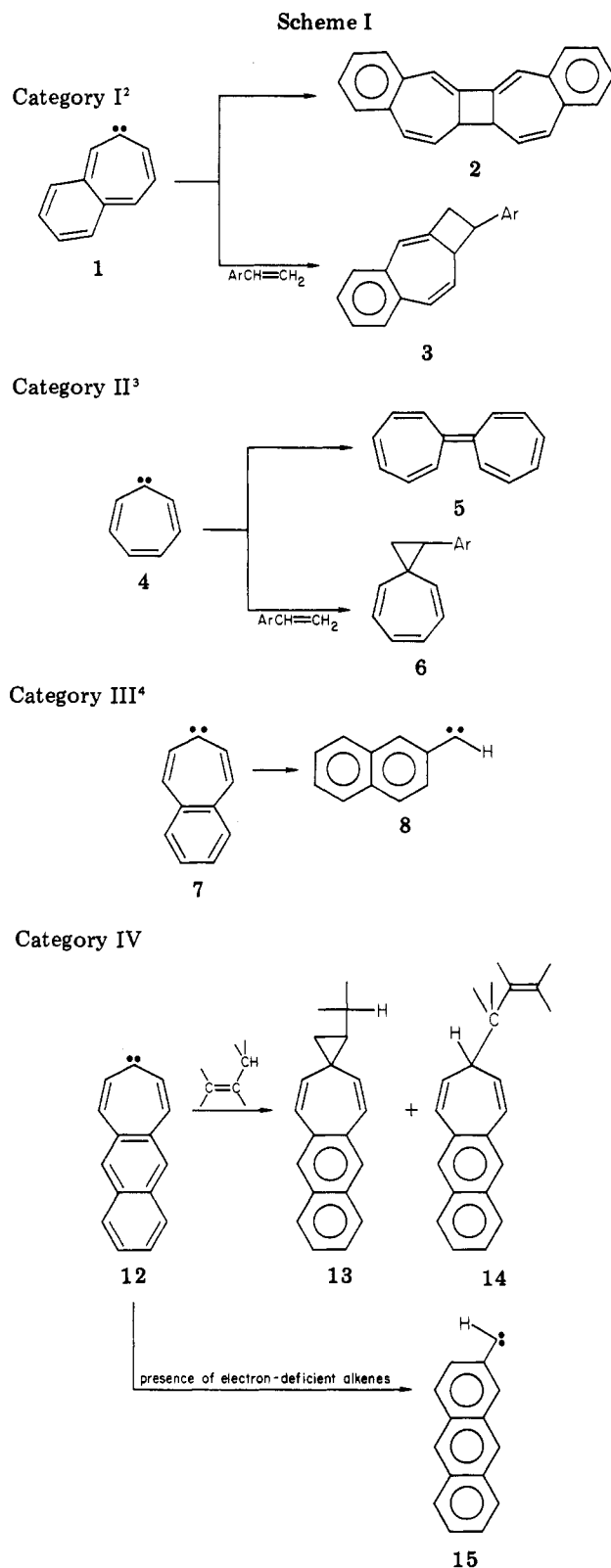
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Received April 22, 1982

A naphthoannelated cycloheptatrienyliene–cycloheptatetraene intermediate has been generated from both the corresponding tropone tosylhydrazone and a mixture of bromocycloheptatrienes. Thermolysis of the tosylhydrazone salt in cyclohexene or benzene gave only a mixture of naphthoannelated heptafulvalenes. Thermolysis of the tosylhydrazone salt in dimethyl fumarate gave the same two dimers along with the expected spirocyclopropane adduct. Thermolysis of the tosylhydrazone salt or dehydrobromination of the mixture of bromocycloheptatrienes (21 and 22) with potassium *tert*-butoxide in the presence of diphenylisobenzofuran gave, in addition to the heptafulvalene dimers, an adduct that is believed to have arisen from rearrangement of an initially formed allene adduct. On the basis of the chemistry reported here as well as INDO calculations on a number of cycloheptatrienyliene–cycloheptatetraene pairs (and the triplets of the carbenes) it is suggested that initially formed singlet carbenes either intersystem cross to their triplet forms and show triplet chemistry (carbenes 12, 32, and 34) or drop to allene ground states to show at least some allene chemistry. The principal unanswered question is whether any bimolecular chemistry originates from any of the singlet carbenes. Calculations of Waali argue for all chemistry coming from the allene while some of the experimental observations are consistent with a carbene.

The chemical properties of seven-membered cyclic conjugated carbenes (most originating from tosylhydrazone

salts) have been found to be highly sensitive to monoannulation by aromatic rings.¹ Prior to the recent report of

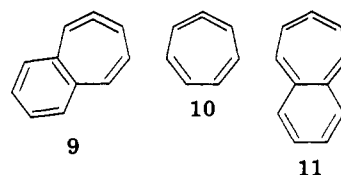


Dürr, the chemistry of the different ring systems fell into three general categories. These are exemplified by reactions shown in Scheme I.

(1) For reviews, see: (a) Jones, W. M.; Brinker, U. H. "Pericyclic Reactions"; Marchand, A., Lehr, R., Eds.; Academic Press: New York, 1977. (b) Jones, W. M. "Rearrangements in Ground and Excited States"; de Mayo, P., Academic Press: New York, 1980. (c) Wentrup, C. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum: New York, 1980. (d) Wentrup, C. *Top. Curr. Chem.* 1976, 62, 175. (e) Dürr, H. *Ibid.* 1973, 4, 103.

(2) Waali, E. E.; Lewis, J. M.; Lee, D. E.; Allen, E. W., III; Chappell, A. K. *J. Org. Chem.* 1977, 42, 3460.

In the early years of this chemistry, the reactions in category I were assigned to an allene valence isomer (9)



while those in categories II and III were assigned to singlet carbenes 4 and 7.³⁻⁵ With the passage of time, however, the role of allene structures 10 and 11 in the chemistry of intermediates in categories II and III as well as category I became increasingly apparent.^{1,6,7} This found theoretical support in INDO calculations⁸ that predicted allenes 9-11 to be more stable than their corresponding singlet carbenes.⁹

Recently, Dürr reported the generation and chemistry of the mononaphthoannulated cycloheptatrienyliene 12.¹⁰ In view of the structural similarity between 12 and 7, it was surprising that most of its chemistry is different not only from 7 but also from the intermediates in the other two categories. The chemistry of Dürr's carbene is summarized in category IV.

When Dürr's work appeared, we had just synthesized 19 for other purposes and thought it would be interesting to compare the calculated and observed properties of its corresponding carbene with Dürr's isomeric carbene 12. In this paper we report the preparation of ketone 19, its corresponding tosylhydrazone, and bromides 20-22 and the chemical properties of the intermediates generated from them. We also report INDO calculations on the carbene and allene structures for this intermediate and the intermediate generated by Dürr using the same assumptions as in our earlier paper.⁸ Finally, we report INDO calculations on a number of carbenes and allenes using optimized geometries as determined by Waali¹¹ using the MNDO method. From the experimental work, we find that the naphthoannulated cycloheptatrienyliene shows properties essentially identical with those of the parent. From a comparison of the two sets of theoretical calculations we conclude that the chemistry of cycloheptatrienyliene and its annelated relatives is dominated in some cases by the allene form and in others by the triplet carbene. The role of the singlet carbene remains uncertain.

Results

Synthesis of ketone 19 is outlined in Scheme II. The tosylhydrazone and its salt were prepared in the usual manner.³ Chemical properties of the salt are summarized in Scheme III. Thermolysis of the salt in cyclohexene or benzene at 105 °C gave no detectable insertion product (as reported for 12);¹⁰ only the two dimers 23 and 24 were

(3) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* 1969, 91, 6391.
 (4) Krajca, K. E.; Mitsuhashi, T.; Jones, W. M. *J. Am. Chem. Soc.* 1972, 94, 3661 Mullen, P. W., unpublished results.

(5) See also: Waali, E. E.; Jones, W. M. *J. Org. Chem.* 1973, 38, 2573 and references cited therein.

(6) Jones, W. M.; LaBar, R. A.; Brinker, U. H.; Gebert, P. H. *J. Am. Chem. Soc.* 1977, 99, 6379 and references cited.

(7) Saito, K.; Omura, Y.; Mukai, T. *Chem. Lett.* 1980, 349.

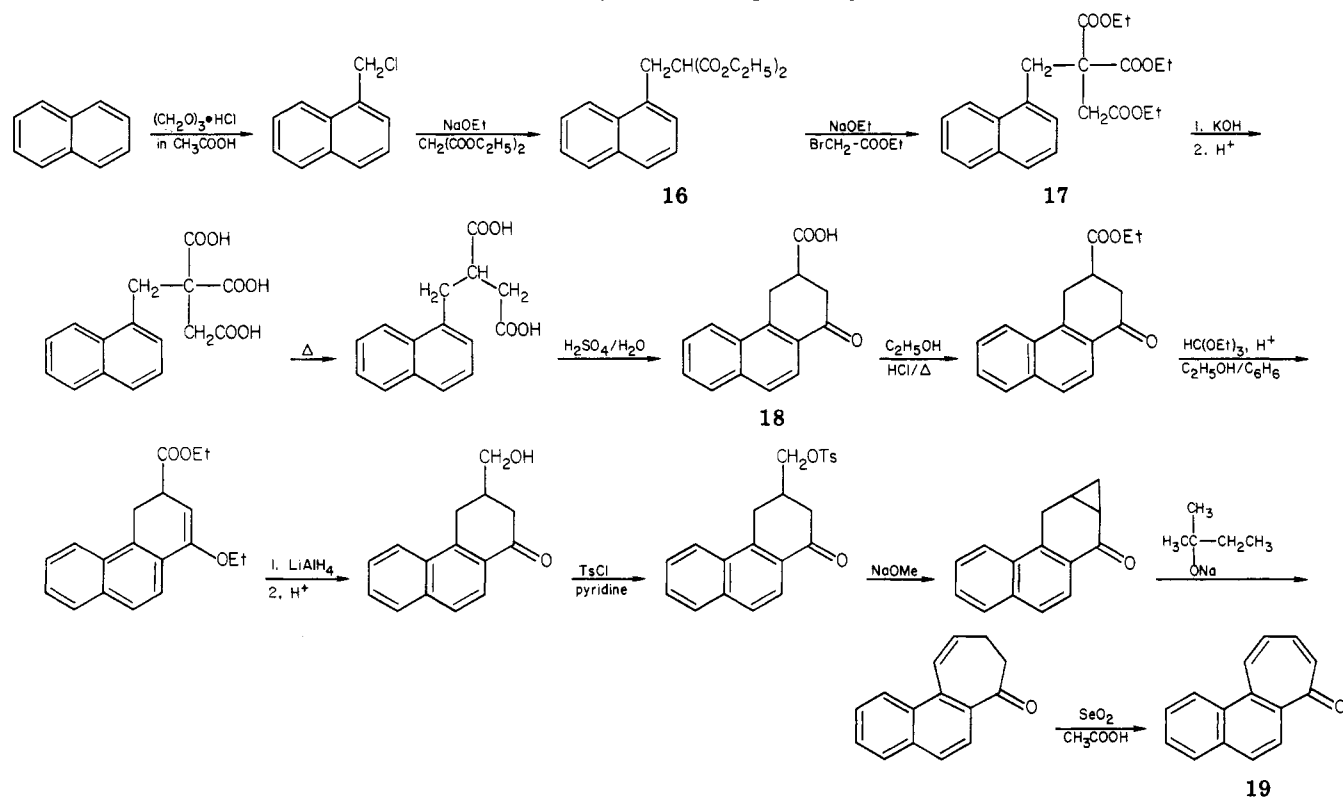
(8) Tyner, R. L.; Jones, W. M.; Ohrn, N. Y.; Sabin, J. R. *J. Am. Chem. Soc.* 1974, 96, 3765.

(9) Subsequent calculations have confirmed the conclusion that 10 is lower energy than 4: Radom, L.; Schaefer, H. F., III; Vincent, M. A. *Nouv. J. Chem.* 1980, 4, 411. Waali, E. E. *J. Am. Chem. Soc.* 1981, 103, 3604.

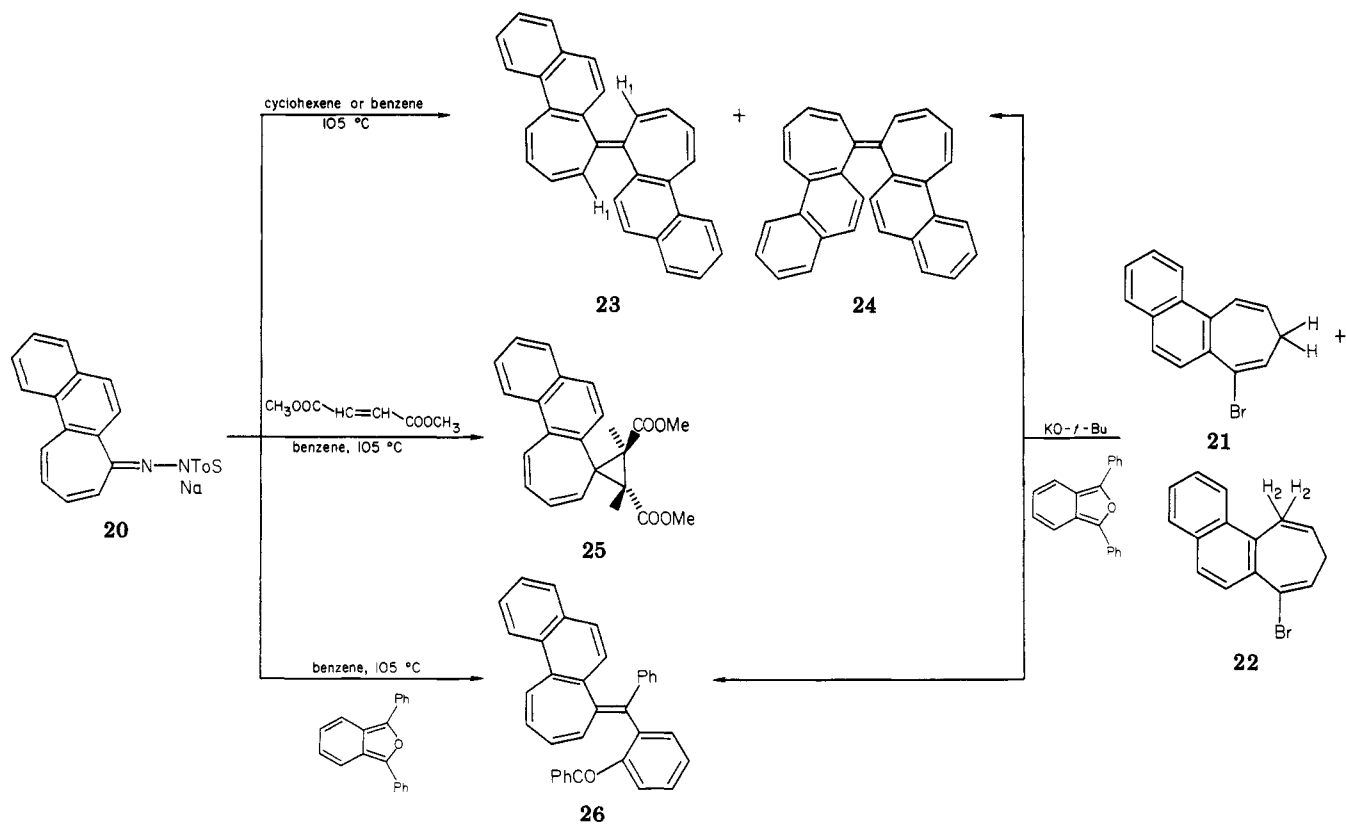
(10) Hackenberger, A.; Dürr, H. *Tetrahedron Lett.* 1979, 47, 4541.

(11) Private communication from Professor. E. E. Waali, University of Montana.

Scheme II. Synthesis of Naphthotropone



Scheme III. Chemistry of 20-22


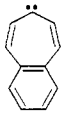
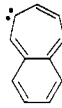

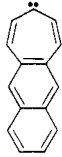
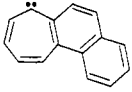
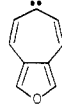
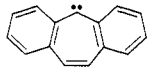

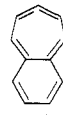
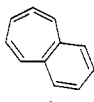

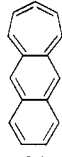
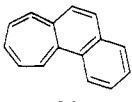
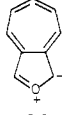
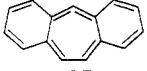


isolated. These dimers correspond to heptafulvalene, the ubiquitous product of the parent intermediate.^{1,3} Thermolysis at 105 °C in the presence of dimethyl fumarate gave 47% of the spirocyclopropane 25 along with a small amount of the dimers. Finally, thermolysis in diphenylisobenzofuran gave the rearranged adduct 26 which presumably arose from Diels-Alder addition of the allene 28

followed by rearrangement as pictured in Scheme IV. An analogous rearrangement of the parent adduct has been reported.¹² However, as expected, more vigorous conditions were required since the parent does not have aro-

(12) Cf.: Duell, B. L.; Jones, W. M. *J. Org. Chem.* 1978, 43, 4901.

Table I. Calculated Energies of Singlet and Triplet Carbenes and Allenes

								
singlet total energy, au (not optimized)	-52.109 25	-81.060 55	-81.054 02	-81.063 71	-110.001 26	-110.013 79	-83.379 40	-110.029 83
singlet total energy, au (optimized)	-52.115 80	-81.077 02	-81.054 56	-81.081 33	-110.032 29	-110.030 112		-110.059 30
								
singlet total energy, au (not optimized)	-52.131 233	-81.072 17	-81.127 63	-81.030 45	-110.005 10	-110.005 63	-83.360 46	-109.934 14
singlet total energy, au (optimized)	-52.191 61	-81.121 12	-81.180 72	-81.122 91	-110.054 42	-110.109 47		-110.053 93
energy difference, kcal (not optimized)	-13.79	-7.29	-46.19	20.87	-2.40	5.12	11.89	60.05
energy difference, kcal (optimized)	-47.57	-27.67	-79.17	-26.09	-13.89	-49.77		3.37
triplet total energy, au	-52.128 42	-81.113 72	-81.115 11	-81.116 75	-110.080 44	-110.059 53	-83.427 90	-110.099 26
singlet-triplet diff, kcal	-7.92	-23.03	-38.00	-22.23	-30.21	-18.46	-30.43	-25.08
allene-triplet diff, kcal	39.65	4.64	41.17	3.87	-16.33	31.33	-42.32	-28.44

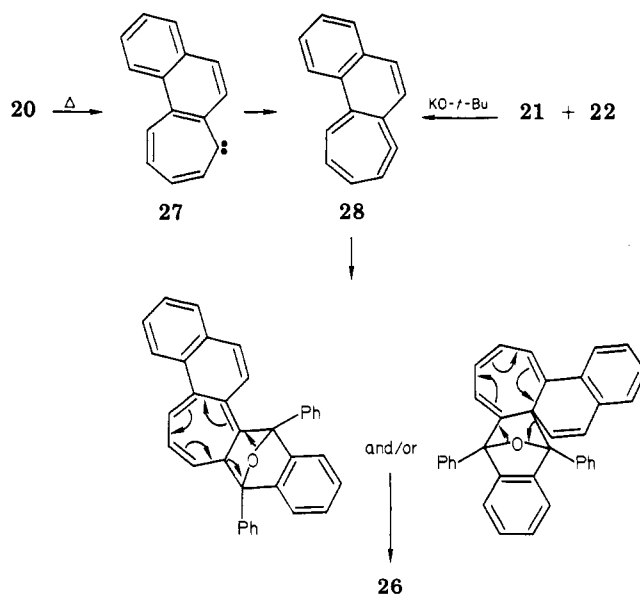
matization of the naphthalene ring as an additional driving force.

The annelated bromocycloheptatrienes **21** and **22** were synthesized by treating the ketone with oxalyl bromide followed by reduction with lithium aluminum hydride.¹² Treatment of the mixture with potassium *tert*-butoxide in the presence of diphenylisobenzofuran gave, in addition to the two dimers **23** and **24**, the same rearranged adduct (**26**) as was observed from the tosylhydrazone salt.

Calculations

Calculations were carried out by using the well-known semiempirical INDO method.¹³ To enable direct comparison with previous results,⁸ we performed initial calculations by concatenation of a planar naphthalene ring to the parent system. For derivatives of cycloheptatrienyliidene this involved replacement of two adjacent hydrogens with a naphthalene ring in the plane of the molecule. Derivatives of cycloheptatetraene were assumed to have a planar concatenated ring bisecting the parent H-C-C-H dihedral angle. No further optimization was attempted at this point. The results of these calculation as well as pertinent earlier results are recorded in Table I.

Models and preliminary calculations showed the derivatives of cycloheptatetraene to be sensitive to relaxing the

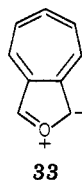
Scheme IV. Possible Origin of **26**

requirement of planarity on the fused ring. Further calculations were therefore performed by using geometries optimized by the MNDO method by Waali.¹¹ These included the parent and benzannelated structures but not the naphthoannelated intermediates. These structures were derived by concatenation of a planar benzene ring to the benzannelated structures, again bisecting the H-

(13) Dobosh, P. A. "INDO"; Quantum Chemistry Exchange; Bloomington, IN; Program No. 141. Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

C-C-H dihedral angle of the corresponding parent structure.

MNDO optimized geometries were not available for the furan-annulated cycloheptatrienyliene and cycloheptatetraene. The structure of the former was derived by annelation of optimized cycloheptatrienyliene with furan, for which the C₄-C₅ bond length had been shortened from 1.44 to 1.40 Å and for which the C-O-C bond angle had been reduced from 106° to 103.3°. For the cycloheptatetraene, the plane of the annelating furan ring was initially assumed to bisect the H-C-C-H angle followed by some geometry optimization. Thus the C₄-C₅ furan bond distance was optimized by holding the C-O-C angle constant, and then the C-O-C angle was optimized. This resulted in the minimum structure 33.

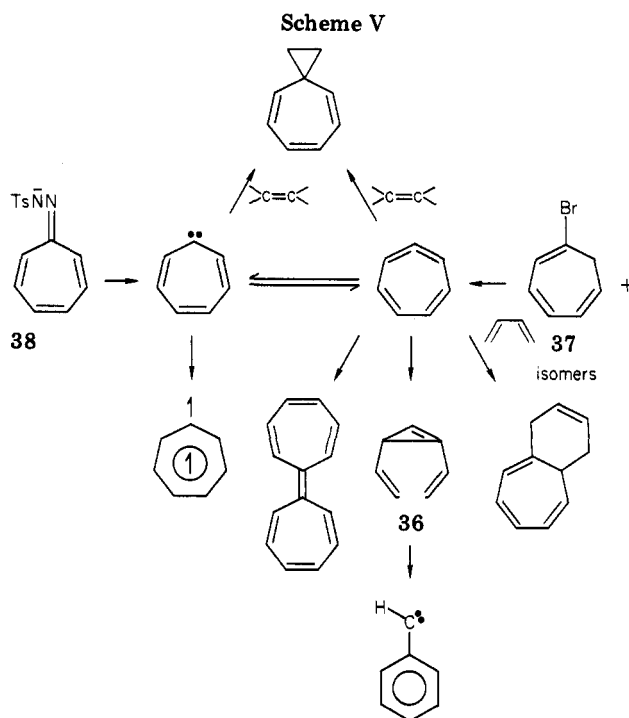


The energies of the triplet configurations were calculated by using the INDO method, and the same geometries were established by MNDO for the singlet carbenes with no further optimization.

Discussion

Most of the chemistry of the monocyclic seven-membered C₇H₆ intermediate and its benzannelated relatives has been explained in terms of two species; the singlet cycloheptatrienyliene and cycloheptatetraene.^{1-5,7-9,14-17} On the assumption of possible equilibria, it seemed reasonable to us to expect theoretical calculations of differences in energy between these species to permit us to qualitatively forecast differences in chemistry. On the basis of this presumption, the nonoptimized data in Table I would predict the properties of 12 to be sandwiched between those of 7 and 27 with the latter possibly similar to 32. And, by no stretch of the imagination would 27 be expected to show properties similar to 4, the parent. Furthermore, from the nonoptimized data, 29 should be quite different from 7. In fact, all of these predictions completely miss the mark; instead, the properties of 7 and 29 are essentially identical as are those of 4 and 27 while properties of 12 are similar to those of 34 and 32.

Since it was felt that MO calculations should shed at least a bit more light on this situation than was indicated by the early work, we undertook to see if there might be a flaw in the assumptions that we made for our original calculations. In fact, thanks to independent MNDO calculations of Waali, it was found that some of the assumed geometries (especially of the allenes) were in serious error. With the aid of optimized geometries provided by Waali,¹¹ new INDO energies were computed. These are recorded in Table I. In addition, the energies of the triplet carbenes



were computed and are recorded in the same table. From these results, the observed groupings make more sense.

First, the chemistry of 1 is clearly that expected of an allene,² and the total energy of the allene form in this case stands out as much lower (relative to its other forms) than any of the others. This, of course, is also what would be expected on the basis of classical resonance considerations. The next group, 7 and 29, shows similar chemistry,⁴ and their energies and energy differences are nearly identical (the probable real significance of this is discussed below). Another pair of intermediates with similar chemistry are 4³ and 27, and, again, the energy differences of the various intermediates are similar. Finally, the three intermediates (12,¹⁰ 32,¹⁸ and 34¹⁹) show the chemistry of typical triplet carbenes, and these are the only intermediates with triplet states highly favored over the other forms.

From the above remarks it is clear that there is at least an empirical correlation between the INDO calculations and the chemical properties of these intermediates. But, does this correlation have chemical significance? In some cases we believe that it does while in others it is doubtful. To develop this, consider the origin and reasonable fate of these intermediates. On the basis of a mass of published and unpublished information as well as the new material included in this paper, we believe the following scenario (Scheme V, pictured for the parent only) comes closest to providing a coherent picture of the chemistry of these intermediates that is consistent with both theory and experiment. When the manifold of the reactive intermediate is entered by either thermolysis or photolysis of a tosylhydrazone salt (or diazoalkane in one case),¹⁹ a singlet carbene is formed. In those instances where calculations predict the triplet to be heavily favored (12, 32, and 34), we believe that intersystem crossing to the triplet occurs and that most of the chemistry originates from this state.^{10,18,19} In all other cases, calculations predict allene ground states, and we believe the initially formed singlet

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(17) (a) Kirmse, W.; Loosen, K.; Sluma, H. D. *J. Am. Chem. Soc.* 1981, 103, 5935. (b) Nitrogen analogues of 4, 10, and 36 have been invoked to rationalize the interconversion of arylnitrenes and pyridyl carbenes (1c,d). The nitrogen analogue of 4 was first suggested by Crow and Wentrup (Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* 1968, 6149); not erroneously reported in ref 1b by Smith.

(18) Unpublished results of T. Ledford, University of Florida.

(19) Murahashi, S. I.; Moritani, I.; Nishino, M. *J. Am. Chem. Soc.* 1967, 89, 1257. Murahashi, S. I.; Moritani, I.; Nishino, M. *Tetrahedron* 1981, 27, 5131. Also see: Durr, H.; Hackenberger, A. *J. Chem. Res.* 1981, 178.

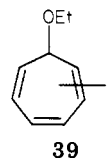
carbene rapidly drops to the allene from which at least some of the chemistry originates. This chemistry probably includes dimerization of 10 and 28 to give the corresponding heptafulvalenes and rearrangement of 10 (at high temperature),²⁰ 11, and 30 (both at low temperature)¹⁴ to their respective arylcarbenes. In the two latter rearrangements, the correlation between this tendency and the allene-singlet carbene separations probably is merely a result of a fortuitous paralleling of these differences with the differences in energy between the allenes and their corresponding norcaratrienes⁹ (e.g., 36, Scheme V) which are the precursors to the arylcarbenes.²¹ Unfortunately, we do not have calculated energies for the norcaratrienes. We believe a similar argument also applies to 10 and 28. Again, if the energy differences between the carbene and allene forms parallel differences between allenes and norcaratrienes, this would explain why carbene-carbene rearrangements are not observed in these cases (except at very high temperature in the case of 10; 27 has not been studied).

The principal unanswered question in all of these systems is that of the structure of the parent intermediate and the naphthoannelated intermediate reported in this paper that are responsible for adduct formation. From the calculations reported here the allene forms should be the ground states, and at least some allene chemistry would be expected. In fact, we have unequivocal evidence²² for cycloheptatetraene (generated by dehydrobromination of 37 and its isomers) as the intermediate that is trapped by diphenylisobenzofuran (and presumably other dienes).²³ Furthermore, the properties of the intermediate generated from 37 and from the tosylhydrazone salt 38 are identical. It therefore appears clear that both 37 and 38 give cycloheptatetraene, which is responsible for at least some of the bimolecular chemistry. We presume the same to be the case for 20-22.

It might be further argued that the bimolecular chemistry of intermediates from both 37 and 38 should originate *only* from the allene because the calculations predict the carbene to be too far above the allene to be accessible. However, it must be remembered that although calculated trends are probably reliable (e.g., allene 10 is lower relative to its singlet carbene than is 11), absolute energies are not. Thus, the important open question in Scheme V is: what are the progenitors of the spirocyclopropanes originating from 37 and 38?

From Waali's MNDO calculations,⁹ cycloheptatrienyliidene represents the transition state for interconversion of enantiomeric cycloheptatetraenes. From this he has quite reasonably concluded that cycloheptatrienyliidene cannot be responsible for bimolecular chemistry; all of it must originate from the allene. However, there remain persistent observations that, although not unequivocal, are so consistent with singlet carbene chemistry as to prevent us from totally excluding the carbene form from the active intermediate manifold. First, of course, is the very formation of spirocyclopropanes from alkenes. Although we agree with Waali's perceptive suggestion^{2,9} that such products would also arise from a [$\pi_2s + \pi_8s$] cycloaddition of the alkene to the allene, we have found in preliminary experiments²⁴ that the spiro-

triene formed from reaction of optically active 10 with styrene has no detectable optical activity; an observation that is admittedly negative evidence but one that is more consistent with an achiral carbene intermediate than a chiral allene requiring a face to face approach. Further, Kirmse¹⁷ generated the intermediate in the presence of MeOD and MeO⁻ and found only the product expected of a carbene (39); none of the vinyl ether expected²⁵ of a strained allene was observed.



Though both of these arguments have their weaknesses, taken together they make a strong enough case to prevent us from discarding the carbene as a reactive intermediate in equilibrium with an allene form that is most likely of lower energy. We are currently engaged in experiments that we hope will answer this question once and for all.

Experimental Section

General Methods. Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Accurate mass measurements were performed on an AEI NS 30 with a DS 30 data system.

Chemical shifts are reported in δ values from an internal tetramethylsilane standard. All chemicals were reagent grade and used as supplied unless otherwise stated.

Naphtho[1,2-*b*]tropone (19). This ketone was prepared by the reactions outlined in Scheme II. Published procedures were used to prepare all intermediates: 17²⁶, 18,²⁷ 19.²⁸

Naphtho[1,2-*b*]tropone Tosylhydrazone and Its Sodium Salt (20). A mixture of 1 g (4.85 mmol) of the ketone 19, 0.903 g (4.85 mmol) of *p*-toluenesulfonyl hydrazide, and 1 drop of concentrated H₂SO₄ in 25 mL of absolute ethanol was stirred at room temperature for 24 h. The ethanol solution was taken up into 50 mL of methylene chloride, and this was washed with two 25-mL portions of saturated NaHCO₃ and finally with 25 mL of H₂O. The methylene chloride was dried (MgSO₄) and concentrated at reduced pressure. The residue (1.8 g) was recrystallized from 5 mL of ethanol to yield 1.100 g (61% after recrystallization) of yellow crystals: mp 151-155 °C dec; ¹H NMR (Me₄Si, CDCl₃) δ 7-8.2 (m, 12 H, 10 aromatic, 1 olefinic, 1 NH), 6.2-6.6 (m, 3 H, olefinic), 2.25 (s, 3 H, CH₃); IR (CHCl₃) 3300, 3080, 1605, 1390, 1335, 1220, 1170, 1100, 1070, 935, 915 cm⁻¹. Anal. Calcd for C₂₂H₁₈N₂O₂S: C, 70.56; H, 4.84; N, 7.48. Found: C, 70.52; H, 4.86; N, 7.45.

To prepare the sodium salt, 1.0 g (2.67 mmol) of the tosylhydrazone was dissolved in 20 mL of dry THF. To this solution was added over a period of ca. 15 min 140 mg of 50% NaH suspension. The salt immediately began to precipitate. The reaction mixture was allowed to stir for an additional hour after which 100 mL of pentane was added. The salt was filtered, washed with 50 mL of pentane, and dried under vacuum to give 1.080 g of the salt.

Thermolysis of 20 in Benzene To Give 23 and 24. A suspension of 80 mg (0.2 mmol) of the sodium salt 20 in benzene was heated in a sealed tube under nitrogen for 20 min at 105 °C. The resulting mixture was poured into methylene chloride and washed twice with water. After being dried over MgSO₄, the solvent was removed and the yellow residue chromatographed over neutral alumina (activity III). Elution with CH₂Cl₂/pentane gave two yellow bands. The first (presumed to be the trans isomer 23) was

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(28) Julia, S.; Bonnet, Y. *Bull. Soc. Chim. Fr.* 1957, 1340.

obtained in 38% yield (15 mg) as yellow crystals from CH_2Cl_2 : mp 288–290 °C; NMR (Me_4Si , CDCl_3) δ 7.1–8.3 (m, 7 H), 6.2–6.9 (m, 3 H); MS, m/e 380 (M^+). Anal. Calcd for $\text{C}_{30}\text{H}_{20}$: C, 94.70; H, 5.30. Found: C, 94.65; H, 5.35.

The second, smaller band (presumed to be the *cis* isomer) gave 9 mg (23%) of yellow crystals (from CHCl_3): mp 280–285 °C; NMR (Me_4Si , CDCl_3) δ 7.6–8.2 (m, 10 H), 5.9–6.9 (m, 3 H); high-resolution mass spectrum calcd for $\text{C}_{30}\text{H}_{20}$ m/e 380.156 50, found m/e 380.154 30. Anal. Calcd for $\text{C}_{30}\text{H}_{20}$: C, 94.70; H, 5.30. Found: C, 94.65; H, 5.34.

Thermolysis of 20 in Cyclohexene. A mixture of 80 mg (0.201 mmol) of the tosylhydrazone salt 20 was heated in a sealed tube at 105 °C for 20 min. The workup yielded only dimers 23 and 24. No other hydrocarbon product was detected.

Thermolysis of 20 in Benzene in the Presence of Dimethyl Fumarate 25. A mixture of 100 mg (0.252 mmol) of the tosylhydrazone salt 20 and 500 mg (3.47 mmol) of dimethyl fumarate in 10 mL of benzene was heated in a sealed tube at 105 °C for 20 min. A yellow precipitate formed. The benzene mixture was poured into 50 mL of CH_2Cl_2 , washed twice with water, dried over MgSO_4 , and concentrated under reduced pressure. The residue was chromatographed over an alumina column (activity grade III; neutral) eluting with 10% ether/pentane (1:3). This gave a fast-moving band (ca. 1 mg of dimer) followed by a second fraction which was dimethyl fumarate. A third fraction gave 38 mg (47%) of the spiro adduct 25 as a white crystalline solid: mp 124–125 °C (pentane/ether); NMR (Me_4Si , CDCl_3) δ 7.1–8.3 (m, 7 H), 6.8 (dd, 1 H), 6.3 (dd, 1 H), 5.1 (d, 1 H), 3.8 (s, 3 H), 3.25 (d, 1 H), 3.2 (s, 3 H), 2.25 (d, 1 H); high resolution mass spectrum calcd for $\text{C}_{21}\text{H}_{18}\text{O}_4$ m/e 334.120 51, found m/e 334.120 45. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_4$: C, 75.43; H, 5.42. Found: C, 75.45; H, 5.41.

Thermolysis of 20 in the Presence of Diphenylisobenzofuran 26. A mixture of 140 mg (0.35 mmol) of the tosylhydrazone salt 20 and 500 mg (1.2 mmol) of diphenylisobenzofuran in 10 mL of benzene was heated at 105 °C in a sealed tube for 20 min. After cooling, the tube was opened and 40 mL of CH_2Cl_2 added. To this was added 300 mg of maleic anhydride (to consume excess furan), and the solution was washed twice with water. The organic layer was dried over MgSO_4 , and the solvent was removed at reduced pressure. The residue was chromatographed on activity grade III neutral alumina. Elution with 1:5 CH_2Cl_2 /pentane gave two yellow bands. The first band yielded 70 mg (43%) of one of the isomers 26: mp 160–164 °C (yellow crystals from benzene/pentane); NMR (Me_4Si , CDCl_3) δ 6.6–8.2 (m, 21 H), 6.5 (t, 1 H), 6.2 (d, 1 H), 5.8 (dd, 1 H); IR (CCl_4) 3080, 3040, 1670, 1605, 1500, 1450, 1320, 1290, 1260, 1220, 940 cm^{-1} ; high-resolution mass spectrum calcd for $\text{C}_{34}\text{H}_{24}\text{O}$ m/e 460.182 72, found, m/e 460.182 65; ^{13}C NMR (Me_4Si , CDCl_3 ; 32 signals) δ 196.72 (CO), 140.79, 140.40, 140.26, 139.04, 137.53, 137.28, 136.46, 136.21, 132.39, 132.22, 131.95, 131.19, 131.09, 130.78, 130.63, 130.29, 130.10, 129.61, 129.12, 128.83, 128.73, 128.32, 128.24, 127.98, 127.29, 126.63, 126.34, 126.10, 125.76, 125.42, 123.98.

The second yellow band yielded 25 mg (15%) of an isomeric adduct: mp 95–98 °C (benzene/pentane); NMR (Me_4Si , CDCl_3) δ 6.1–8 (m, 23 H), 5.8 (dd, 1 H). IR (CCl_4) 3080, 3045, 2980, 1670, 1270 cm^{-1} ; high-resolution mass spectrum calcd for $\text{C}_{34}\text{H}_{24}\text{O}$ m/e

460.182 72, found m/e 460.182 35.

To gain more information about the structure of these products, we reduced 25 mg of the more abundant isomer in MeOH with H_2 in the presence of Pd/C. Following filtration and concentration, the residue was chromatographed on a short silica gel column eluted with CH_2Cl_2 to give 24 mg (95%) of the tetrahydro product: mp 160–162 (MeOH/ CH_2Cl_2); NMR (Me_4Si , CDCl_3) δ 6.6–8.1 (m, 20 H), 1.2–2.6 (m, 10H); IR (CHCl_3) 3020, 2980, 2940, 1670, 1600 cm^{-1} ; high resolution mass spectrum: Calcd for $\text{C}_{34}\text{H}_{28}\text{O}$: 464.21402; Found, 464.21351.

Synthesis of Mixture of Naphthobromocycloheptatrienes 21 and 22. A solution of 850 mg (4.13 mmol) of the ketone 19 in 20 mL of CH_2Cl_2 was cooled to 0 °C. A solution of 1 g (4.63 mmol) oxalyl bromide in 10 mL of CH_2Cl_2 was added over 15 min. After stirring for an additional 20 min at 0 °C, the mixture was permitted to warm to room temperature, and stirring was continued for 1.5 h. Solvent was removed, and the residue taken up in 10 mL of dry THF. This was cooled to 0 °C, and 250 mg of LiAlH_4 was added in small portions. The mixture was allowed to warm to room temperature and stirred for an additional 20 min. Excess LiAlH_4 was destroyed with water and the mixture extracted with CH_2Cl_2 . After the mixture was washed and dried over MgSO_4 , the oily residue was chromatographed over silica gel. Elution with 10:1 pentane/ether gave 750 mg (67%) of a mixture of two isomers: NMR (Me_4Si , CDCl_3) δ 7.0–8.3 (m), 6.3 (t, 1 H), 5.6–6.1 (m), 3.3 (br d, 2 H), 2.1 (t, 2 H); high-resolution mass spectrum calcd for $\text{C}_{15}\text{H}_{11}\text{Br}$ m/e 270.003 49, 272.001 04, found m/e 270.004 41, 272.002 37.

Reaction of Mixture of Bromonaphthocycloheptatrienes with Potassium *tert*-Butoxide in the Presence of Diphenylisobenzofuran. To a solution of 170 mg (0.62 mmol) of a mixture of bromonaphthocycloheptatrienes 21 and 22 in 15 mL of dry THF was added 500 mg (1.85 mmol) of diphenylisobenzofuran and 125 mg (1.11 mmol) of potassium *tert*-butoxide. The mixture was refluxed for 1.5 h. After the mixture cooled to room temperature, water was added and the mixture extracted with CH_2Cl_2 . The organic layer was washed and dried over MgSO_4 . After removal of the solvent, the residue was chromatographed over alumina, eluting with 1:4 CH_2Cl_2 /pentane. This gave a fast moving yellow band (40 mg, 30%) of the dimers 23 and 24, a fraction containing an unidentified hydrocarbon, and a yellow band that proved to be a mixture of 26 and its isomer (21.8%).

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Registry No. 9, 52783-97-8; 10, 52783-93-4; 11, 52783-98-9; 19, 83477-24-1; 20, 83477-33-2; 20-Na, 83477-25-2; 21, 83477-26-3; 22, 83477-27-4; 23, 83477-28-5; 24, 83477-29-6; 25, 83477-30-9; (*E*)-26, 83477-31-0; (*Z*)-26, 83477-32-1; H_4 -26, 83477-37-6; 28, 83477-35-4; 30, 52783-96-7; 31, 83477-34-3; 32, 53247-52-2; 35, 52784-03-9; dimethyl fumarate, 624-49-7; diphenylisobenzofuran, 5471-63-6.

Photochemical Transformations. 31. Photorearrangements and Photoreactions of Some Benzobicyclooctadienyl Systems¹

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Irradiations of esters of the *exo*- and *endo*-6,7-benzobicyclo[3.2.1]octa-3,6-dien-2-ols lead only to the di- π -methane rearrangement products, even under conditions where the 3-chloro derivatives lead to photosolvolysis and Wagner–Meerwein reaction products. A tentative rationalization of the chlorine-atom effect is offered.

Members of our research group have been interested for some time² in certain photochemically induced Wagner–

Meerwein rearrangements and attendant photosolvolyses. Evidence is strong in these systems, all of which contain