The Reaction of Benzenediazonium-2-carboxylate with 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene[1]

THOMAS J. BARTON,* A. JAMES NELSON,[2] AND JON CLARDY

Contribution No. 2737 from the Department of Chemistry, Iowa State University, and Ames Laboratory of the U. S. Atomic Energy Commission, Ames, Iowa 50010

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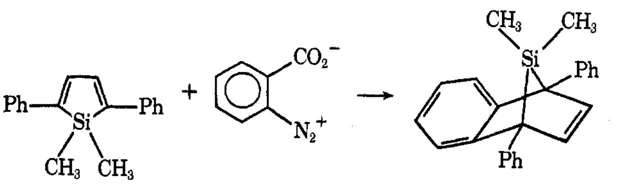
The attempted addition of benzyne, produced thermally from benzenediazonium-2-carboxylate, to 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (1) did not yield the expected Diels-Alder product, 2,3-benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (2). Instead, further reaction with benzenediazonium-2-carboxylate afforded an adduct (8) which had resulted from silicon-carbon bond cleavage concomitant with silicon-oxygen bond formation. While this reaction formally amounted to addition of the often proposed 1,4-dipolar species 3 to the silanorbornadiene, it was conclusively established that benzenediazonium-2-carboxylate is itself the attacking species. The driving force for this reaction is attributed to the great strength of the silicon-oxygen bond. The structure of 8 was determined by X-ray diffraction.

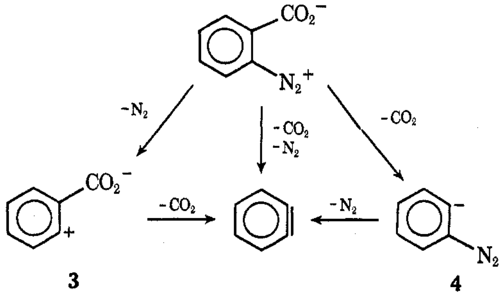
As part of a program which involves the preparation of silicon-bridged hydrocarbons, we undertook the synthesis of 2,3-benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (2) from 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (1) and benzyne. No particular difficulties were foreseen, as a similar addition between benzyne and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene had been reported[3] to proceed in yields up to 60%. However, when an equimolar solution of the hydrochloride salt of benzenediazonium-2-carboxylate, propylene oxide (to remove the hydrogen chloride),[4] and 1 were refluxed in 1,2-dichloroethane, much of the silacyclopentadiene was recovered unreacted, along with a small amount of a colorless adduct. Use of a threefold molar excess of the benzyne precursor afforded, after chromatography on silica gel, a 77% yield of the same colorless, crystalline solid, mp 278-279°, as the sole isolable product derived from the silacyclopentadiene.

The mass spectrum (base and parent ion *m/e* 458) and combustion analysis clearly indicated that the adduct was composed of the elements of one molecule of 1, one molecule of benzyne, and a molecule of benzenediazonium-2-carboxylate less a molecule of nitrogen. For an explanation of this type of adduct formation we turned to the mechanism of benzyne formation.



1 2

While it has been known for the last decade that benzenediazonium-2-carboxylate will thermally decompose to benzyne,[5] the detailed mechanism of this decomposition in solution has not been fully elucidated. Three possibilities must be considered: (a) concerted loss of carbon dioxide and nitrogen; (b) loss of nitrogen to afford the dipolar species 3 followed by loss of carbon dioxide or attack on some trapping agent before loss of carbon dioxide; and (c) initial loss of carbon dioxide to provide 4, which may either lose nitrogen or react directly with the trapping molecule.



3 4

Intermediate 4 has never been seriously implicated in this decomposition, but 3 has several times been suggested as a possible intermediate. Both Knorr[6] and Yaroslavsky[7] have isolated phthalimides from the reaction of isocyanides with benzenediazonium-2-carboxylate, and 3 has been postulated as the reactive intermediate which adds across the carbon-nitrogen multiple bond. The formation of phthalic anhydride from the reaction of nickel tetracarbonyl and benzenediazonium-2-carboxylate may also proceed through 3.[6] A search of the literature reveals that the only situation where 3, although in these cases generated from the pyrolysis of diphenyliodonium-2-carboxylate[8] or potassium 2-halogenobenzoates,[9] might be involved in an addition to a carbon-carbon multiple bond is in the reaction with benzyne itself to produce 3,4-benzocoumarins and xanthones. In each of these cases, the products could also be explained by a series of substitution reactions in which benzyne attacks benzenediazonium-2-carboxylate. However, benzocoumarin has never been observed during the decomposition of benzenediazonium-2-carboxylate.[10] Other evidence for the existence of 3 comes from trapping by nucleo-

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(1) (a) Heterocyclopentadienes. II. For the previous paper in this series, see T. J. Barton and A. J. Nelson, *Tetrahedron Lett.*, 5037 (1969). (b) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 29.

(2) NASA Predoctoral Fellow, 1969-present.

(3) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

(4) For an example of the use of this particular technique in the synthesis of triptycene, see R. M. Roberts, J. C. Gilbert, L. B. Rodewald, and A. S. Wingrove, "An Introduction to Modern Experimental Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1969, pp 196-201.

(5) (a) M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, **82**, 3802 (1960); (b) R. S. Berry, G. N. Spokes, and R. M. Stiles, *ibid.*, **82**, 5240 (1960); (c) M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963); (d) R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963); (e) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).

(6) R. Knorr, *Chem. Ber.*, **98**, 4038 (1965).

(7) S. Yaroslavsky, *Chem. Ind.* (*London*), 765 (1965).

(8) F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).

(9) E. McNelis, *ibid.*, **28**, 3188 (1963).

(10) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 77.

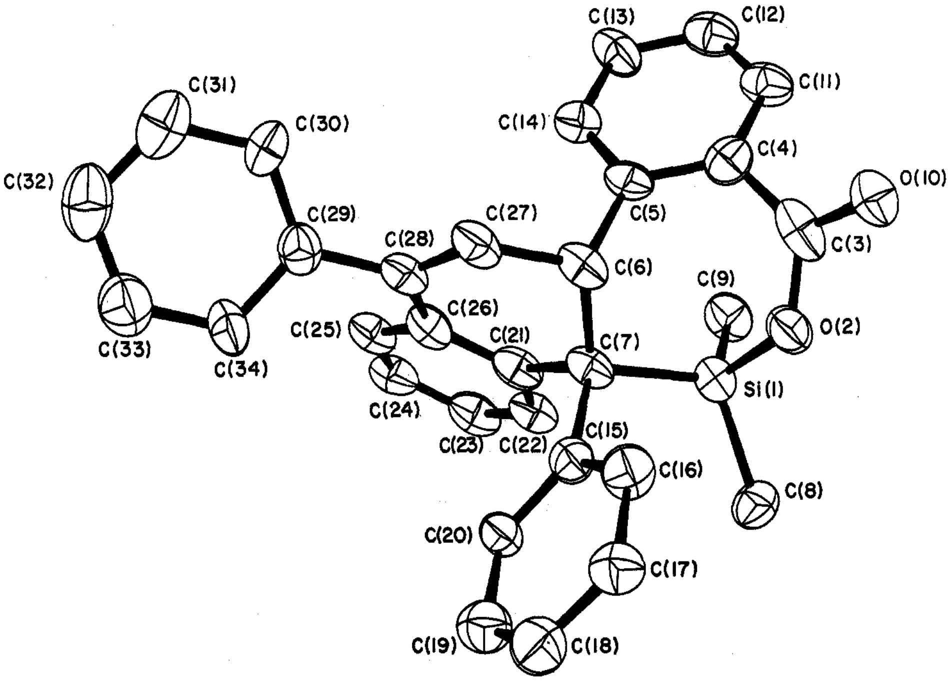
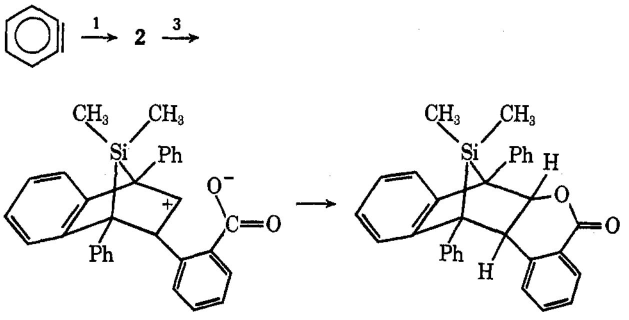


Figure 1.—The molecular structure of adduct **8**.

philic solvents, *e.g.*, in water to provide salicyclic acid in 88% yield,[5a,11] and observed greater than unity ratios of nitrogen to carbon dioxide evolution upon decomposition of benzenediazonium-2-carboxylate in a variety of solvents in the absence of suitable trapping agents.[5a,c] Perhaps the most frequently quoted work which has been offered as evidence for the intermediacy of **3** (or some isomer of **3**) is that of Gompper.[12] When benzenediazonium-2-carboxylate was decomposed in acetonitrile–water–furan mixtures the ratio of products derived from water (salicylic acid) and furan (1,4-epoxy-1,4-dihydronaphthalene, from a Diels–Alder reaction with benzyne) was found to be dependent upon the water concentration but independent of the furan concentration. These results were interpreted as being consistent with the formation of both products from a common intermediate, namely **3** or some isomer of **3**.

In view of this information it was tempting to assign a structure such as **6** [ir 1729 (lactone carbonyl) and 1327 cm^{-1} (lactone C–O stretch)] as it is mechanistically simple to account for the inclusion of the elements of **3** in the product. However, although the striking upfield position of one of the *Si*-methyl groups (δ −0.33) in the nmr spectrum was in keeping with this assignment, a one-proton doublet at δ 5.78 (J = 6.8 Hz) was difficult to assign to anything other than an olefinic proton. Also this addition would represent the only suggested example of the trapping of intermediate **3** by a simple olefinic system. Current evidence has characterized 1,4-dipolar cycloaddition[13] as a two-step process proceeding through a zwitterionic intermediate such as **5**. However, it has been generalized that only dipolarophiles possessing strong nucleophilic or electrophilic reactivity will combine with 1,4 dipoles.[13] It would be quite difficult to rationalize these observations with the formation of **6**, as no pronounced reactivity of this type would be expected from either **1** or **2**. Lastly, and most importantly, there was no loss of CO_2 from the parent ion observed in the mass spectrum, as would be expected from **6**. Consequently it was deemed necessary to determine the structure of the reaction product by X-ray diffraction techniques.



5 **6**

Single crystals of the adduct from **1** and benzenediazonium-2-carboxylate suitable for X-ray analysis were grown from diisopropyl ether. The course of the analysis was routine and the details are given in the Experimental Section. A computer drawing of the final X-ray model is given in Figure 1.[14] The bond distances and angles (Tables I and II) agree satisfactorily with generally accepted values.[15] The seven-membered ring containing silicon and oxygen (atoms 1–7) is in a boat conformation. The silicon atom is tetrahedrally coordinated and the four atom fragments of the carboxyl group [O(2), C(3), C(4), and O(10)] and C(3), C(4), C(5), and C(6) are all planar. C(6) and C(7) are tetrahedral. The bond distances to C(7) all seem slightly long. The six-membered ring [C(6), C(7),

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[11] R. Howe, *J. Chem. Soc. C*, 478 (1966).

[12] R. Gompper, G. Seybold and B. Schmolke, *Angew. Chem., Int. Ed. Engl.*, **7**, 389 (1968).

[13] R. Huisgen and K. Herbig, *Justus Liebigs Ann. Chem.*, **688**, 98 (1965); R. Huisgen, M. Morikawa, K. Herbig, and E. Brunn, *Chem. Ber.*, **100**, 1094 (1967); R. Huisgen, K. Herbig, and M. Morikawa, *ibid.*, **100**, 1107 (1967).

[14] C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report No. 3794, Oak Ridge, Tenn. (1965).

[15] "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

TABLE I

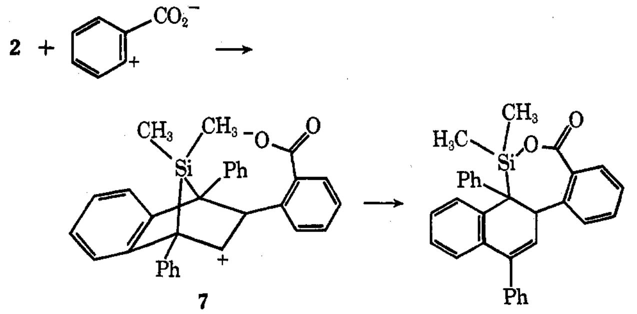
BOND DISTANCES, Å[a]

Si(1)–O(2)	1.685(4)	C(17)–C(18)	1.388(8)
Si(1)–C(8)	1.848(6)	C(18)–C(19)	1.394(9)
Si(1)–C(9)	1.862(6)	C(19)–C(20)	1.392(8)
Si(1)–C(7)	1.901(6)	C(20)–C(15)	1.391(6)
C(7)–C(15)	1.580(7)	C(21)–C(22)	1.384(7)
C(7)–C(21)	1.545(7)	C(22)–C(23)	1.433(8)
C(7)–C(6)	1.576(8)	C(23)–C(24)	1.400(9)
C(6)–C(5)	1.538(7)	C(24)–C(25)	1.370(8)
C(6)–C(27)	1.489(8)	C(25)–C(26)	1.395(7)
C(5)–C(4)	1.411(7)	C(21)–C(26)	1.415(8)
C(5)–C(14)	1.384(7)	C(26)–C(28)	1.467(7)
C(14)–C(13)	1.377(7)	C(27)–C(28)	1.348(7)
C(13)–C(12)	1.419(8)	C(28)–C(29)	1.476(8)
C(12)–C(11)	1.378(8)	C(29)–C(30)	1.398(8)
C(11)–C(4)	1.373(7)	C(30)–C(31)	1.375(8)
C(4)–C(3)	1.509(8)	C(31)–C(32)	1.385(9)
C(3)–O(10)	1.221(6)	C(32)–C(33)	1.414(10)
C(3)–O(2)	1.357(7)	C(33)–C(34)	1.383(9)
C(15)–C(16)	1.390(7)	C(34)–C(29)	1.405(7)
C(16)–C(17)	1.414(7)		

[a] The estimated standard deviation, as computed by the inverse least-squares matrix, is given in parentheses.

C(21), C(26), C(28), and C(27)] is fused to the seven-membered heterocyclic ring in a cis diequatorial manner. The hydrogen of C(6) is axial as is the phenyl ring [C(15) through C(20)]. The conformation about the double bond [C(27)–C(28)] is cis relative to the C(6)–C(28) ring. All four aromatic rings are planar within experimental error.

Therefore the adduct resulting from **1** and benzenediazonium-2-carboxylate is the siloxapinone **8**. In view of the previously mentioned proposals for the mechanism of thermal decomposition of benzenediazonium-2-carboxylate it appeared that a logical mechanism for the formation of **8** would involve attack on the olefinic bond of **2** by **3**, to generate **7**, followed by carboxylate anion attack upon the silicon atom. Given this mechanism, it is apparent from the stereochemistry of **8** that attack by the benzenium cation must be exo, as only this mode would result in the proper orientation for carboxylate attack upon the silicon atom. It would of course be possible for the reaction to proceed in a concerted fashion.



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8

The isolation of this unique adduct (**8**) by a process which the similar reaction between cyclopentadiene and benzyne generated from benzenediazonium-2-carboxylate does not undergo[16] appears to indicate that a likely driving force is the formation of the silicon–oxygen bond, which is well established to be far stronger than the carbon–oxygen bond.[17] Upon consideration of the fact that the mechanism presented above for the formation of **8** does not depend upon the

TABLE II

BOND ANGLES[a]

C(7)–S(1)–C(8)	113.3(3)
C(7)–Si(1)–O(2)	103.9(2)
C(7)–Si(1)–C(9)	114.0(2)
C(9)–Si(1)–O(2)	110.0(2)
C(9)–Si(1)–C(8)	110.8(3)
O(2)–Si(1)–C(8)	103.8(2)
Si(1)–O(2)–C(3)	127.4(4)
O(2)–C(3)–O(10)	118.4(6)
O(10)–C(3)–C(4)	123.4(5)
O(2)–C(3)–C(4)	118.0(4)
C(3)–C(4)–C(5)	121.4(5)
C(3)–C(4)–C(11)	116.7(5)
C(11)–C(4)–C(5)	121.6(5)
C(4)–C(11)–C(12)	120.2(5)
C(11)–C(12)–C(13)	119.1(5)
C(12)–C(13)–C(14)	119.5(6)
C(13)–C(14)–C(5)	121.8(5)
C(14)–C(5)–C(4)	117.3(5)
C(14)–C(5)–C(6)	122.4(5)
C(4)–C(5)–C(6)	120.0(5)
C(5)–C(6)–C(7)	113.1(4)
C(5)–C(6)–C(27)	112.6(5)
C(27)–C(6)–C(7)	110.0(4)
C(6)–C(7)–Si(1)	108.0(3)
C(6)–C(7)–C(15)	108.9(4)
C(6)–C(7)–C(21)	109.2(5)
Si(1)–C(7)–C(15)	107.3(3)
Si(1)–C(7)–C(15)	114.3(3)
C(15)–C(7)–C(21)	108.7(3)
C(7)–C(15)–C(16)	118.5(4)
C(7)–C(15)–C(20)	122.0(4)
C(16)–C(15)–C(20)	119.3(5)
C(15)–C(16)–C(17)	120.3(5)
C(16)–C(17)–C(18)	118.9(6)
C(17)–C(18)–C(19)	120.8(6)
C(18)–C(19)–C(20)	119.2(5)
C(19)–C(20)–C(15)	120.9(5)
C(6)–C(27)–C(28)	123.2(5)
C(27)–C(28)–C(29)	120.8(5)
C(27)–C(28)–C(26)	119.9(5)
C(29)–C(28)–C(26)	119.2(5)
C(28)–C(26)–C(25)	123.2(5)
C(28)–C(26)–C(21)	119.0(5)
C(21)–C(26)–C(25)	117.6(5)
C(26)–C(25)–C(24)	123.3(6)
C(25)–C(24)–C(23)	119.8(6)
C(24)–C(23)–C(22)	117.7(6)
C(22)–C(21)–C(26)	119.7(5)
C(22)–C(21)–C(7)	120.6(5)
C(7)–C(21)–C(26)	119.4(5)
C(28)–C(29)–C(34)	119.5(5)
C(28)–C(29)–C(30)	122.5(5)
C(34)–C(29)–C(30)	117.8(6)
C(29)–C(34)–C(33)	119.3(6)
C(34)–C(33)–C(32)	122.8(6)
C(33)–C(32)–C(31)	116.4(6)
C(32)–C(31)–C(30)	121.5(7)
C(31)–C(30)–C(29)	121.9(6)

[a] The estimated standard deviation, as estimated from the inverse least-squares matrix, is given in parentheses.

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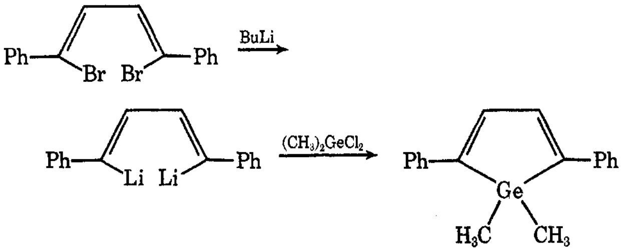
[16] This reaction provides the normal Diels–Alder adduct in 78% yield: F. M. Logullo, A. Seitz, and L. Friedman, personal communication quoted in ref 10, p 210.

[17] The observed bond energy of a Si–O bond is *ca.* 112 kcal/mol as compared with a value of 85.5 kcal/mol for a C–O bond: E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 51.

silicon–oxygen bond formation for a driving force, it was decided to put that point to a test. The intermediate strength of a germanium–oxygen bond[17] compared with the carbon–oxygen and silicon–oxygen bonds made the prospect of performing this reaction with a system where silicon had been replaced by germanium especially intriguing. For this purpose we prepared 1,1-dimethyl-2,5-diphenyl-1-germacyclopentadiene (**9**)[18] by a route exactly analogous to that used by Atwell and Weyenberg[19] for the synthesis of 1,1-dimethyl-2,5-diphenyl-1-stannacyclopentadiene.



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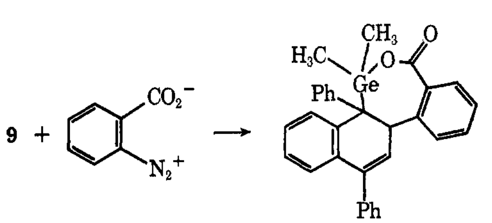
If the thermodynamics of this bond formation were really the controlling factor in the trapping of **3**, we might expect not to obtain any products resulting from addition of **3**. However, when the reaction between benzenediazonium-2-carboxylate and **9** was run under exactly the same conditions as for **1**, a single isolable product was obtained whose spectra and elemental analysis corresponded to **10**. The nmr spectrum of **10** virtually identical with that of **8** [δ *ca.* 7.75–7.1 (complex aromatic multiplet, 18 H), 5.85 (olefin doublet, J = 6.8 Hz, 1 H), 4.84 (methine doublet, J = 6.8 Hz), 0.33 (methyl singlet, 3 H), and −0.12 (methyl singlet, 3 H)]. The mass spectrum showed a strong parent ion and a *very* small fragment ion resulting from loss of carbon dioxide, in keeping with structure **10**.



10

Although the use of **3** was mechanistically convenient, the very inability of this mechanism to account for the driving force derived from Si–O or Ge–O bond formation argued against its operation. Therefore it appeared wise to reevaluate the reported evidence for the two-step decomposition of benzenediazonium-2-carboxylate. In most instances it appears that **3** is invoked simply as a matter of convenience and to be in step with the contemporary thought regarding the reactions of aryldiazonium cations. Indeed, if we center our attention upon the work of Gompper[12] (*vide supra*), it may be easily shown that his results can be equally well explained by a combination of bimolecular displacement of nitrogen by water to afford salicylic acid and simultaneous loss of nitrogen and carbon dioxide to give benzyne, which then reacts solely with furan. Why displacement of nitrogen by water through a one-step process was not considered may be understood only when one examines the history of the mechanism of denitrogenation of benzenediazonium salts in solution.

In 1942, Waters[20] first proposed that the benzenediazonium cation reacted through the unstable phenyl cation intermediate with no participation of the adding nucleophile in the rate-determining step. This two-step mechanism was generally accepted because of its ability to explain the lack of anion or acidity dependence and because of the observed first-order kinetics of the reaction.[21] However, in 1969 Lewis reported that in the reaction of diazonium salts with nucleophiles rate accelerations could be observed from a variety of added salts.[22] These results were therefore interpreted as a result of a bimolecular displacement reaction which consequently did not involve any intermediate such as the phenyl cation. Since Lewis found the relative reactivities of the different nucleophiles toward the diazonium ion to vary only slightly, it was pointed out that the general unselectivity led to an inherent difficulty in distinguishing between a single-step reaction and a two-step reaction which proceeded through a reactive intermediate. Interestingly, Swain has recently presented rather convincing evidence that this reaction proceeds by rate-determining unimolecular cleavage to a singlet phenyl cation.[23] This conclusion was reached on the basis of results which showed only unrearranged products, first-order rate constants which varied less than tenfold with anion change, and large secondary kinetic hydrogen isotope effects for each ortho position. The situation therefore appears to be somewhat in a state of flux but it is now obvious why, in light of the then-accepted Waters' mechanism, Gompper did not consider a nitrogen displacement reaction in the production of salicylic acid from benzenediazonium-2-carboxylate.

In order to determine whether the 7-silanorbornadiene (**2**) was reacting directly with benzenediazonium-2-carboxylate or with some intermediate (*e.g.*, **3**) derived from benzenediazonium-2-carboxylate, it would be desirable to prepare **2** and attempt to react it with benzenediazonium-2-carboxylate under conditions where the inner salt does not decompose. To achieve this purpose the method of benzyne generation chosen was the lead tetraacetate oxidation of 1-aminobenzotriazole (**11**).[24] However, reaction of the silole **1** with benzyne generated in this fashion yielded only 1,4-diphenylnaphthalene (**12**) upon normal work-up. While this represents a drastic difference in thermal stability between **2** and the tetraphenyl adduct reported by Gilman,[3] we have often noted that the Diels–Alder adducts of **1** and acetylenes were far less stable than the analogous adducts resulting from 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene.[25] We

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[18] The photochemical properties, but not the synthesis, of this "germole" were briefly reported in ref 1 and A. J. Nelson, J. C. Clardy, and T. J. Barton, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN-92.

[19] W. H. Atwell, D. R. Weyenberg, and H. Gilman, *J. Org. Chem.*, **32**, 885 (1967).

[20] W. A. Waters, *J. Chem. Soc.*, 266 (1942).

[21] D. F. DeTar and A. R. Ballentine, *J. Amer. Chem. Soc.*, **78**, 3916 (1956).

[22] E. S. Lewis, L. D. Hartung, and B. M. McKay, *ibid.*, **91**, 419 (1969).

[23] C. G. Swain, J. E. Sheats, K. G. Harbison, and D. G. Gorenstein, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 34.

[24] C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964).

[25] T. J. Barton, unpublished observations.

have attributed this to the fact that with phenyls only at the bridgeheads of the silanorbornadiene, as in **2**, these rings are much less restricted with regard to their ability to properly orient themselves to stabilize cleavage of the bridge. When the reaction of **1** and benzyne, generated from 1-aminobenzotriazole, was performed at −78° and the reaction mixture was examined by nmr (at *ca.* −50°), it was revealed that *ca.* one-half of the silole **1** was consumed and two new singlets of equal intensity appeared slightly upfield, therefore presumably corresponding to the two methyl groups in **2** (Figure 2). After establishing that the relative concentrations of **1** and **2** did not noticeably change after several hours at −50°, a slight excess of benzenediazonium-2-carboxylate was added to the reaction mixture and the mixtrue was allowed to stand at 0° overnight. Work-up of the reaction afforded both **12** and **8** in *ca.* a 2:1 ratio. As the solubility of benzenediazonium-2-carboxylate in the solvent used, dichloromethane, was probably not high at these temperatures, it is likely that there was an insufficient amount of this reagent to react with **2** before the thermal decomposition of **2** to **12**. The key point is that **2** apparently reacts with benzenediazonium-2-carboxylate to form the siloxapinone **8** *at temperatures where benzenediazonium-2-carboxylate is quite stable.* Possibly more conclusive evidence that **8** arises solely from reaction between **2** and benzenediazonium-2-carboxylate comes from experiments where **2** was first formed from **1** and the benzotriazole **11** at low temperatures, benzenediazonium-2-carboxylate was added, and the reaction mixture was allowed to warm slightly below room temperature. After only 10 min at 20° gas evolution from this sample was essentially quantitative for loss of only nitrogen. At the same time and under identical thermal conditions, solutions containing benzenediazonium-2-carboxylate and (a) only solvent (dichloroethane), (b) lead diacetate, (c) lead tetraacetate and lead diacetate, or (d) **1** evolved either no gas or only a *very* small fraction of the amount obtained from the sample containing preformed **2**. Therefore, it can be conclusively stated that **8** is the result of reaction between **2** and benzenediazonium-2-carboxylate with *no* involvement of any intermediate derived from prior decomposition of the latter named compound.

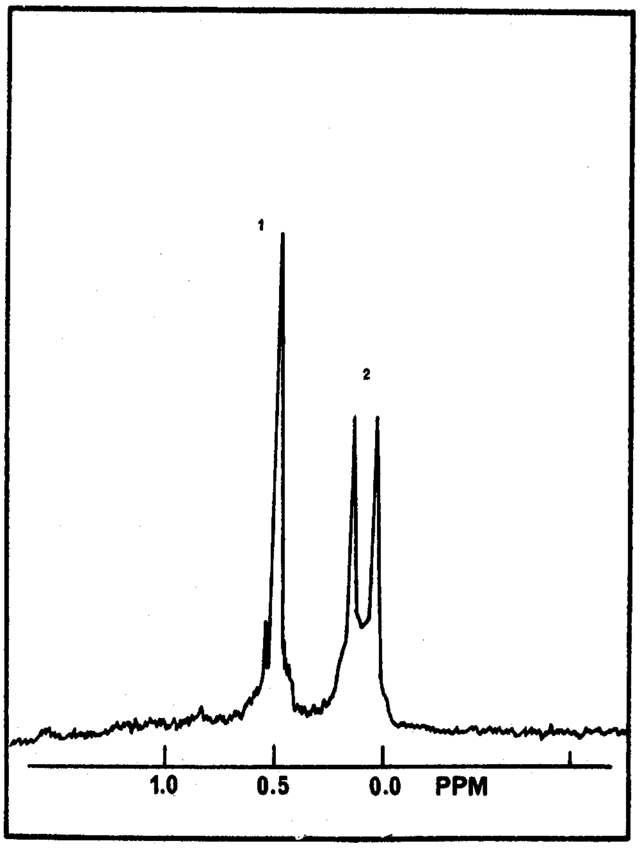
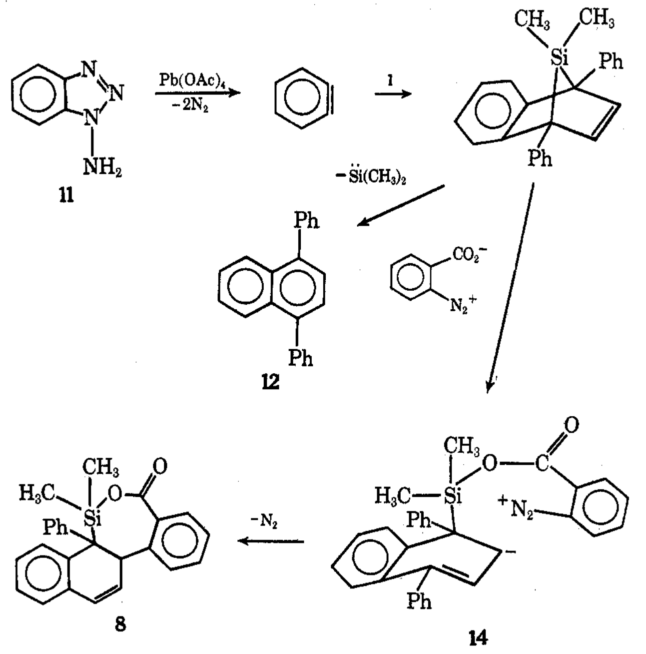
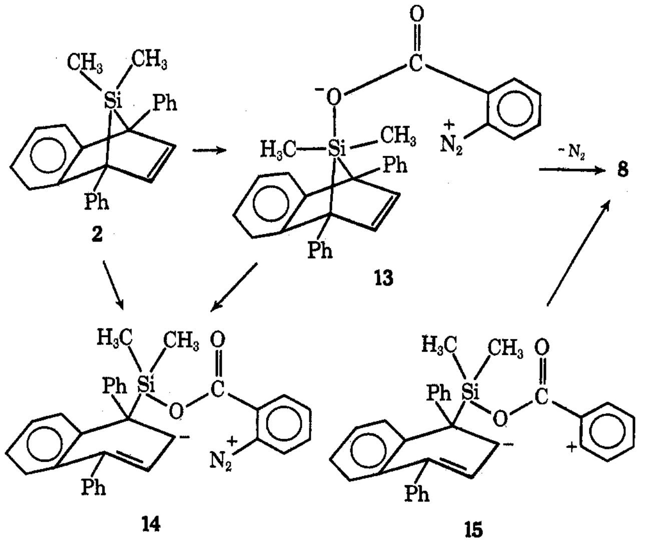


Figure 2.—60-Hz nmr spectrum of a mixture of **1** and **2** at *ca.* −50°.

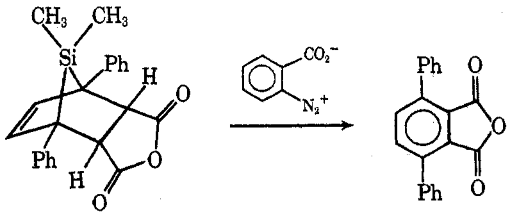


After attack of **2** by the carboxylate anion of benzenediazonium-2-carboxylate we cannot know the intimate details of this reaction. Several courses are available: (a) formation of a pentavalent silicon anion (**13**) which may either go directly to **8** or collapse to the allylic anion (**14**); (b) going directly by carbon displacement to **14** followed either by nitrogen loss to **15**, and then final bond formation to give **8**, or displacement of nitrogen by the anionic portion to provide **8** directly; or (c) an essentially concerted process leading



to **8**. No decision can be made at this time as to which terminal route this reaction follows.

The discovery of a high-yield reaction with benzenediazonium-2-carboxylate which could easily have been explained in mechanistic terms involving the intermediate **3**, but instead has been shown to involve only benzenediazonium-2-carboxylate itself, casts serious doubt upon the evidence which has been offered for the existence of **3** in the thermal decomposition of this useful benzyne precursor. However, it should be noted that this work has no bearing upon the mechanism of benzyne formation from benzenediazonium-2-carboxylate, since the reaction of **2** → **8** and the corresponding reaction leading to **10** do not involve decomposed benzenediazonium carboxylate. We seem to have accidentally hit upon an optimum system for this type reaction which depends not only on the presence of a bridged silicon or germanium but also on the particular substitution of the bicyclic system. As mentioned previously,[3] 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene does not undergo this reaction—presumably for steric reasons. The same is true for 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene.[26] Also, the maleic anhydride adduct of **1**, **16**, gives no isolable products resulting either from the addition of benzyne or benzenediazonium-2-carboxylate; indeed the reaction of **16** and benzenediazonium-2-carboxylate afforded reasonable yields of 1,4-diphenylphthalic anhydride under conditions where **16** is quite stable alone. The nature of this reaction, including the dehydrogenation step, is under investigation.



16

Experimental Section[27]

X-Ray Data Collection.—Single crystals of **8** can be grown from isopropyl ether as long needles with square cross sections. Cubes roughly 0.08 mm on an edge were cut from the needles for diffraction work. No crystal decomposition was noticed during the course of the study.

Weissenberg photographs displayed $2/m$ reciprocal lattice symmetry. The systematic absence $0k0$ for k odd and $h0l$ for $h+l$ odd establish the space group as $P2_1/n$. The goniometer head was then transferred to a fully atutomated Hilger-Watts four circle diffractometer. Lattice constants were determined using Cu Kα radiation (1.5418 Å). The unit cell dimension are $a = 10.725 \pm 0.003$ Å, $b = 10.775 \pm 0.003$ Å, $c = 20.888 \pm 0.005$ Å, and $\beta = 87.76 \pm 0.08°$. The calculated density is 1.26 g/cm^3 for $Z = 4$ and molecular formula $C_{31}H_{26}O_2Si$. The measured density (flotation) was 1.24 g/cm^3.

The intensity data were collected using the stationary-crystal stationary-counter technique with two 5-sec backgrounds and a 10-sec peak height count. Ni-filtered Cu Kα radiation was employed. Two hundred reflections were measured with the θ–2θ scan mode and these were used to convert the peak height intensities to integrated intensities. The net intensity of each reflection was assigned an eror, $\sigma(I)$ = [total count + background + 5% (total count)^2 + 5% (background)^2]$^{1/2}$. Reflections for which $\sigma(I)/I \geq 0.33$, or for which a negative net count was observed, were omitted from refinement. These omitted reflections constituted roughly one-third of the total reflections measured. Periodically monitored check reflections showed no decomposition. Since $\mu = 10$ cm^{-1} no absorption corrections were made. The 2136 observed reflections were corrected for Lorentz and polarization factors to give F_o^2.

Solution and Refinement.—A three-dimensional Patterson synthesis gave the Si coordinates unambiguously. The 33 remaining nonhydrogen atoms were located in subsequent electron density syntheses. Several cycles of full-matrix least-squares refinement in which all atomic coordinates were varied and all atoms had anisotropic thermal parameters (307 total parameters of which 200 could be varied in each cycle) reduced the conventional discrepancy index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ to 0.089 for the 2136 independent reflections.[28] Hydrogen atoms were not included in these calculations.

The weighted discrepancy index, $wR = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$, was 0.113. The w's were calculated from $\sigma(F_o) = (F_o^2 + \sigma(I)/Lp)^{1/2} - |F|_o$. A final electron density difference map showed no peaks greater than 0.8 e/Å.^{3} Some of these were attributed to hydrogens but a detailed analysis was not attempted. The final atomic parameters are given in Table III[29] along with the least squares estimated standard deviations. The anisotropic thermal parameters are listed in Table IV.[29] Bond distances and angles are given in Tables I and II.

Reaction of Benzenediazonium-2-carboxylate with 1.—A mixture of 2.02 g (7.7 mmol) of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene,[19] 4.26 g (23.2 mmol) of benzenediazonium-2-carboxylate hydrochloride, and 2.24 g (38.6 mmol) of propylene oxide in 1,2-dichloroethane (40 ml) was stirred at reflux for 2 hr.[4] The solvent was removed *in vacuo* and the resultant solid was redissolved with difficulty in the minimum amount of chloroform. The solution was put on a 30-in. (1.15-in. i.d.) chromatographic column of silica gel packed in hexane. The column was first flushed with hexane to remove any hydrocarbon byproducts and then eluted with methylene chloride. Continuous monitoring by tlc revealed the complete absence of starting material and only one product. The methylene chloride fractions were combined and the solvent was removed *in vacuo* to afford 2.72 g (77%) of yellow-brown product which was shown to be at least 90% pure by nmr. A single recrystallization from acetone yielded 1.52 g (43%) of white, crystalline **8**, mp 275–276°. Repeated recrystallization from acetone gave analytically pure material, mp 278–279°.

Anal. Calcd for $C_{31}H_{26}SiO_2$: C, 81.18; H, 5.71; Si, 6.13. Found: C, 81.04; H, 5.67; Si, 6.27.

1,1-Dimethyl-2,5-diphenyl-1-germacyclopentadiene (9).[18]—*n*-Butyllithium, 13.0 ml of a 1.6 *M* solution in hexane, was added dropwise under argon to a stirred, ice-bath cooled solution of 1,4-dibromo-1,4-diphenylbutadiene,[19] 3.62 g (10 mmol), in 40 ml of ether freshly distilled from lithium aluminum hydride. All glassware was previously flame dried under argon. After the addition was complete, the reaction mixture was allowed to warm to room temperature and then added dropwise to a stirred solution of dimethylgermanium dichloride, 1.77 g (10 mmol), in 80 ml of dry ether also under an argon atmosphere. The resulting yellow solution was percolated through a short column packed with neutral alumina to remove the lithium chloride. The residue was crystallized from ether–hexane to afford yellow, crystalline **9**: yield 2.35 g (65%); mp 128°; nmr ($CDCl_3$) δ 0.68 (methyl singlet, 6 H), 7.15–7.40 (complex multiplet for both aromatic and olefinic protons, 12 H); mass spectrum[30] (16 eV) m/e

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[26] H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 5584 (1964). We have confirmed this result by attempting to react the Diels–Alder adduct of 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene and benzyne with benzenediazonium-2-carboxylate. No reaction took place.

[27] Melting points are uncorrected. The analyses were performed by Ilse Beetz, Mikroanalytisches Laboratorium, 8640 Kronach, Postfach 460, West Germany.

[28] W. R. Busing, K. O. Martin, and A. A. Levy, ORFLS, A Fortran Crystallographic Least-Squares Program, ORNL-TM-305 (The Oak Ridge National Laboratory, Oak Ridge, Tenn.), 1962.

[29] Listings of structure factors and atomic and thermal parameters (Tables III and IV) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[30] We thank the National Science Foundation for funds contributed toward the purchase of an Atlas CH-4 mass spectrometer.

310 (17%, parent ion, Ge^{76}), 308 (100%, Ge^{74}), 307 (17%, Ge^{73}), 306 (75%, Ge^{72}), 304 (50%, Ge^{70}), 206 (100%).

Anal. Calcd for $C_{18}H_{18}Ge$: C, 70.44; H, 5.91. Found: C, 70.61; H, 6.12.

Reaction of Benzenediazonium-2-carboxylate with 9.—A solution consisting of 0.731 g (2.1 mmol) of **9**, 1.44 g (7.8 mmol) of benzenediazonium-2-carboxylate hydrochloride, and 1.2 ml of propylene oxide in 30 ml of 1,2-dichloroethane was refluxed for 2 hr. The dark reaction product was filtered through silica gel, the solvent was removed *in vacuo*, and the residue was crystallized from acetone to afford 0.155 g of white, crystalline **10**, mp 254–262°. A second crop of 0.108 g was obtained from addition of pentane to the filtrate, yield 0.263 g (0.48 mmol, 23%). Repeated recrystallization from acetone gave analytically pure material: mp 267.5–269.5°; ir absorption 1682 (C═O), 1274 (CO), 1118 cm (GeO?).

Anal. Calcd for $C_{31}H_{26}GeO_2$: C, 74.00; H, 5.21; Ge, 14.43. Found: C, 74.05; H, 5.34; Ge, 14.35.

Preparation of 2 from 1-Aminobenzotriazole (11)[31] and 1.—A solution containing 0.444 g (3.7 mmol) of 1-aminobenzotriazole (**11**) in 10 ml of dry dichloromethane was added dropwise to a stirred solution of 1.64 g (3.7 mmol) of lead tetraacetate, 0.96 g (3.7 mmol) of **1**, and *ca.* 15 ml of dry dichloromethane under nitrogen at −78°. After 40 min the addition was complete and an aliquot was removed for low-temperature nmr investigation. Two new singlets at δ 0.04 and 0.14 corresponding to the nonequivalent methyls in **2** (Figure 2) were observed. The reaction mixture was then warmed to 0° while simultaneously adding 0.39 g (2.6 mmol) of benzenediazonium-2-carboxylate.[5c] The mixture was heterogeneous and stirring was difficult. After allowing the reaction mixture to stand under N_2 at 0° for 8 hr, the mixture was worked up by immediate filtration through silica gel, evaporation of solvent *in vacuo*, and chromatography on a 2.3 × 45 cm column packed with silica gel in hexane: fraction A, hexane eluent, 0.320 g (1.22 mmol, 33%) of **1**; fraction B, 5% ether–hexane, 0.306 g (1.1 mmol, 49%) of **13**; fraction C, 20% ether–hexane, 0.122 g (15%) of **8**, mp 277–279°.

Reaction of 11 and 1 with Room Temperature Work-Up.—A solution containing 0.350 g (2.89 mmol) of 1-aminobenzotriazole (**11**) in 30 ml of dry dichloromethane was added dropwise to a stirred solution of 1.512 g (2.93 mmol) of lead tetraacetate and 0.757 g (2.89 mmol) of **1** in 50 ml of dry dichloromethane at 0°. After *ca.* 40 min, the addition was complete and gas evolution had ceased. The reaction mixture was immediately filtered through silica gel and the solvent was removed *in vacuo*. Chromatography of the residue on a 2.2 × 30 cm silica gel column packed in hexane afforded two fractions: 0.14 g (18.5%) of yellow, crystalline **1**, mp 131–133° (lit.[19] mp 130–133°), and 0.297 g (36.8%) of white, crystalline **12**, mp 132–134° (lit.[32] mp 134–135°, *m/e* 280).

Reaction of 2 with Benzenediazonium-2-carboxylate.—A solution containing 0.195 g (1.5 mmol) of **11** in 10 ml of dry 1,2-dichloroethane was added dropwise to a stirred solution of 0.390 g (1.5 mmol) of **1** and 0.626 g (1.41 mmol) of lead tetraacetate in 10 ml of dry 1,2-dichloroethane held at −50° under nitrogen. After completion of addition the reaction vessel (flask A) was removed from the Dry Ice bath and placed in a 20° water bath. At the same time two flasks (flasks B and C), each containing 20 ml of dry 1,2-dichloroethane, were lowered into the same water bath. To each of the three flasks was then added 0.170 g (1.15 mmol) of dry benzenediazonium-2-carboxylate and to flask B was added 0.400 g (1.5 mmol) of lead diacetate. The three flasks were immediately capped with a condenser and a gas outlet tube which led in each case to a 50-ml gas burette filled with water and having a leveling bulb. Each of the mixtures was stirred magnetically. The evolution of gas from flask A was essentially complete after 10 min, during which time 11.9 ml (0.484 mmol) of gas was collected. Assuming that a maximum of 50% **2** had been formed, this represented 65% of the theoretical volume of nitrogen to be expected with no correction being made for solubility. During the same time period flasks B and C gave off *no* gas. After stirring the three solutions for 40 min at 20°, 0.176 g (0.67 mmol) of **1** was added to flask C and a catalytic amount of lead tetraacetate was added to flask B. No evolution of gas from new flask C was observed over a 5-hr period. Slow gas evolution from new flask B was, however, observed—15.6 ml (0.64 mmol) after 4.2 hr but only 0.9 ml (0.037 mmol) after 10 min. Isolation of **8** from flask A by filtration through silica gel, evaporation of the solvent *in vacuo*, and crystallization of the residue from hexane–methanol afforded 0.251 g (0.55 mmol) of **8**, mp 275–277°). Therefore, based on isolated **8**, the 11.9 ml (0.484 mmol) of nitrogen collected represented 88% of theoretical. Thin layer chromatography of the solid revealed the absence of **12**. This is probably due to the homogeneity of the reaction mixture at this higher temperature and the resultant more efficient stirring.

Reaction of 1 with Maleic Anhydride.—A mixture of 1.31 g (5 mmol) of **1** and 0.49 g (5 mmol) of maleic anhydride was refluxed for several minutes in benzene (*ca.* 15 ml). The solution was cooled and filtered to afford 1.80 g (5 mmol, 100%) of white, crystalline **16**: mp 179–181°; nmr ($DCCl_3$) δ 0.12 (methyl singlet, 3 H), 0.18 (methyl singlet, 3 H), 4.38 (singlet methine α to carbonyl, 2 H), 6.62 (vinyl singlet, 2 H), 7.33 (singlet, aromatic, 10 H); ir (KBr) 5.40 and 5.65 (anhydride carbonyl), 8.20 μ (anhydride C–O stretch). In the mass spectrometer **16** apparently undergoes a retrograde Diels–Alder reaction, as the spectrum observed is essentially that of **1**. The highest *m/e* observed is 300, corresponding to 1,4-diphenylphthalic anhydride, but this peak has an intensity of *ca.* 0.07% of the base peak at *m/e* 262 (**1**).

Reaction of 16 and Benzenediazonium-2-carboxylate.—A solution containing 0.525 g (1.46 mmol) of 7,7-dimethyl-1,4-diphenyl-2,3-dicarboxy-7-sila-5-norbornene anhydride (**16**) and 0.22 g (1.49 mmol) of dry benzenediazonium-2-carboxylate in *ca.* 25 ml of dry 1,2-dichloroethane was stirred at 15–20° for 2.7 hr. Gas evolution from the reaction was measured using a gas burette and leveling bulb filled with water. During a period of 8 min, 7.3 ml (0.297 mmol) of gas were evolved. The evolution ceased after 62 min, giving a total gas volume of 24.2 ml (1 mmol). The mixture was then filtered through silica gel using ether, the solvent was evaporated *in vacuo*, and three fractions were separated by chromatography on a 2.8 × 25 cm column of silica gel packed in hexane: fraction A, 25% ether–hexane, 0.162 g (0.54 mmol, 37%) of 1,4-diphenylphthalic anhydride, mp 223–225°, recrystallized to 227° (lit.[33] mp 228–230°), *m/e* 300; fraction B, 10% acetone–ether; fraction C, methanol. B and C gave only uncharacterizable tars.

Registry No. 1, 7688-03-1; **8**, 33069-00-0; **9**, 28124-19-8; **10**, 33070-29-0; **16**, 33122-21-3; benzenediazonium carboxylate, 1608-42-0.

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