^{1}H and ^{19}F Nmr Spectra. All pmr spectra were recorded at both 60 and 100 MHz using Varian Associates Model A56/60A and HA-100 spectrometers equipped with variable-temperature probes. ^{19}F nmr spectra were recorded at 56-MHz $\delta_{^1H}$ relative to TMS (δ ^{19}F relative to CCl_3F).

^{13}C Nmr Spectra. ^{13}C spectra were obtained by irradiation of the 100-MHz proton spectrum with a swept 25.1-MHz frequency source (indor method). The detailed techniques employed have been described previously.[20] ^{13}C shifts were computed with respect to TMS as a reference and converted to the carbon disulfide standard.

Raman Spectra. Raman spectra were recorded on a Cary-81 Raman spectrophotometer with laser source (50-mW gas laser using the 6328-Å He–Ne line) equipped with a variable-temperature Raman cell.[11]

Alkylation Reactions. Heteroorganic (n Donor) Bases. The bases used in these alkylation experiments were commercially available. Liquids were distilled and solids recrystallized to ensure purity. A general procedure for the alkylation reactions was used. A calculated amount of n donor base was added to an nmr tube and then cooled to −78° in a Dry Ice–acetone bath. An equivalent amount of the freshly prepared solution of RF (R = CH_3, CH_3CH_2)–SbF_5–SO_2 (SO_2ClF) at *ca.* −60° was then added. The mixture was then stirred at *ca.* −40° until a clear, colorless solution was observed. Pmr spectra of these solutions[3r] were then used to identify the "onium" ions generated.

π Bases. To a solution of excess RF (R = CH_3, CH_3CH_2)–SbF_5–SO_2(SO_2ClF) at −78° in an nmr tube was added with stirring 0.5 equiv of olefin or aromatic π base in SO_2 (SO_2ClF) at *ca.* −60°. The resulting solutions were clear and usually highly colored. These solutions were studied by pmr spectroscopy. In the case of aromatic alkylations the σ complexes were then quenched with aqueous $NaHCO_3$ at 0°. The resulting mixtures were extracted with diethyl ether and the combined extracts dried over $MgSO_4$. The methyl and ethyl aromatic products were then analyzed by capillary gas–liquid chromatography.

σ Bases (Alkanes). Reactions of RF (R = CH_3, CH_3CH_2)–SbF_5–SO_2 with alkanes were run at low temperature according to the same procedure described above for n donor bases. Reactions run at room temperature (or above) were carried out in stainless steel, Teflon-lined pressure cylinders. Normal reaction time at room temperature was about 0.5 hr. At the termination of the reaction, gaseous products were collected and studied by mass spectroscopy. The residual solutions were quenched with $NaHCO_3$–H_2O at −78° and extracted with diethyl ether. The resulting ether solutions were studied by glc.

Acknowledgment. Partial support of the work by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged. We also thank Esso Research and Engineering Corporation for their help.

5-Dibenzosemibullvalenylcarbinyl Carbene and Carbonium Ion. Some Observations on the Fate of Reactive Groups Attached to the Bridgehead Carbon of a Nonfluxional Semibullvalene

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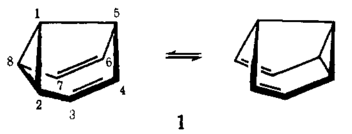
Abstract: The decomposition of 5-dibenzosemibullvalenylcarboxaldehyde tosylhydrazone (**7**) was examined under a variety of conditions. Under aprotic conditions in diglyme, benzo[*b*]fluorene (**8**) was the only product formed. Base-induced decomposition in protic ethylene glycol took an almost totally different course; **8** was again produced, but the 2-hydroxyethyl ether (**9**) predominated by a sizable margin. The reaction mechanisms which best correlate with these results are presented. It is concluded that the derived carbene is the reactive species in aprotic solvent and that the carbinyl cation intervenes in proton-donating media. Independent generation of diazonium ion **25** was found to give rise to a similar product distribution. Mechanistically revealing information was also derived from reactions of **7** in ethylene glycol-d_2. Insight into the behavior of the 5-dibenzosemibullvalenylcarbinyl cation was gained from acetolysis and deamination studies. Tosylate **10** was seen to solvolyze very slowly as a result of the adverse inductive effects of the attached phenyl and cyclopropane rings. Ring expansion was seen under both sets of conditions, with phenyl migrating to the exclusion of cyclopropyl. The factors underlying this phenomenon are discussed and other considerations relating to the neopentyl and rearranged tertiary cations are offered for consideration.

The semibullvalene molecule **1**, restricted for structural reasons to undergo the Cope rearrangement *via* a boatlike transition state,[1] exhibits an activation energy for degenerate rearrangement which is the lowest recorded to this time.[2–4] As a result, the rapid valence tautomerism of this hydrocarbon results



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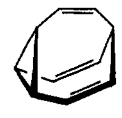

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in the equivalence of carbon atoms 2, 4, 6, and 8, and of 1 and 5 (3 and 7 remain vinyl throughout). Thus, any substituent attached to C_5 of **1**, for example, will be subject to rapid interconversion between two sites of

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[1] Stereochemically unconstrained acyclic 1,5-hexadienes are known to undergo Cope rearrangement preferentially *via* chair transition states. In a typical case, the boatlike form was shown to be at least 5.7 kcal/mol less stable than the chair counterpart: W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

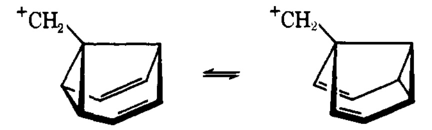
[2] The 60-MHz nmr spectrum of 1 is invariant from −110 to +117°: H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. L. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

[3] Recent MINDO/2 calculations have produced an estimated activation energy of 2.3 kcal/mol for the degenerate rearrangement of 1: M. J. S. Dewar and W. W. Schoeller, *ibid.*, **93**, 1481 (1971).

[4] The free energy of activation for the degenerate Cope rearrangement of octamethylsemibullvalene has been measured, *ca.* 6.4 kcal mol: F. A. L. Anet and G. E. Schenk, *Tetrahedron Lett.*, 4237 (1970).

nonidentical chemical character (in this instance, sp^3- and sp$^{2.27}$-hybridized carbon). As outlined in an earlier paper,[5] this unique property of **1** and its higher homolog, bullvalene (**2**), has caused us to undertake an in-depth investigation of the capability of these polyenes to function as neighboring groups in a variety of chemical reactions. Because of the prevailing Cope rearrangements, however, the problem takes on a number of complicating features. Chief among these is the fact that the result of generating a -CH$_2^+$, -CH:, or similar reactive functionality adjacent to one of the ring positions may be difficult to rationalize on the basis of a specific structure at the height of the particular rate-determining transition state. Some knowledge of the reactivities of appropriate model compounds would go far in resolving such a dilemma and may be considered, in fact, the logical line of development to the ultimate resolution of such questions.

Previously, we characterized the mode of reaction of a carbene center attached to C$_1$ of a semibullvalene in which the condition of nonfluxionality was imposed.[5] This paper reports on the consequences of generating carbonium ion and carbene centers adjacent to C$_5$ in a semibullvalene of equivalent structural rigidity. These data, in conjunction with information bearing on the behavior of the 1-dibenzosemibullvalenylcarbinyl cation,[6] now provide the foundation upon which the chemical reactivity of the interesting cation **3**[7] is to be quantitatively assessed.[8]



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Results

The initial phase of this investigation was concerned with the transformation of ester **4**[9] to tosylhydrazone **7** (Scheme I). Reduction of **4** with lithium aluminum hydride readily afforded **5**, oxidation of which under Pfitzner–Moffatt conditions[10] proved to be highly efficient, leading to the isolation of aldehyde **6** in 96% yield. Conversion of **6** to **7** was most expeditiously carried out (90% yield) by separately dissolving equimolar amounts of **6** and tosylhydrazide in minimal amounts of hot ethanol, combining these, and adding 2 drops of concentrated hydrochloric acid. Under these conditions, **7** precipitates very quickly from the solution and is not subject to deleterious side reactions.

Scheme I

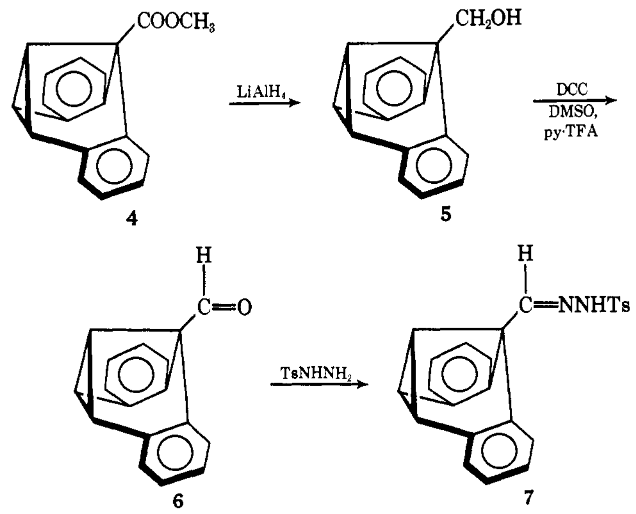
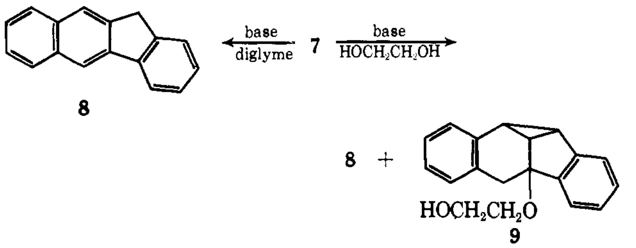


Table I. Decomposition of Dibenzosemibullvalene 5-Carboxaldehyde Tosylhydrazone (**7**)

Run no.	Reactant, mmol	Base	Base, mmol	Solvent	% composition[d] **8**	% composition[d] **9**
1	0.50	NaOCH$_3$	0.75	Diglyme	31	
2	2.50	NaOCH$_3$	3.75	Diglyme	50	
3	1.00	*n*-BuLi	3.00	Diglyme	90.5	
4	1.00	*n*-BuLi	1.80	Ethylene glycol	12	*a*
5	4.00	*n*-BuLi	12.00	Ethylene glycol	11.5	87.5
6	1.00	*n*-BuLi	3.00	Ethylene glycol-d_2	30[b]	*a*
7	1.62	*n*-BuLi	2.43	Ethylene glycol-d_2	40[b]	45[c]

[a] No attempt was made to isolate **9** in these runs. [b] In these cases, **8**-d_3 was the product. [c] Obtained as **9**-d_2. [d] Values cited are actual yields determined after initial chromatography on silica gel.

Reaction of **7** with varying amounts of sodium methoxide in anhydrous diglyme at 125° resulted in the formation of benzo[*b*]fluorene (**8**) in yields ranging from 31 to 50% (Table I). When a threefold molar excess of *n*-butyllithium was substituted for the alkoxide base, the same hydrocarbon was obtained in 90.5% yield. Confirmation of the structural assignment to **8** was based on the identity of infrared[11] and nmr spectra[12] with those reported for authentic material. In contrast, decomposition of **7** in highly protic ethylene glycol using its lithium alkoxide as the base proceeded to give **8** only as a minor product (~12%). The major constituent of such reaction mixtures was identified as alcohol **9**, the result of skeletal rearrangement and solvent capture. This solid exhibited the anticipated infrared band at 3450 cm^{-1} which attests to the presence of the hydroxyl group. Particularly com-



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(5) L. A. Paquette and G. V. Meehan, *J. Amer. Chem. Soc.*, **92**, 3039 (1970).

(6) D. R. James, results to be published.

(7) Cation **3** has recently been subjected to theoretical scrutiny: R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, submitted for publication.

(8) This study is currently in progress.

(9) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

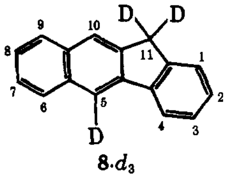
(10) K. E. Pfitzner and G. G. Moffatt, *ibid.*, **87**, 5670 (1965).

(11) Sadtler infrared spectrum no. 1191.

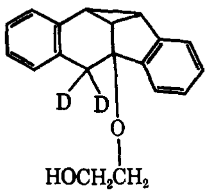
(12) B. Deubzer, E. O. Fischer, H. P. Fritz, C. G. Kreiter, N. Kriebitzsch, H. D. Simmons, Jr., and B. R. Willeford, Jr., *Chem. Ber.*, 100, 3084 (1967).

mensurate with the ring-expanded structure of **9** is the appearance in its nmr spectrum of a characteristic AB pattern (J_{AB} = 16 Hz; $\Delta\nu$ = 39 Hz) unequivocally assignable to its ring methylene group. Specifically, the rather sizable difference in chemical shift of protons A and B, a phenomenon which is also seen in such allied structures as **15** and **16**, results from the high level of rigidity associated with this particular carbon framework and the attendant positioning of H_A and H_B in substantially different chemical environments. On the other hand, 5-dibenzosemibullvalenyl derivatives of type **5** and **11**, in which the methylene group quite likely is an almost freely spinning rotor, exhibit overlapping singlet absorptions for H_A and H_B (see Experimental Section).

When tosylhydrazone **7** was decomposed in ethylene glycol-d_2 to which had been added somewhat greater than 1 equiv of *n*-butyllithium, **8**-d_3 and **9**-d_2 were produced. Under these conditions, isotopic exchange of the benzofluorenyl CH_2 protons with the medium was anticipated. The absence of the two-proton singlet at δ 4.02 in the nmr spectrum (in $CDCl_3$) of **8**-d_3 revealed in fact that two deuterium atoms were bonded to C_{11}.[12] The point of attachment of the remaining isotopic label was easily established as C_5 due chiefly to the fortunate coincidence that the unique environment of H_5 in **8** causes this proton to appear at δ 8.17 (in $CDCl_3$), a position substantially downfield shifted from the remaining aromatic protons.[12,13] The virtually complete absence of this absorption in **8**-d_3, coupled with the proper relative integration of the two remaining aryl proton multiplets, fixes C_5 as the other site of deuterium incorporation.



8-d_3

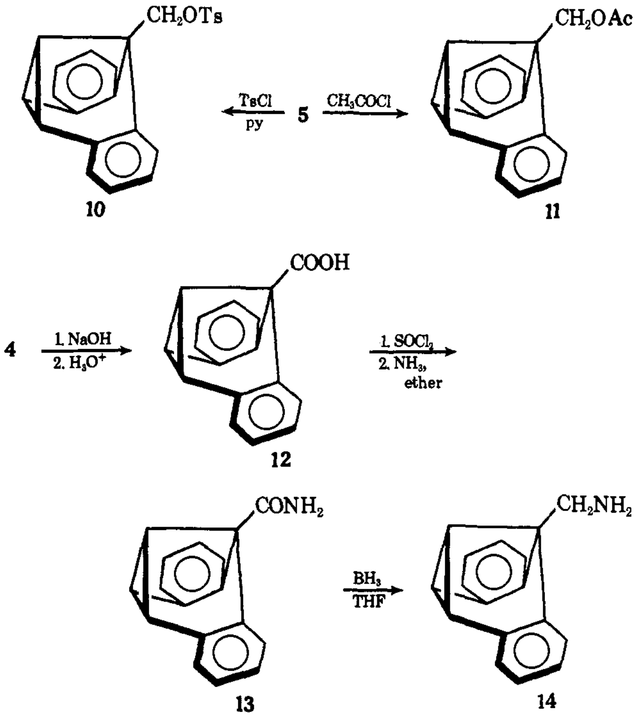


9-d_2

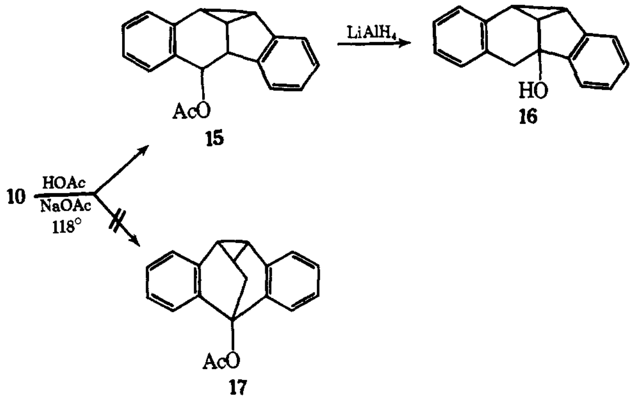
In an attempt to intercept the intermediate believed to be involved in the conversion of **7** to **8** (see Discussion), the dry sodium salt of **7** was prepared and pyrolyzed at 130° (0.5 mm) in an apparatus designed to remove all volatile material from the heating zone as it was produced. The white crystalline solid which began to appear immediately in the cool zone of the apparatus was found to be uniquely benzo[*b*]fluorene (90% yield).

Insight into the behavior of the 5-dibenzosemibullvalenylcarbinyl cation was gained from two directions: acetolysis experiments and deamination studies. To these ends, alcohol **5** was converted to the tosylate derivative **10**. The synthesis of the requisite amine **14** could be satisfactorily achieved by saponification of **4** to acid **12**, followed by conversion to the acid chloride and reaction with ethereal ammonia. Amide **13** was most efficiently reduced to **14** with diborane in tetrahydrofuran solution[14] (Scheme II).

Scheme II



Not unexpectedly,[15] tosylate **10** proved to be appreciably unreactive toward acetolysis. Thus, heating a solution of **10** in acetic acid buffered with sodium acetate at 118° for 432 hr succeeded in returning approximately one-fourth of the tosylate in unreacted form. The only other substance isolated was tertiary acetate **15**. This new acetate as well as its derived alcohol **16** were shown not to be identical with **11** and **5**, respectively. The possibility was considered that the ring-expanded product was **17**. The nmr spectrum of the acetate shows an AB pattern assignable to the methylene protons for which J_{AB} = 14.5 Hz and $\Delta\nu$ = 48 Hz. The widely differing chemical shifts observed for H_A and H_B are consistent with structure **15** but inconsistent with the isomeric dibenzohomosemibullvalene formulation **17** because of the plane of symmetry inherent in the latter molecule. It follows, therefore, that phenyl migration proceeds to the virtual exclusion of cyclopropyl migration.



Despite the considerable strain which must be encountered in the skeletal rearrangement of this bridge-

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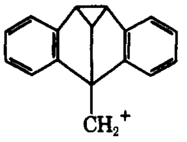
(13) The other aryl protons fall into two groups: the downfield multiplet at *ca.* δ 7.88 encompasses H-4, -6, -9, and -10, while the upfield multiplet at *ca.* δ 7.53 is due to H-1, -2, -3, -7, and -8.

(14) H. C. Brown and P. Heim, *J. Amer. Chem. Soc.*, **86**, 3566 (1964).

(15) (a) B. R. Ree and J. C. Martin, *ibid.*, **91**, 5882 (1969); **92**, 1660 (1970); (b) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965), and references cited therein.

head neopentyl system, no unrearranged products were detected, in agreement with earlier studies on other cations of similar type.[16,17] Such an observation clearly attests to the instability of the primary carbonium ion **18**. We have no information on whether neopentyl-like cation **18** is a discrete intermediate or is bypassed in favor of a concerted 1,2-alkyl shift to give **19** directly.



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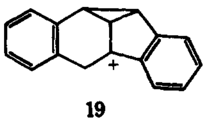

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When the acetolysis of **10** was carried out in a sealed tube at 220° for 24 hr, the only product isolated was benzo[*b*]fluorene (**8**). Subjection of **15** to similar treatment was found to give **8** in 56% yield together with 36% recovered acetate. These results attest to the propensity of carbonium ion **19** for aromatization and proton loss at more elevated temperatures.

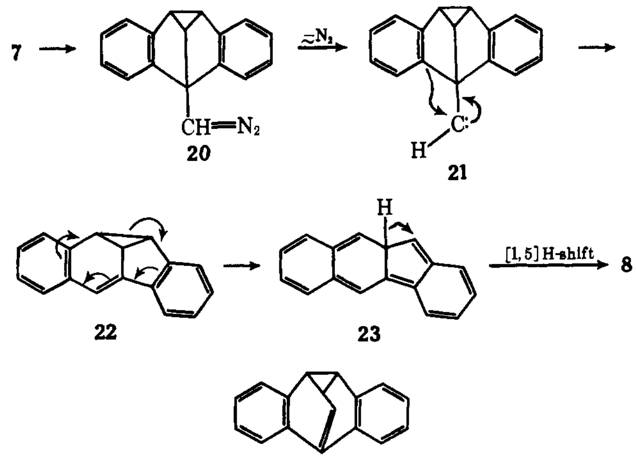
$$\mathbf{10} \xrightarrow[\substack{\text{NaOAc} \\ 220°}]{\text{HOAc}} \mathbf{8} \xleftarrow[\substack{\text{NaOAc} \\ 220°}]{\text{HOAc}} \mathbf{15}$$

Deamination of the perchlorate salt of **14** in acetic acid containing sodium nitrite afforded **15** in 58% yield. Aprotic diazotization[18] of **14** with isoamylnitrite in diglyme containing 1 equiv of acetic acid led to a product mixture consisting of benzo[*b*]fluorene (**8**, 2%) and ring-expanded acetate **15** (41%). In the presence of 10 equiv of acetic acid, the yield of **8** was slightly depressed and that of **15** increased slightly. The deaminative behavior of **14** is similar to that experienced in the solvolysis of **10** with phenyl migration occurring sufficiently rapidly (and perhaps even concertedly with the loss of nitrogen) to preclude possible reactions of the primary diazonium ion or its derived cation (if produced).

Discussion

Although the alkaline decomposition of tosylhydrazones in aprotic solvents is a sensitive process demanding that strict attention be paid to several reaction variables in order to preclude the insurgence of cationic mechanisms,[19] the base-promoted decomposition of **7** in diglyme almost certainly proceeds *via* diazo compound **20** to carbene **21** (Scheme III).[20] We base this claim chiefly on the observation that the dry vacuum pyrolysis of the sodium salt of **7** likewise resulted only in the high-yield production of benzo[*b*]fluorene (**8**). The interesting passage of **21** to **8** can arise by 1,2 rearrangement in which one of the flanking phenyl rings migrates to the carbenoid center.[21] The highly strained nature of the double bond in the resulting bridgehead olefin (**22**)[22] will endow this molecule with a ground-state energy sufficiently high that its conversion to **8** (*via* **23**) is endothermic or, at worst, mildly exothermic.

Scheme III



From these results, it is clear that carbene **21** demonstrates little tendency for 1,2 insertion into the neighboring bond positioned exocyclic to the cyclopropane ring.[23] Examination of Prentice-Hall framework molecular models suggests that **22** is capable of *trans*-stilbene-like π-orbital conjugation, albeit to a minimal extent due to twisting, whereas the other possible bridgehead olefin **24** is essentially cross conjugated. However, the ring expansion of **21** is probably not controlled significantly by product stability considerations since the migratory aptitude of a phenyl group to a carbenoid center is known to be kinetically faster than that of a cyclopropyl substituent.[24,25]

When **7** was decomposed in ethylene glycol, the rearrangement took an almost totally different course. Benzo[*b*]fluorene was again formed, but the major product was now the 2-hydroxyethyl ether **9**. This behavior lies in dramatic contrast to that of 1-dibenzosemibullvalenylcarboxaldehyde tosylhydrazone which leads to essentially identical product compositions in both protic and aprotic solvents.[5]

Mechanistic rationalization of the formation of **9** involves either solvent capture by rearranged cationic

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[16] (a) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958); (c) C. A. Grob, R. M. Hoegerle, and M. Ohta, *ibid.*, **45**, 1823 (1962); (d) W. G. Dauben and J. B. Rogan, *J. Amer. Chem. Soc.*, **79**, 5002 (1957); (e) S. J. Cristol and D. K. Pennelle, *J. Org. Chem.*, **35**, 2357 (1970).

[17] (a) In the acetolysis of bicyclo[2.1.1]hexane-1-methyl tosylate, 2% of unrearranged acetate was observed: K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963); (b) a true carbonium ion equilibrium has been demonstrated in the adamantylcarbinyl–homoadamantyl interconversion: J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *ibid.*, **88**, 4475 (1966); (c) the hydrolysis of norbornyl-1-carbinyl and norbornenyl-1-carbinyl tosylates in acetone–water (60:40) lacking collidine leads exclusively to ring-expanded products. In contrast, when collidine is present, 8.5 and 42% unrearranged alcohols, respectively, are produced: J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

[18] L. Friedman and J. H. Bayless, *J. Amer. Chem. Soc.*, **91**, 1790 (1969).

[19] J. A. Smith, H. Shechter, J, Bayless, and L. Friedman, *ibid.*, **87**, 659 (1965).

[20] In particular, it is recognized that an increase in base concentration increases the carbene nature of the reaction and decreases the contribution due to cationic intermediates. An increase in solvent proton-donating ability reverses this trend: R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 1442 (1967).

[21] 1,2-Alkyl migrations of a related type have been noted previously: R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969); M. H. Fisch and H. D. Pierce, Jr., *ibid.*, 503 (1970); R. D. Allan and R. J. Wells, *Aust. J. Chem.*, **23**, 1625 (1970).

[22] See, for example: J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969); J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967); **92**, 948 (1970); J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970); G. Köbrich and H. Heinemann, *Chem. Commun.*, 493 (1969).

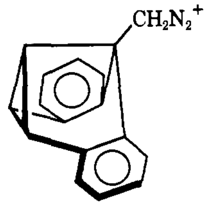
[23] There appears to be no reasonable pathway from **24** to **8**.

[24] A. R. Kraska, L. I. Cherney, C. G. Moseley, G. M. Kaufman, and H. Shechter, submitted for publication.

[25] In the present instance, a twofold statistical advantage for phenyl migration needs also to be considered.

intermediate **19**[26] or solvent interception of **22**[21] subsequent to its formation from carbene **21**. The utilization of ethylene glycol-d_2 has not provided a clear distinction between carbene and cationic mechanisms. However, these experiments do reveal deuterium incorporation at the "aldehydic" proton and require that this carbon atom become C_5 in **8**. This exchange of isotopic label quite likely does not involve either **7** or its anion since tosylhydrazones are normally completely converted to their anions under such conditions and exchange at the sp^2-hybridized carbon under these conditions is recognized to be sluggish.[27] Rather, exchange in the diazo compound **20** most probably is achieved by deuteration at carbon to give the corresponding diazonium ion **25** in reversible fashion.[28] Perhaps the strongest testimony to carbonium ion intervention in the genesis of **9** is the similarity in product distribution which is observed in the independent generation of diazonium ion **25**.

The structural rigidity of the dibenzosemibullvalene ring system strictly fixes the orientation of the phenyl and cyclopropyl rings relative to a given substituent. In the case of a developing carbinyl cation at C_5, for example, no conjugative interaction with either the cyclopropane or phenyl rings is possible. In fact, the geometric requirements are such that phenyl migration necessarily must proceed by way of a σ-bonded species (*cf.* **26**) rather than a phenonium ion. Understandably, therefore, the additive inductive effects of these proximate electron-withdrawing rings in **10** and **25** will exert a substantial strengthening of the carbinyl carbon leaving group bond.[15] Such an effect would be reflected primarily in the activation enthalpy and in rate retardation in the solvolysis of **10** as has already been noted. Also, the transition state is probably attained late in the reaction coordinate and, consequently, product stabilities will be reflected to a greater degree.[29]



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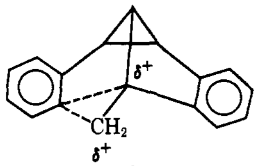

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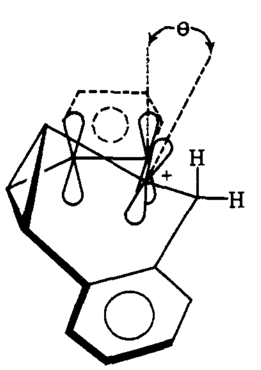
Two bicyclic ions are possible by rearrangement in this instance, but they are not equally likely. To begin with, phenyl assistance in neopentyl solvolyses is approximately five times faster than cyclopropyl neighboring group participation, at least under normal circumstances.[30] Secondly, molecular models disclose that a 1,2-phenyl shift leads to cation **27** (= **19**) which is capable of appreciable stabilization ($\theta_{27} \approx 30°$) while cyclopropyl migration would lead to cation **28** which is not ($\theta_{29} \approx 80°$). The conclusion may be drawn, then, that cation **27** is more likely than ion **28**. Furthermore, although **27** must be a highly strained ion, it seems clear that it must be more stable than primary carbonium ion **18**.



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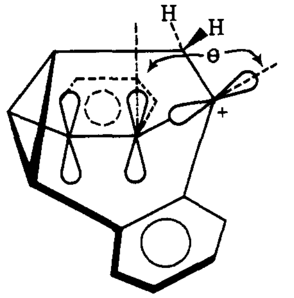
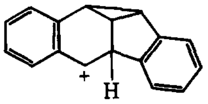


28

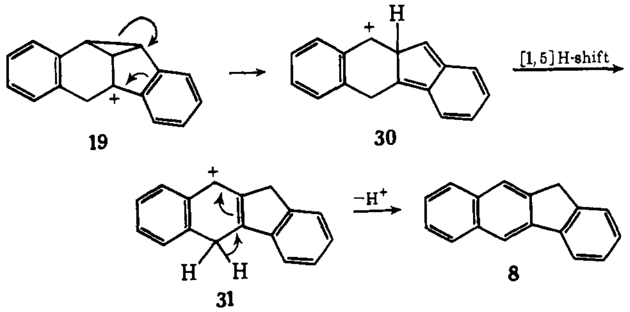
The absence of any interconversion between **27** (= **19**) and benzylic cation **29** by a 1,2-hydride shift is not unexpected. The carbon–hydrogen bonds which would be involved in migration are positioned 45° out of plane to the p orbital of the cationic center. The superstructure of **27** is very rigid and therefore the energy barrier to such a migration must necessarily be significantly greater than those involved in the capture of **27** by nucleophile.[31]



29

The 220° acetolysis experiments gave evidence that ion **19** (= **27**) could, however, undergo bond reorganization at more elevated temperatures. Apparently under these conditions the cyclopropane ring is cleaved to give **30** (Scheme IV) which is subject to [1,5]sigmatropic shift. The ease with which this latter ion **31** or its solvent-captured counterpart can aromatize would be expected to favor only the isolation of **8**, as was observed.

Scheme IV



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(26) J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959); J. W. Wilt, C. A. Schneider, H. A. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, 31, 1543 (1966).

(27) K. B. Wiberg and J. M, Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

(28) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, p 45.

(29) Due to the higher energy content of the product-forming ions (either diazonium or carbonium) generated during deamination reactions, their activated complexes resemble reactants to a greater degree than those encountered in solvolyses.

(30) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **92**, 5270 (1970).

(31) Similar rationale has been employed to explain the lack of rearrangement of: (a) the 2-adamantyl cation to the more stable 1-adamantyl cation on acetolysis [P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182, 2700 (1961)]; (b) the behavior of 1-aminodibenzobicyclo[2.2.2]octadiene on deamination [W. R. Benson, Ph.D. Thesis, University of Colorado, 1958]; (c) the like behavior of 1-aminomethyltriptycene.[16e]

Experimental Section[32]

5-Carbomethoxydibenzosemibullvalene (4).[9,33] A mixture of 50.0 g (0.281 mol) of anthracene, 150 ml of nitrobenzene, and 30 ml (44.6 g, 0.351 mol) of oxalyl chloride was placed in a 500-ml flask and refluxed for 7 hr. After this time, the excess oxalyl chloride was removed *in vacuo* and the mixture was then transferred to a steam distillation apparatus and the nitrobenzene removed. To the remaining mixture was added 100 ml cf 10 *N* sodium hydroxide solution and the entire solution was refluxed for 1 hr. The cooled solution was filtered to remove suspended solids and the filtrate was neutralized with 10% sulfuric acid. The precipitated solid was collected by suction filtration, washed with water, and dried *in vacuo* at 150°. This solid was dissolved in 1 l. of acetone, decolorized with charcoal, concentrated to 75 ml, and cooled. There was obtained 40 g (64%) of 9-anthroic acid as yellow needles, mp 215 dec (lit.[34] mp 208–212°).

Treatment of 22.2 g (0.10 mol) of 9-anthroic acid with ethereal diazomethane afforded, after recrystallization of the crude solid from methanol, 23 g (97.5%) of 9-methyl anthroate as yellow prisms, mp 111–112° (lit.[35] mp 114, 115°).

1-Carbomethoxy-7,8-dichlorodibenzobicyclo[2.2.2]octadiene was obtained by heating 20.0 g (0.985 mol) of the above ester and 70 g of *cis*-1,2-dichloroethylene in a thick-walled sealed glass tube at 195° (total immersion) for 28 hr. After cooling, the tube was opened, the solution was removed, the tube was rinsed with methanol (10 ml), and the combined solutions were evaporated to dryness. Recrystallization of the solids from isopropyl alcohol yielded 14 g (49.5%) of white needles, mp 156–157° (lit.[36] mp 159–160°). The combined filtrates from these recrystallizations generally contained 9-methyl anthroate and adduct in a ratio of 7:3 (nmr analysis). This mixture was suitable for recycling.

A mixture of 16.8 g (0.05 mol) of the adduct, 30 g of Zn–Cu couple,[37] and 250 ml of absolute ethanol was refluxed for 8 hr. The hot solution was filtered and the solids were washed twice with 10-ml portions of hot ethanol. The filtrate was evaporated and the residue was recrystallized from isopropyl alcohol. There was obtained 12.5 g (95%) of 1-carbomethoxydibenzobicyclo[2.2.2]-octatriene as white needles, mp 137–138° (lit.[36] mp 139–140°).

A solution of 10 g (3.8 mmol) of this ester in 500 ml of acetone was photolyzed through Pyrex with a 450-W Hanovia lamp for 10 hr. The solvent was removed on a rotary evaporator and the resulting yellow oil was chromatographed on Florisil (500 g). The elution solvent was 9% benzene–hexane and 100-ml fractions were taken. Fractions 1–150 were blank; fractions 151–350 contained 3.91 g of **4**; fractions 351–441 contained 2.11 g of the 2 isomer. Recrystallization of both samples of benzene–hexane gave 40% of **4**, mp 128–129° (lit.[9,36] mp 129–130°), and 21% of the 2 isomer, mp 99–102° (lit.[9,36] mp 101–102°).

5-Dibenzosemibullvalenylmethanol (5). A slurry of 0.95 g (0.025 mol) of lithium aluminum hydride in 35 ml of dry tetrahydrofuran cooled to 0° was treated dropwise with a solution of 1.31 g (0.005 mol) of **4** in 10 ml of the same solvent. After 1.5 hr at this temperature, the mixture was stirred at room temperature for 1 hr. Hydrolysis was achieved by dropwise addition of 0.95 ml of water, 0.95 ml of 30% sodium hydroxide solution, and 2.85 ml of water at 0°. The customary processing gave 0.80 g (69%) of **5** as white crystals: mp 136–137° (from aqueous methanol); ν_{max}^{KBr} 3300 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.80–7.30 (m, 8, aryl), 4.28 (s, 2, –C*H*$_2$O–), 3.63 (dd, *J* = 6.5 Hz, 1, cyclopropyl), 3.02 (d, *J* = 6.5 Hz, 2, cyclopropyl), and 2.07 (s, 1, –OH).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.16; H, 6.06.

5-Dibenzosemibullvalenylcarboxaldehyde (6). To a solution of 2.15 g (9.2 mmol) of **5** in 20 ml of dimethyl sulfoxide and 20 ml of benzene was added 5.68 g (27.8 mmol) of dicyclohexylcarbodiimide, 0.73 ml of pyridine, and 0.37 ml of trifluoroacetic acid. After standing overnight at room temperature, the mixture was treated with ether (100 ml) and stirred for 1 hr at which point 3.50 g of oxalic acid was added. After 30 min, the precipitate was filtered and washed with ether (two 50-ml portions). The combined ether layers were washed with saturated sodium bicarbonate solution (two 100-ml portions) and water (100 ml), dried, and evaporated. Chromatography of the resulting oil on Florisil (elution with hexane) gave 2.04 g (95%) of **6** as white needles, mp 124–125°, after recrystallization from benzene: ν_{m}^{KBr} 1720 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 10.20 (s, 1, –C*H*O), 6.90–7.50 (m, 8, aryl), 3.95 (t, *J* = 6.5 Hz, 1, cyclopropyl), and 3.22 (d, *J* = 6.5 Hz, 2, cyclopropyl).

Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.74; H, 5.23.

5-Dibenzosemibullvalenylcarboxaldehyde Tosylhydrazone (7). To a hot solution of 2.00 g (8.6 mmol) of **6** in 30 ml of 95% ethanol was added a hot solution of 1.60 g (8.6 mmol) of tosylhydrazide in 15 ml of 95% ethanol. Upon addition of 2 drops of concentrated hydrochloric acid, a precipitate developed immediately. The mixture was cooled and the solid was collected and washed with ethanol (three 10-ml portions). There was obtained 3.09 g (90%) of **7**: mp 230–231° dec; $\delta_{TMS}^{CDCl_3}$ 6.80–8.00 (m, 14, aryl, –C*H*=N<, and >N—H), 3.78 (t, *J* = 6.0 Hz, 1, cyclopropyl), 3.18 (d, *J* = 6.0 Hz, 2, cyclopropyl), and 2.38 (s, 3, methyl).

Anal. Calcd for $C_{24}H_{20}N_2O_2S$: C, 71.98; H, 5.03; N, 7.00. Found: C, 71.60; H, 4.97; N, 7.00.

Base-Induced Decomposition of 7 with Sodium Methoxide. Dry, powdered tosylhydrazone **7** (1.00 g, 2.5 mmol) was added in one portion to a suspension of 203 mg (3.75 mmol) of sodium methoxide in 20 ml of dry diglyme. The flask was immersed in a preheated oil bath and the temperature was raised rapidly. At *ca.* 90°, vigorous gas evolution commenced; by 115°, gas evolution was essentially complete and the reaction mixture became red. The temperature was then raised to 125° and maintained there for 15 min. The cooled solution was added to ice water (100 ml) and extracted with ether (four 80-ml portions). The combined pink ethereal layers were washed with water, dried, and evaporated. Chromatography of the red oil on silica gel and elution with pentane yielded 250 mg (50%) of **8**, white plates, mp 207–209° (from hexane) (lit.[12] mp 208°). The infrared and nmr spectra of **8** were identical with those reported for benzo[*b*]fluorene.[11,12]

Base-Induced Decomposition of 7 with *n*-Butyllithium. To a stirred slurry of 1.60 g (4.0 mol) of **7** in 20 ml of dry ethylene glycol was added dropwise during 5 min a 5-ml sample of 1.21 *N* *n*-butyllithium in hexane (6.0 mmol). The reaction flask was immersed in a preheated oil bath and the temperature was raised rapidly to 125° and maintained there for 15 min. The mixture was worked up as above to give after silica gel chromatography: (a) elution with pentane, 91 mg (11%) of **8**; (b) elution with ether–pentane (1:1), 700 mg (87.5%) of **9**: mp 96–97°; ν_{max}^{KBr} 3450 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.76–7.25 (m, 8, aryl), 3.50–3.83 (m, 4, –C*H*$_2$O–), 3.50 and 2.90 (AB pattern, J_{AB} = 14.5 Hz, $\Delta\nu$ = 37 Hz, 2, methylene), and 2.50–3.30 (m, 3, cyclopropyl).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.89; H, 6.42.

Base-Induced Decomposition of 7 in Ethylene Glycol-*d*$_2$. To a slurry of 650 mg (1.62 mmol) of **7** in 8 ml of ethylene glycol-*d*$_2$ was added under nitrogen 2.10 ml of 1.16 *M* *n*-butyllithium (2.44 mmol) in hexane *via* a syringe. As above, the mixture was heated rapidly to 130°, maintained at that temperature for 15 min, and quenched by the addition of water (20 ml). The milky suspension was worked up as described earlier to afford upon elution with hexane 120 mg (40%) of **8**-*d*$_3$ and upon elution with ether–hexane (1:1) and ether 202 mg (45%) of **9**-*d*$_2$.

8-*d*$_3$ showed: combustion analysis (falling drop method, Josef Nemeth, Urbana, Ill., 2.89 D per molecule; *m*/*e* 219; $\delta_{TMS}^{CDCl_3}$ 7.70–8.05 (m, 4, H-4, -6, -9, -10) and 7.18–7.70 (m, 5, H-1, -2, -3, -7, -8).

9-*d*$_2$ showed: δ_{TMS}^{CDCl} 6.75–7.25 (m, 8, aryl), 3.50–3.83 (m, 4, C*H*$_2$O), and 2.50–3.30 (m, 3, cyclopropyl).

Vacuum Pyrolysis of the Sodium Salt of 7. To a suspension of 800 mg (2.0 mmol) of **7** in 10 ml of dichloromethane was added 84 mg of 57% sodium hydride–mineral oil suspension (2.0 mmol) in one portion. Hydrogen was evolved gradually while the mixture was stirred at room temperature for 6 hr. The precipitated solid was filtered but not dried completely and transferred while moist to

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(32) Melting points are corrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Nuclear magnetic resonance spectra were recorded with a Varian-A60A spectrometer.

(33) The *Chemical Abstracts* name for **4** is methyl 5-dibenzotricyclo[3.3.0.0^{2,8}]octadienylcarboxylate. Throughout this paper, the dibenzosemibullvalenyl nomenclature is employed for convenience.

(34) H. G. Lantham, Jr., E. L. May, and E. Mosettig, *J. Amer. Chem. Soc.*, **70**, 1079 (1948).

(35) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **30**, 927 (1965); R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 2221 (1961).

(36) We thank Dr. Ciganek for providing us with details of his procedure in advance of publication.

(37) Prepared by treating 38 g of zinc powder with three 100-ml portions of 2% aqueous copper sulfate solution, and washing with 500 ml of ethanol.

a beaker where it was kept *in vacuo* overnight. There was obtained 680 mg (81%) of white solid.

This solid (90 mg, 0.21 mmol) was introduced into a pyrolysis flask to which was applied a vacuum of 0.5 mm. Upon lowering the apparatus into a preheated (130°) oil bath, a white solid appeared immediately in the cool zone of the vessel. After 30 min, these white plates were collected (43 mg, 90%) and examined by nmr spectroscopy. The spectrum was identical with that of benzo[*b*]fluorene.

5-Tosyloxymethyldibenzosemibullvalene (10). A solution of 234 mg (1.0 mmol) of **5** and 381 mg (2.0 mmol) of freshly recrystallized *p*-toluenesulfonyl chloride in 6 ml of pyridine was maintained at 0° for 45 hr. The reaction was quenched by addition of 10 g of ice-water, extraction with ether (three 25-ml portions), and washing of the combined ether layers with 6 *N* hydrochloric acid (two 25-ml portions) and water (two 30-ml portions). The ether layer was dried and evaporated and the resulting oil was crystallized from hexane (15 ml). The yield of dried crystals was 328 mg (85%): mp 139.5–141°; $\nu_{\max}^{\mathrm{KBr}}$ 1360, 1193, and 1180 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.70–7.90 (m, 12, aryl), 4.75 (s, 2, C*H*$_2$O), 3.58 (t, *J* = 6.5 Hz, 1, cyclopropyl), 3.08 (d, *J* = 6.5 Hz, 2, cyclopropyl), and 2.42 (s, 3, methyl).

Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19; S, 8.25. Found: C, 74.45; H, 5.31; S, 8.14.

5-Acetoxymethyldibenzosemibullvalene (11). A solution of 234 mg (1.0 mmol) of **5** and 71.5 μl (1.0 mmol) of acetyl chloride in 10 ml of pyridine was stirred at room temperature for 2 hr and 50 ml of water was then added. The product was extracted with ether and the ether layers were dried and evaporated. Recrystallization of the residue from hexane–benzene afforded 200 mg (70%) of **11** as colorless prisms: mp 155–156°; $\nu_{\max}^{\mathrm{KBr}}$ 1727 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.90–7.40 (m, 8, aryl), 4.91 (s, 2, C*H*$_2$O), 3.62 (t, *J* = 6.0 Hz, 1, cyclopropyl), 3.10 (d, *J* = 6.0 Hz, 2, cyclopropyl), and 1.98 (s, 3, methyl).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.35; H, 5.91.

5-Dibenzosemibullvalenecarboxylic Acid (12). A solution of 1.00 g (3.9 mmol) of **4** in 5 ml of methanol and 30 ml of 20% aqueous sodium hydroxide was refluxed overnight. Neutralization was effected with 10% sulfuric acid and the resulting milklike suspension was digested on a steam bath for 30 min. The white plates so produced were collected, washed with water, and dried to give 880 mg (91%) of **12**. Recrystallization from hexane–benzene yielded fluffy white needles: mp 202–203°; $\nu_{\max}^{\mathrm{KBr}}$ 1698 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.90–7.60 (m, 8, aryl), 4.10 (t, *J* = 6.5 Hz, 1, cyclopropyl), and 3.18 (d, *J* = 6.5 Hz, 2, cyclopropyl).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 81.93; H, 4.80.

5-Dibenzosemibullvalenecarboxamide (13). To a suspension of 2.08 g (8.4 mmol) of **12** in 7 ml of benzene was added 2.00 g (16.8 mmol) of thionyl chloride and 600 mg (8.4 mmol) of pyridine. After being stirred for 20 hr at room temperature, the solvent and excess thionyl chloride were removed *in vacuo*. The residual tan solid was dissolved in ether and added in one portion to 200 ml of ether previously saturated with ammonia. After 30 min, water (150 ml) was added, and the ether layer was separated, washed with water (100 ml) and saturated sodium chloride solution (100 ml), and dried. After evaporation of the ether, the crude solid was recrystallized from benzene–hexane to afford 1.98 g (96%) of **13** as white needles: mp 181–182°; $\nu_{\max}^{\mathrm{KBr}}$ 1625–1695 cm^{-1} (broad); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.90–7.50 (m, 8, aryl), 6.45 (br, 2, -NH$_2$), 3.78 (t, *J* = 6.0 Hz, 1, cyclopropyl), and 3.21 (d, *J* = 6.0 Hz, 2, cyclopropyl).

Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.78; H, 5.43; N, 5.31.

5-Dibenzosemibullvalenylmethylamine (14). To a solution of 1.00 g (4.05 mmol) of **13** in 15 ml of anhydrous tetrahydrofuran was added dropwise 32 ml (32.0 mmol) of diborane in the same solvent (*ca.* 1 *M*) during 15 min under nitrogen. The mixture was subsequently refluxed for 8 hr, cooled, and treated carefully with 16 ml of 6 *N* hydrochloric acid. The tetrahydrofuran was evaporated and the resulting paste was brought to pH 10 with 5 *N* sodium hydroxide. Extraction with ether (three 50-ml portions) was followed by washing, drying, and evaporation of the organic layer. The resulting oil was dissolved in ether and treated with 70% perchloric acid–ethanol (1:1). There was obtained 850 mg (63%) of perchlorate salt, mp 246–248° dec.

Anal. Calcd for $C_{17}H_{16}ClNO_4$: C, 61.18; H, 4.83; N, 4.20. Found: C, 60.92; H, 4.83; N, 4.08.

Alternatively, the free amine can be obtained as white needles, mp 117–118°, by direct crystallization of the oil initially produced from hexane: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.90–7.40 (m, 8, aryl), 3.60 (t, *J* = 6.0 Hz, 1, cyclopropyl), 3.55 (br s, 2, C*H*$_2$N), 3.10 (d, *J* = 6.0 Hz, 2, cyclopropyl), and 1.35 (br, 2, -NH$_2$).

Acetolysis of 10. A. A solution of 60 mg (0.154 mmol) of **10** and 14 mg (0.132 mmol) of anhydrous sodium carbonate in 5 ml of dry acetic acid was refluxed (118°) for 432 hr. Aliquots (1 ml) were removed after 24- and 216-hr periods; the first of these showed only unreacted **10**, while the latter indicated but minimal (~15%) conversion to a single product. The acetic acid was removed *in vacuo* and the residual solid was shown by nmr to consist only of **10** and **15**. Preparative tlc of this solid on silica gel G afforded 9 mg (26%) of recovered **10** and 11 mg (43%) of **15** (elution with 10% ether–hexane, R_{f}**10** = 0.71; R_{f}**15** = 0.80). This acetate was obtained as white prisms, mp 117–118°, from hexane: $\nu_{\max}^{\mathrm{KBr}}$ 1748 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.82–7.30 (m, 8, aryl), 3.82 and 3.02 (AB pattern, J_{AB} = 14.5 Hz, Δν = 48 Hz, 2, methylene), 2.55–3.08 (m, 3, cyclopropyl), and 2.06 (s, 3, methyl).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.42; H, 5.85.

B. A mixture of 49 mg (0.126 mmol) of **10**, 12 mg (0.10 mmol) of anhydrous sodium carbonate, and 2 ml of dry acetic acid was sealed in a tube and kept at 220° (total immersion) for 24 hr. The tube was cooled and the contents were treated with 20 ml of water. The milky suspension was extracted with ether (two 25-ml portions) and the combined ether layers were washed with water (two 30-ml portions) and saturated sodium bicarbonate solution (two 30-ml portions), and dried. The yellow oil remaining on evaporation was subjected to tlc purification as above. The only identifiable product was benzo[*b*]fluorene (**8**, 14 mg, 50%). The remainder consisted of a viscous yellow-brown gum.

A control experiment in which 27.6 mg (0.10 mmol) of **15** was substituted for **10** led under the same reaction conditions and work-up to a 60:40 mixture of **8** and **15**.

Reduction of 15. To a stirred suspension of 63 mg (1.65 mmol) of lithium aluminum hydride in 4 ml of anhydrous tetrahydrofuran was added dropwise at 0–5° a solution of **15** (91 mg, 0.33 mmol) in 2.5 ml of the same solvent. After 1 hr at room temperature, the reaction mixture was quenched with water and processed as predescribed to yield 42 mg (55%) of **16** as white crystals, mp 174–176°, from benzene–hexane: $\nu_{\max}^{\mathrm{KBr}}$ 3510–3125 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.80–7.30 (m, 8, aryl), 3.45 and 2.89 (AB pattern, J_{AB} = 14.5 Hz, Δν = 33.5 Hz, 2, methylene), and 2.40–2.90 (m, 3, cyclopropyl).

Deamination of 14 Perchlorate. To a suspension of 300 mg (0.90 mmol) of the perchlorate salt of **14** in 10 ml of dry acetic acid was added 120 mg (1.74 mmol) of sodium nitrite in small portions. The solid gradually dissolved, nitrogen was liberated, and the solution became yellowish orange. Benzene (30 ml) and water (30 ml) were added and the water layer was extracted with additional benzene (two 30-ml portions). The combined organic layers were washed in turn with saturated sodium bicarbonate (two 80-ml portions) and sodium chloride solutions (two 80-ml portions) and dried. The solvent was evaporated and the resulting oil was chromatographed on silica gel. The yellow oil which eluted with 20% ether–hexane was further purified by tlc (silica gel G) to afford a faint yellow solid. Two recrystallizations from hexane furnished 54 mg (58%) of **15** as white prisms, mp 117–118°.

Aprotic Deamination of 14. A solution of 270 mg (1.16 mmol) of **14** in 20 ml of diglyme was treated with 60 μl of freshly distilled isoamyl nitrite and then heated rapidly to 130°. When gas evolution ceased, the flask was cooled and 50 ml of water was added. The products were extracted with ether (50 ml) and this organic layer was washed with water (50 ml), dried, and evaporated. The resulting yellow oil was chromatographed on a preparative tlc plate (silica gel G, elution with 20% ether–pentane). The higher R_f band yielded 6 mg (2.4%) of **8** and the lower R_f band furnished 130 mg (41%) of **15**. The remaining material which did not migrate from the origin was an ill-defined yellow gum.

When a tenfold increase in the amount of acetic acid was utilized, there was obtained 4 mg (1.7%) of **8** and 138 mg (43.5%) of **15**.