Table IV. Summary of Analysis Data, Melting Points, and Spectral Characteristics of Triphenylmethylsulfenyl Phenyl Esters (Ph_3CSOPh-X-*p*)

X	Mp, °C		%					λ_{max}, mμ	ϵ_{max}
			C	H	S	N	Cl		
H	92.5–93.5	Found	81.44	5.37	8.70			276[a]	2,524
		Calcd	81.48	5.47	8.70				
NO_2	161–162	Found	72.48	4.62	7.80	3.68		308	11,220
		Calcd	72.61	4.63	7.76	3.39			
Cl	116.5–117	Found	74.44	4.70	8.00		8.83	274[a]	2,297
		Calcd	74.52	4.75	7.96		8.80		
CH_3	96–97	Found	81.83	5.83	8.40			284[a]	2,804
		Calcd	81.63	5.80	8.38				

[a] Shoulder.

centers. It is worth noting that the only two cases[8] where formation of a pentacovalent intermediate has been postulated meet at least some of these requirements.

Experimental Section

Materials. Pure, peroxide-free *p*-dioxane was prepared according to the method described by Vogel,[28] kept over sodium under nitrogen atmosphere, and distilled immediately before use. Deionized water was distilled from potassium permanganate. Reagent grade sodium hydroxide, hydrochloric acid, and borax were used without further purification. All commercial phenols, *i.e.*, *p*-Cl, *p*-Br, H, *p*-CH_3, and *p*-OCH_3, have been purified by repeated sublimations and had good melting points. *p*-Acetylphenol was kindly provided by Professor Da Re and purified by sublimation; mp, 110°.[29]

All the sulfenyl esters have been prepared according to the method of Vorländer and Mittag.[30] Yields in purified product ranged from 20 to 40% and no attempts have been made to increase them. Table IV is a summary of analysis data, melting points, and spectral characteristics.

Kinetic Methods. The reactions were followed at the appropriate wavelength corresponding to the maximum absorption of the product phenoxide by a spectrophotometric technique at 25.0 ± 0.1° with a SP 800 Unicam spectrophotometer. The faster reactions were followed with a Durrum stopped-flow apparatus. All reactions were studied under pseudo-first-order conditions.

Boric acid–borate buffers have been prepared according to Bates.[31] pH measurements were performed with a Metrohm Herisau pH meter equipped with XL glass electrode.

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(28) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., Ltd., London, 1964, p 717.

(29) K. W. Rosenmund and W. Schnurr, *Ann.*, **460**, 56 (1928).

(30) D. Vorländer and E. Mittag, *Chem. Ber.*, **52**, 413 (1919).

(31) R. G. Bates, "Determination of pH," John Wiley & Sons, Inc., New York, N. Y., 1964, pp 160–161.

Mechanistic Features of the Base-Induced Decomposition of Dibenzosemibullvalene 1-Carboxaldehyde Tosylhydrazone

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Abstract: The decomposition of dibenzosemibullvalene 1-carboxaldehyde tosylhydrazone (**7a**) and its α-d_1 analog (**7b**) with several bases was examined under a variety of conditions. In each case, only 3,4-benzofluorene (**8**) and terminal allene **9** were produced and the ratio of these hydrocarbons was consistently found to be approximately 2:1. Decomposition of **7b** under aprotic conditions gave rise to **8** containing deuterium only at the methylene position; likewise, **9** contained covalently bound deuterium uniquely at the terminal allene position. The locations of the isotope were established by nmr spectroscopy. Base-induced rearrangement of **7a** with *n*-butyllithium in diglyme, followed by quenching of the reaction mixture with deuterium oxide afforded **8** with greater than 80% d_1 incorporation; allene **9** contained no measurable deuterium. When decomposed in ethylene glycol-d_2, both **8** and **9** were found to be dideuterated at the methylene and terminal allene positions, respectively. The reaction mechanisms which best correlate with these results are presented. It is concluded that the unique geometry of the semibullvalene nucleus in **7** results in rearrangement of the derived carbene principally by a pathway which involves an unprecedented 1,3-aryl shift to what is formally a *trans*-disposed carbon atom.

The capability of the bullvalene molecule (**1**) to undergo rapid and reversible Cope rearrangements and thereby scramble in phantasmagoric fashion the constituent cyclopropyl, vinyl, and bridgehead carbon atoms has no equal in the realm of organic chemistry.[2] The capability of each carbon in bullvalene to partition

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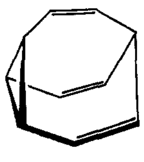
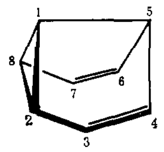
(1) The Ohio State University Postdoctoral Fellow, 1967–1969.

(2) (a) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963); (b) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); (c) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (d) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *ibid.*, **23**, 3943 (1967).



1



2

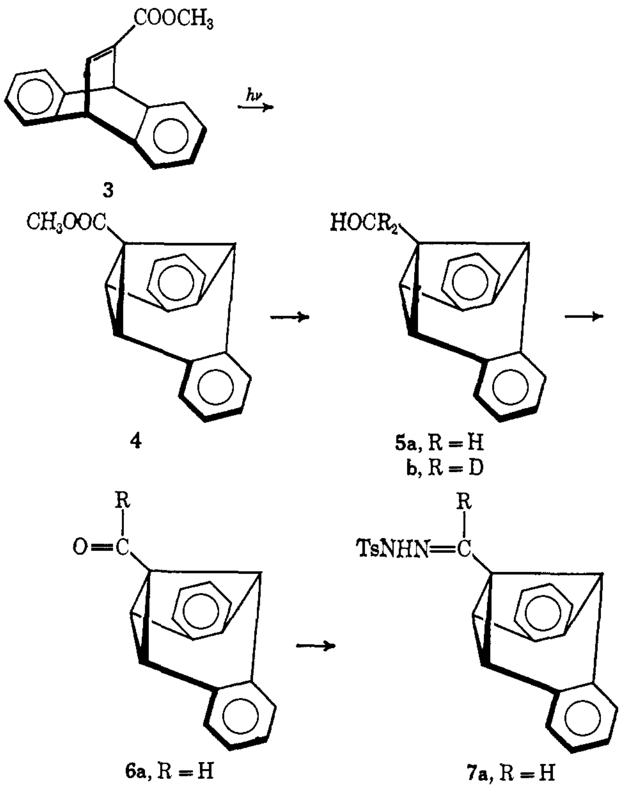
itself between several widely differing chemical environments in a finite period of time is attested to by the single nmr band displayed by **1** at 120°.[3] Semibullvalene (**2**), the lower homolog of **1**, likewise is endowed with fluxional character but to a lesser degree.[4] The valence tautomerism of **2** results in the equivalence of carbon atoms 2, 4, 6, and 8, and of 1 and 5, while 3 and 7 remain vinyl but also equivalent. An interesting property of **2** is the invariant nature of its 60-MHz nmr spectrum from −110 to +117°; on this basis, it is seen to exhibit the most rapid degenerate Cope rearrangement of any known homotropilidine.

It is thus a property of the individual carbon atoms in bullvalene (**1**) and semibullvalene (**2**) that they are subject to ready interconversion between two or three sites of nonidentical chemical character.[5] This unique feature suggested to us that investigation of the capability of **1** and **2** to function as neighboring groups in a wide range of organic reactions would be of considerable interest. More specifically, the question may be asked: if a $-CH_2^+$, $-CH:$, $-N_2^+$, or other reactive group were generated adjacent to one of the bullvalene or semibullvalene ring positions, would this carbon atom undergo subsequent reaction from an sp^3 (bridgehead), $sp^{2.25}$ (cyclopropyl), of sp^2 (vinyl) hybridized state? It is obvious that the possibility for substantial variation exists and that every nuance of chemical behavior might be encountered.

However, the problem is also a complex one. Thus, as a consequence of the prevailing Cope rearrangements, a given result may be difficult to rationalize in terms of a specific structure at the height of the particular rate determining transition state, at least in the absence of knowledge regarding the reactivities of appropriate model compounds. Necessarily, therefore, the logical line of development to the ultimate resolution of such questions must commence with an investigation of the chemical behavior of nonfluxional derivatives of **1** and **2**. In this paper, we wish to characterize the reactivity of a carbene positioned at C_1 in semibullvalene when the stringent condition of nonfluxionality is imposed. For this purpose, the base-induced decomposition of dibenzosemibullvalene 1-carboxaldehyde tosylhydrazone was examined.

Results

Photoisomerization of readily available dibenzobarrelene **3** according to the procedure of Ciganek[6] afforded 1-carbomethoxydibenzosemibullvalene (**4**) in good yield. Reduction of **4** with lithium aluminum hydride gave alcohol **5a**, controlled oxidation of which with chromium trioxide–pyridine led to the nicely crystalline aldehyde **6a**. Similar treatment of **4** with lithium aluminum deuteride afforded dideuterio alcohol **5b**; as expected, the oxidation of **5b** with Sarett's reagent was subject to pronounced rate retardation because of the operation of a primary deuterium isotope effect. Nevertheless, longer durations of exposure of **5b** to the oxidant served to provide good yields of aldehyde without the formation of excessive amounts of carboxylic acid. Tosylhydrazones **7a** and **7b** were prepared in the customary fashion from the derived aldehydes.



3

4

5a, R = H
b, R = D

6a, R = H
b, R = D

7a, R = H
b, R = D

Thermal decomposition of **7a** with a 50% excess of sodium methoxide in diglyme gave a mixture of two hydrocarbons in a ratio of 2:1 (Table I). Separation of these products was achieved by column chromatography on silica gel impregnated with silver nitrate. The major, more rapidly eluted substance was characterized as 3,4-benzofluorene (**8**). Of significance is the fact that **8** displays, *inter alia*, a two-proton singlet for the benzylic hydrogens at δ 3.81 and two five-line multiplets (1 H each) centered at 8.3 and 8.7 due to H_a and H_b. The second hydrocarbon was seen to decompose on standing at room temperature; its further purification by sublimation or recrystallization was also precluded for this reason. However, its spectral properties were commensurate with structure **9**. Thus, this solid exhibited infrared bands at 1931 and 855 cm^{-1} which are characteristic of terminal allenes and nmr absorptions due to allenic (s, δ 5.13), vinyl (s, δ 6.81), and aryl protons (m, δ 7.2–7.5). Unambiguous characterization of **9** was achieved by catalytic hydrogenation; the 5-ethyl-10,11-dihydro-5H-dibenzo[*a*,*d*]cycloheptene (**10**) so obtained was identical in all respects with a sample prepared in unequivocal fashion from ketone **11**.

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(3) R. Merenyi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964).

(4) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Am. Chem. Soc.*, **91**, 3316 (1969); H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

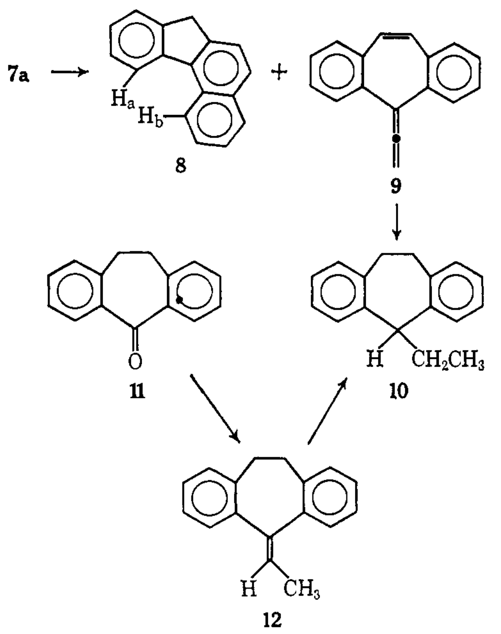
(5) The only exceptions to this generality are carbon atoms 3 and 7 of semibullvalene.

(6) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 2882 (1966); see also P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968).

Table I. Decomposition of Dibenzosemibullvalene 1-Carboxaldehyde Tosylhydrazones **7a** and **7b**

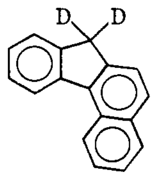
Run no.	Re-actant	Reactant, mmoles	Base	Base, mmoles	Solvent	Temp, °C	Combined yield, %[a]	% composition **8**	% composition **9**	Deuterium content[b] **8**	Deuterium content[b] **9**
1	**7a**	4.00	$NaOCH_3$	6.00	Diglyme	120	52	66	34		
2		1.00	*n*-BuLi	1.50	Ethylene glycol	130	38	69	31		
3		1.00	*n*-BuLi	0.75	Ethylene glycol	130	22	68	32		
4		3.00	*n*-BuLi	4.50	Ethylene glycol-d_2	130	49	69	31	1.96	1.96
5		3.00	*n*-BuLi	4.50	Diglyme[c]	150	68	64	36	0.84	0.01
6	**7b**	2.50	$NaOCH_3$	3.75	Diglyme	120	61	63	37	0.45	0.48
7		3.00	*n*-BuLi	4.50	Ethylene glycol	130	41	70	30	0.06	0.07
8		3.00	*n*-BuLi	4.50	Diglyme	140	75	64	36	0.32	0.26

[a] Yields of hydrocarbons were determined after initial chromatography on silica gel (pentane elution). [b] The percentages of deuterium in **8** and **9** were determined in the following manner: in the case of **8**, integration of the residual methylene protons was compared with that of protons H_a and H_b in the mixture of **8** and **9**. In all runs, the integration of the remaining aryl protons in the mixture was too complex for evaluation. Recrystallization of the mixture from ethanol gave pure **8**; the combined areas of H_a and H_b were then compared quantitatively with that of the aryl protons (invariably 8 H) and the residual methylene protons. These latter values are cited in the table. With **9**, integration of the residual allenic protons was compared with that of the stilbene protons in the reaction mixture. All values are the average of seven to ten integrations and are supported by mass spectral evidence at 15 eV. [c] Reaction mixture quenched with deuterium oxide.

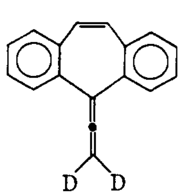


The nmr bands of **8** and **9** were sufficiently well separated to permit unambiguous integration of each, thereby allowing for a quantitative assay of the product distribution. With the unlabeled compounds, repeated integrations of the δ 3.81, 8.3 and 8.7 absorptions of **8** and 5.13 and 6.81 bands of **9** gave the indicated ratios. In the deuterium labeled runs, the δ 8.3 (1 H), 8.7 (1 H), and 6.81 (2 H) signals were employed as internal standards and the area under the absorptions at 3.81 and 5.13 provided the deuterium content of **8** and **9**, respectively.

When tosylhydrazone **7a** was decomposed in a protic medium (ethylene glycol) with excess or insufficient *n*-butyllithium, the ratio of **8** to **9** remained unchanged relative to the diglyme reactions. However, the overall yields of the hydrocarbons understandably were seen to decrease as the quantity of base was lowered below the stoichiometric level. Decomposition of **7a** in ethylene glycol-d_2 under otherwise identical conditions afforded 8-d_2 and 9-d_2. The nmr spectra of these products clearly revealed the complete absence of the δ 3.81 and 5.13 absorptions, respectively, thereby establishing the points of attachment of the isotope as shown. Therefore, the pathways which lead from **7a** to **8** and **9** result in positionally specific incorporation of two deuterium atoms from the hydroxylic medium. This conclusion is further substantiated by the observation that treatment of **7b** with *n*-butyllithium in protoethylene glycol gives **8** and **9** with only trace amounts of isotopic label remaining (Table I). However, when **7a** is exposed to *n*-butyllithium in diglyme and the reaction mixture is subsequently quenched with deuterium oxide, appreciable incorporation of *one* deuterium atom into **8** is seen. This finding establishes that inclusion of one external deuterium can be achieved *after* formal rearrangement to **8**. In contrast, the near absence of monodeuterated allene illustrates that exchange into this product is unimportant at this stage of the rearrangement.



8-d_2



9-d_2

The reaction of **7b** with sodium methoxide and *n*-butyllithium in diglyme was also examined. It is interesting that in these decompositions 50–75% of the deuterium label is lost to the medium, with exchange being more pronounced in the latter case (Table I). Clearly, the formation of **8** and **9** by decomposition of **7b** is subject also to a base-catalyzed exchange which decreases significantly the deuterium content of the labeled carbon.

Discussion

In view of ample precedent,[7] it would appear certain that the anionic decomposition of **7** proceeds *via* the

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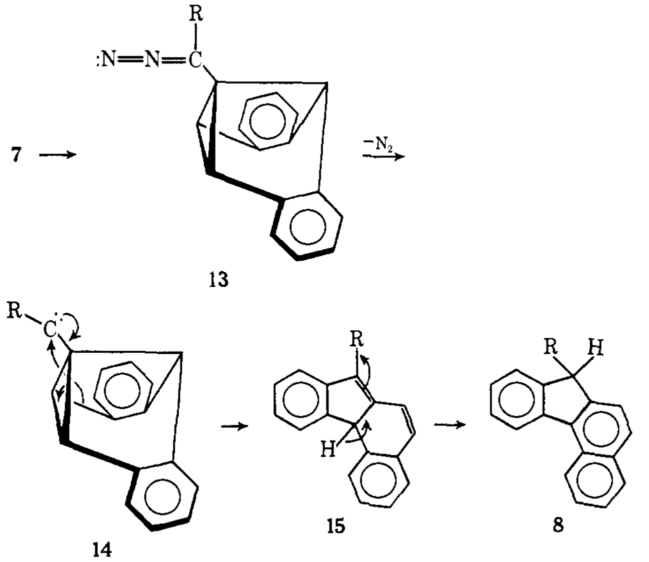
(7) See, for example: (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, 81, 5512 (1959); (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959); (c) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, 87, 659 (1965); (d) K. B. Wiberg and J.

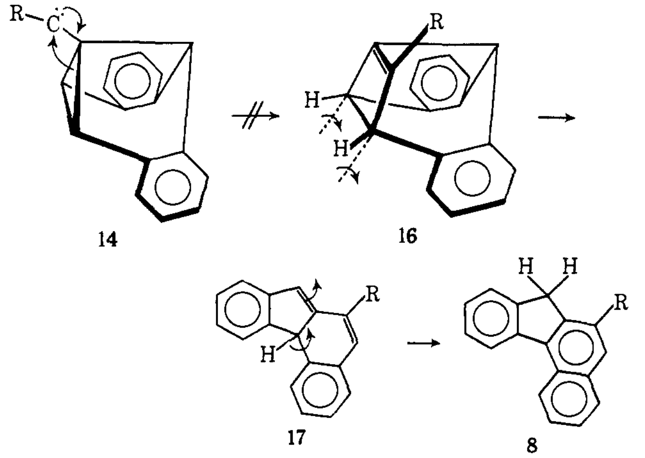
derived diazo compound **13**. The further reaction of **13**, at least in "aprotic" media, likely involves intermediate carbene **14**. Rearrangement of this cyclopropylcarbinyl carbene by a process involving a nonsynchronous (see below) six-electron shift leads to diene **15**, prototropic shift in which affords **8** (Scheme I).

Scheme I



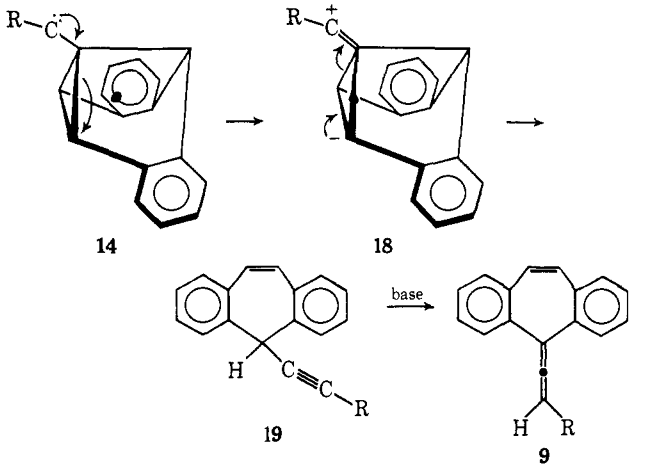
Although the transposition of **13** to **8** has no existing parallel, the indicated mechanism uniquely accounts for the fact that the deuterium label in **7b** ultimately is attached *only* to the methylene group of **8**. In fact, the alternative pathway which utilizes the well-established cyclopropylcarbinyl carbene–cyclobutene rearrangement[8] is immediately seen to be nonoperative in this instance since it requires placement of deuterium at an aryl site (Scheme II). The absence of this mode of rearrangement is perhaps due to the extremely severe strain in cyclobutene intermediate **16** (conclusion based on careful examination of Prentice-Hall models).

Scheme II



The conversion of **14** to **9** is best rationalized in terms of electron shifts of the type illustrated in **18**[9] (Scheme III) which eventuate in the formation of acetylene **19**.

Scheme III



A concerted fragmentation of **14** to **19** cannot, of course, be ruled out. Base-catalyzed isomerization of **19** can be expected to give the observed allene (**9**).[10]

It is particularly interesting and significant that the ratios of **8**:**9** in both protic and aprotic runs vary only insignificantly. The earliest studies of base-induced tosylhydrazone decompositions revealed a strong solvent dependence and led to the generalization that cationic paths prevail under protic conditions.[11] However, complexities uncovered by subsequent investigations have made it quite clear that skeletal rearrangements, hydride shifts, and insertion reactions can arise equally well from carbenes and energetic cations and therefore that product ratios are not reliable criteria for the existence of carbenoid or cationic precursors. In the case of **7**, however, the constant product ratio observed under all the reaction conditions examined would appear most consistent with the intervention of a common intermediate. Of further relevance is the fact that a mechanistic scheme which can adequately account for the conversion of the 1-dibenzosemibullvalenylcarbinyl cation (**20**) to **8** is not easily formulated (Scheme IV).[12] Thus, of the two rearrangement pathways initially available to **20**, one leads to highly strained cyclopropyl cation **21** and is therefore unlikely, while the other could perhaps lead *via* **22** to **19** and **9**. Consequently, it would seem that **7** rearranges to a significant extent by way of carbene **14**, irrespective of the conditions of generation.

Importantly, the experiments with **7b** and with **7a** in ethylene glycol-d_2 reveal more intimate facts about the nature of the intermediates. First, the deuterium incorporation observed in run 4 and the loss of isotopic label noted in runs 6–8 quite likely do not directly involve either **7** or its anion since tosylhydrazones are

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M. Lavanish, *ibid.*, **88**, 365, 5272 (1966); (d) K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 365, 5272 (1966); (e) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

[8] See, for example: (a) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965); (b) J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *ibid.*, **30**, 1052 (1965); (c) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967); (d) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968); (e) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **7**, 823 (1968).

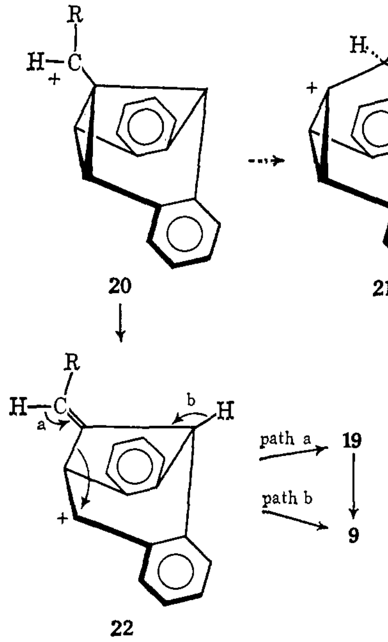
[9] Similar mechanistic rationales have been previously employed; see, for example, (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960); (b) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963); (c) ref 8a.

[10] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, New York, N. Y., 1955, pp 134–139.

[11] For relevant observations and comments, see W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 3.

[12] The reactions of independently generated **20** are presently under investigation in this laboratory.

Scheme IV



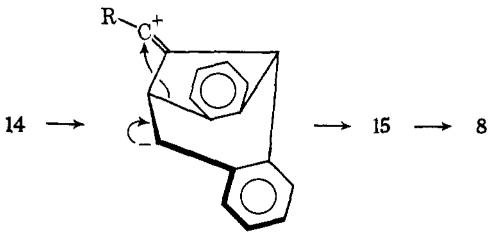
normally completely converted to their anions by such bases and exchange at the sp^2-hybridized carbon under these conditions is known to be sluggish.[7d,e] However, because protons α to a diazo group are acidic,[13] diazomethylcyclopropane **13** is entirely capable of undergoing facile base-catalyzed exchange, and a deuterium atom can be incorporated from, or lost to, the medium at this stage. In those runs in which a protic solvent was employed, exchange in the diazo compound could also be achieved by protonation or deuteration at carbon to give the corresponding diazonium ion in reversible fashion. In any event, exchange in the diazo intermediate is certainly implicated. Furthermore, the obtention of **8**-d_2 and **9**-d_2 demonstrates that additional exchange with the medium is important at a later stage of the rearrangement sequence.

As outlined in Scheme I, rearrangement of carbene **14** with concomitant phenyl migration leads initially to **15**. Conversion of **15** to **8** requires removal of the angular proton by base. Loss of this proton will give rise to the stabilized 3,4-benzofluorenyl anion. Substantiation of the intervention of this anion along the reaction coordinate was achieved by deuterium oxide quenching of the reaction mixture obtained by treating **7a** with *n*-butyllithium in diglyme (run 5); the isolated 3,4-benzofluorene (**8**) contained greater than 80% d_1 at the methylene group. Additionally, when **7a** was decomposed in ethylene glycol-d_2, the resulting **8** was dideuterated at this position (run 4). Therefore, incorporation of a second external deuterium atom in passing from **7** to **8** can be attributed to protonation of the anion of 3,4-benzofluorene.

Allene **9** is seen to incorporate no deuterium when the reaction mixture in run 5 is quenched with deuterium oxide. In contrast, decomposition of **7a** in ethylene glycol-d_2 affords **9** totally substituted with deuterium at the two allenic positions. As noted earlier, the formation of allene **9** can best be explained in terms of base-catalyzed isomerization of acetylene **19**. Two factors contribute to the observed labeling patterns. Under aprotic conditions, equilibrium is ultimately established and the allene anion which is initially generated, being more basic than **8**, gains a proton and attains neutrality. As a result, quenching by deuterium oxide results in no incorporation of the label in **9**. In a deuterium labeled protic solvent, the capability of acetylene **19** rapidly to exchange the acetylenic proton for deuterium becomes clearly evident; furthermore, although proceeding at a somewhat slower rate, the acetylene–allene interconversion is clearly intermolecular. This order of molecularity is entirely consistent with the results of Cram and coworkers,[14] who have shown that base-catalyzed 1,3-proton transfer in 1,3,3-triphenylpropyne with methoxide–methanol or *t*-butoxide–*t*-butyl alcohol is only 18–19% intramolecular at 27–28°.

In conclusion, therefore, the effect of the unique geometry of the semibullvalene nucleus on the reactivity of a carbinylcarbene generated at position 1 (*i.e.*, **14**) is seen to be very pronounced. Although a certain amount of fragmentation to an acetylenic intermediate is seen, no ring expansion to a cyclobutene is encountered. Rather, the principal mode of rearrangement involves an unprecedented 1,3-migration of a phenyl group to what is formally a *trans*-disposed carbon atom (Scheme I). Such a bond reorganization may initially appear unexpected. As a result of the very probable nonconcertedness of the migration, however, reasonable distances for the 1,3-aryl migration are available to the system. As rehybridization in **14** commences on the reaction profile leading to **18**, the original carbene center approaches a spatial orientation which now permits relatively facile allylic migration of the rear-disposed (see Scheme V) phenyl group.

Scheme V



18

We propose that **18** is a likely common intermediate in the rearrangement of **7** to both **8** and **9**. The twofold greater preference of **18** to partition itself in the direction of **8** is interesting and is to be examined further.

Experimental Section[15]

1-Carbomethoxydibenzosemibullvalene (4). A solution of 8.50 g of **3**[16] in 500 ml of acetone was irradiated for 4.5 hr under nitrogen using a 450 W Hanovia mercury arc and Pyrex filter. The solvent was evaporated *in vacuo* and the resulting solid was recrystallized from ethanol to give 7.53 g (88.5%) of **4**, mp 165.5–167.5° (lit.[6] mp 169.5–170.5°).

1-Dibenzosemibullvalenylmethanol (5a). A solution of 1.31 g (5.0 mmoles) of **4** in 10 ml of anhydrous tetrahydrofuran was added dropwise during 30 min to a cold (ice bath), stirred slurry of lithium aluminum hydride (0.95 g, 25.0 mmoles) in 35 ml of the same solvent. The mixture was stirred at 0° for 1.5 hr and then at room

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

(14) D. J. Cram, F. Willey, H. P. Fischer, H. M. Relles, and D. A. Scott, *J. Am. Chem. Soc.*, 88, 2759 (1966).

(15) Melting points were determined with a Thomas-Hoover melting point apparatus and are corrected.

(16) W. Vaughan and K. Milton, *J. Am. Chem. Soc.*, 74, 5628 (1952).

temperature for 1 hr. Water (0.95 ml), 30% sodium hydroxide solution (0.95 ml), and water (2.85 ml) were added in that order with constant ice cooling. Filtration of the solids and evaporation of the solvent *in vacuo* gave 1.14 g (97.5%) of a white solid, mp 142–145°. Recrystallization from methanol–water gave **5a** as broad needles: mp 146–147°; $\nu_{max}^{CHCl_3}$ 3520, 3355, 1464, 1025, and 1010 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 2.20 (s, 1 H, -OH), 2.96 (s, 2 H, cyclopropyl), 3.76 (s, 2 H, -CH$_2$O), 4.42 (s, 1 H, benzylic), and 6.8–7.5 (m, 8 H, aryl).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.92; H, 6.12.

1-Dibenzosemibullvalenylcarboxaldehyde (6a). A solution of 936 mg (4.0 mmoles) of **5a** in 5 ml of dry pyridine was added in one portion to a cooled (ice) slurry of the chromium trioxide–pyridine complex prepared from 1.20 g (12.0 mmoles) of chromium trioxide and 15 ml of dry pyridine. The reaction mixture was stirred at room temperature for 12 hr; methylene chloride was added and the chromium salts were removed by filtration. The methylene chloride solution was washed with three 50-ml portions of 1 *N* hydrochloric acid, three 50-ml portions of 5% sodium bicarbonate solution, water, and dried. Evaporation of the solvent *in vacuo* afforded a dark yellow residue which was purified by elution (CH_2Cl_2) through a short column of silica gel; there was obtained 675 mg (73%) of crystalline **6a**. Recrystallization from benzene–hexane afforded pure **6a** as colorless needles: mp 178–181°; $\nu_{max}^{CHCl_3}$ 1685, 1460, 1182, and 1120 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 3.86 (s, 2 H, cyclopropyl), 5.05 (s, 1 H, benzylic), 6.9–7.5 (m, 8 H, aryl) and 9.34 (s, 1 H, -CHO).

Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.95; H, 5.21.

Acidification of the sodium bicarbonate washings afforded 160 mg (16%) of dibenzosemibullvalenecarboxylic acid: mp 229–232° dec (from aqueous methanol); $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 3.86 (s, 2 H, cyclopropyl), 4.97 (s, 1 H, benzylic), 6.9–7.5 (m, 8 H, aryl), and 10.57 (s, 1 H, -COOH).

Tosylhydrazone 7a. A mixture of 464 mg (2.0 mmoles) of **6a** and 372 mg (2.0 mmoles) of *p*-toluenesulfonylhydrazide in 25 ml of dry tetrahydrofuran was refluxed with stirring for 14 hr. Benzene (50 ml) was added, and most of the solvent was removed by distillation. After the addition of pentane, the insoluble solid was filtered and dried to give 800 mg (100%) of crude **7a**, mp 164° dec. Recrystallization from methanol–water gave faintly yellow needles: mp 167–169° dec; ν_{max}^{KBr} 1618, 1595, 1345, 1165, 765, and 738 cm^{-1}.

Anal. Calcd for $C_{24}H_{20}N_2O_2S$: C, 71.98; H, 5.03; N, 7.00. Found: C, 71.53; H, 5.07; N, 6.87.

1-Dibenzosemibullvalenylmethanol-α,α-d_2 (5b). Reduction of 1.06 g (4.04 mmoles) of **4** with 510 mg (12.12 mmoles) of lithium aluminum deuteride as described for **5a** afforded 945 mg (98%) of **5b**, mp 142–145°. The nmr spectrum of this material was identical with that of **5a** except for the complete absence of the δ 3.76 peak and the appearance of the hydroxyl proton at δ 2.07.

1-Dibenzosemibullvalenylcarboxaldehyde-α-d_1 (6b). The oxidation of **5b** was performed as described for **5a** except that a larger excess of oxidant and a longer reaction time were needed. Thus, oxidation of 450 mg (1.91 mmoles) of **5b** with the complex from 0.80 g (8.00 mmoles) of chromium trioxide and 20 ml of pyridine for a total reaction time of 46 hr yielded 335 mg (75%) of **6b**. The nmr spectrum was identical with that of **6a** except for the total absence of the δ 9.34 absorption. Tosylhydrazone **7b** was obtained in 97% crude yield in the manner reported for **7a**.

Base-Induced Decomposition of 7a with Sodium Methoxide. Dry, powdered tosylhydrazone **7a** (1.60 g, 4.0 mmoles) was added in one portion to a suspension of 324 mg (6.0 mmoles) of sodium methoxide in 15 ml of dry diglyme. The flask was immersed in an oil bath and stirred under nitrogen while the temperature was raised rapidly. At *ca.* 90°, the reaction mixture became dark green and vigorous gas evolution commenced; by 100°, gas evolution was almost complete. The temperature was then raised to 120° and maintained there for 15 min. The cooled solution was added to ice water (60 ml) at which point a dramatic green to red color change took place. The products were extracted with three 100-ml portions of ether and the ether solution was washed with five 50-ml portions of water, dried, and evaporated. Thin layer chromatography (silica gel–hexane) of the residual dark red gum showed the presence of two nonpolar components and several minor colored components of much lower R_f. Chromatography of the crude product on silica gel and elution with pentane gave 450 mg (52%) of a crystalline residue consisting (tlc) only of the above two-components in a ratio of 66:34 (nmr analysis, see below). Separation of the two substances was achieved with difficulty by chromatography on silica gel impregnated with silver nitrate.[17]

In one experiment, 200 mg of this mixture was chromatographed on 10 g of silica gel–silver nitrate (elution with 5% benzene–hexane, 100-ml fractions). Fractions 4–7 yielded 100 mg of colorless plates. Recrystallization from ethanol afforded 80 mg of pure **8**: mp 125.5–126.5° (lit.[18] mp 124–125°); $\lambda_{max}^{isooctane}$ 231 (47,400), 300 (11,900), 310 (15,800), 321 (13,600), 327 (11,800), and 335 nm (ϵ 17,200);[19] $\delta_{TMS}^{CDCl_3}$ 3.81 (s, 2 H, benzylic), 7.1–8.0 (m, 8 H, "normal" aryl), 8.3 and 8.7 (five-line m, 1 H each, H_a, H_b).

Fractions 8–12 consisted of 44 mg of **8** and **9**. Fractions 13–22 yielded 53 mg of yellow solid, mp 76–80°. This substance decomposed rapidly on standing at room temperature and could not be purified either by sublimation or recrystallization. However, this sample was free from **8** and showed the following spectral properties commensurate with structure **9**: $\nu_{max}^{CHCl_3}$ 1931 and 855 cm^{-1} (terminal allene); $\delta_{TMS}^{CDCl_3}$ 5.13 (s, 2 H, allenic), 6.81 (s, 2 H, vinyl), and 7.2–7.5 (m, 8 H, aromatic).

Hydrogenation of 9. A sample of **9** (40 mg, direct from chromatography) in 30 ml of dry tetrahydrofuran was hydrogenated over 5% palladium on charcoal at atmospheric pressure. The catalyst was removed by filtration and the solvent was evaporated. The residual colorless oil was purified by preparative vpc (5 ft × 0.25 in. Al column packed with 5% SE-30 on 60–80 mesh Chromosorb W at 145°). This substance was identical in all respects with an authentic sample of **10**.

5-Ethylidene-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (12). A solution of 1.6 *M n*-butyllithium in hexane (6.26 ml, 10.0 mmoles) was added dropwise to a stirred suspension of 4.18 g (10.0 mmoles) of ethyltriphenylphosphonium iodide in 50 ml of anhydrous tetrahydrofuran under a nitrogen atmosphere. The red solution was stirred for 30 min, whereupon the solution of 1.04 g (5.0 mmoles) of 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (**11**, Aldrich) in 10 ml of anhydrous tetrahydrofuran was added dropwise and the mixture was refluxed with stirring for 10 hr. The major portion of the solvent was evaporated, water was added, and the mixture was extracted with two 10-ml portions of ether. Evaporation of the dried ether solution afforded an oily residue which was chromatographed on silica gel. Elution with pentane yielded 1.00 g (96%) of **12** (homogeneous by vpc) from which the analytical sample was prepared by molecular distillation (95–100° (0.2 mm)): $\nu_{max}^{CHCl_3}$ 1477, 1437, 1355, 946, 892, 845 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.72 (d, J = 7.0 Hz, 3 H methyl), 3.06 (br s, 4 H, benzylic), 5.95 (q, J = 7.0 Hz, 1 H, vinyl), and 6.9–7.4 (m, 8 H, aryl).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.61; H, 7.00.

5-Ethyl-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (10). A solution of 660 mg (3.0 mmoles) of **12** in 60 ml of methanol–tetrahydrofuran (1:1) was hydrogenated at atmospheric pressure over 5% palladium on carbon. The reaction mixture was filtered, the solids were washed thoroughly with solvent, and the combined filtrates were evaporated. There was obtained 650 mg of **10** which was purified by molecular distillation and preparative vpc on a 3 ft × 0.25 in. Al column packed with 5% SE-30 on Chromosorb W (145°): $\nu_{max}^{CHCl_3}$ 1480, 1445, 1370, 1357, 1305, 1105, 1075, 910, 870, and 845 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 0.85 (t, J = 7.0 Hz, -CH$_2$C*H*$_3$), 2.09 (q of d, 2 H, -C*H*$_2$CH$_3$), 3.14 (14 line m, 4 H, benzylic), 3.85 (t, J = 7.8 Hz, H_b), and 6.9–7.3 (m, 8 H, aryl).

Anal. Calcd for $C_{17}H_{18}$: C, 91.89; H, 8.16. Found: C, 91.55; H, 7.78.

Base-Induced Decompositions with *n*-Butyllithium. The required volume of 1.85 *M n*-butyllithium in hexane was added *via* a syringe to a stirred suspension of tosylhydrazones **7a** or **7b** in the chosen solvent under nitrogen and the mixture was stirred about 5 min at room temperature. The reaction flask was immersed in an oil bath maintained at the indicated temperature and stirred for 15 min after which gas evolution had ceased. The reaction mixture was worked up as described above (except for run no. 5 which was quenched in D_2O) and the mixture of **8** and **9** was isolated by chromatography on silica gel (elution with pentane). Both nmr and tlc analyses indicated that **8** and **9** were the only hydrocarbons formed in each instance.

Subsequently, it was found that **8** could be separated from the unstable allene **9** by three recrystallizations from ethanol.

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(17) T. Norin and L. Westfelt, *Acta Chem. Scand.*, 17, 1828 (1963).

(18) J. W. Cook, A. Dansi, C. L. Hewett, J. Iball, W. V. Mayneord, and E. Roe, *J. Chem. Soc.*, 1319 (1935).

(19) For the ultraviolet spectrum of 3,4-benzofluorene in 95% ethanol, see R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, spectrum no. 430.