

The Dehydrocyclopentadienyl Anion. A New Aryne¹

J. C. Martin* and Daniel R. Bloch²

Contribution from the Department of Chemistry,
University of Illinois, Urbana, Illinois 61801. Received June 22, 1970

Abstract: Evidence for the intermediacy of the dehydrocyclopentadienyl anion (**2**) is seen in trapping experiments involving the Diels–Alder dienes tetraphenylcyclopentadienone and 1,4-diphenyl-*sym*-tetrazine. The thermal or photolytic decompositions of the diazocyclopentadiene-2-carboxylate anion (**1**) under a variety of conditions yield carbon dioxide and nitrogen, presumably to give **2**. Products from the pyrolysis of **1** at *ca.* 200° in the presence of the above named dienes give the products expected from the reaction of **2**. The negative ion mass spectra of the conjugative acid of **1** show peaks with *m/e* appropriate for **2**.

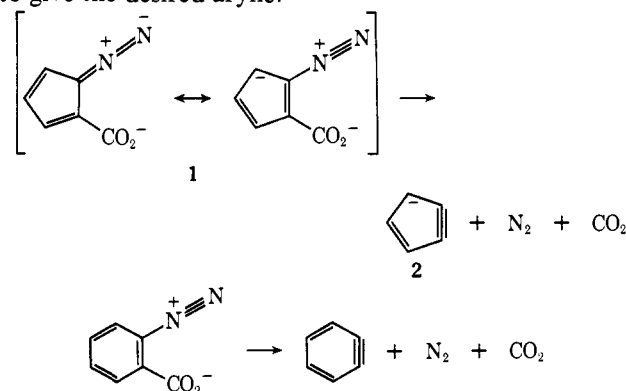
Structure–reactivity relationships and synthetic applications involving arynes intermediates have continued³ to generate widespread interest since Roberts' ⁴ demonstration of the intermediacy of the parent member of the series, benzyne⁴ (or dehydrobenzene⁵). One of the more characteristic reactions of benzyne, which has been widely used to provide evidence for its intermediacy, is the Diels–Alder addition to dienes, such as anthracene,^{6–8} tetracyclone,^{8,9} α -pyrone,¹⁰ diphenyl-*sym*-tetrazine,¹¹ and others,¹² to give characteristic isolable products.

The dehydrocyclopentadienyl anion (**2**), a very interesting but hitherto unknown analog of benzyne, is related to the aromatic 6π -electron cyclopentadienyl anion as benzyne is related to benzene. Its theoretical interest and potential synthetic utility prompted us to attempt to generate and characterize it.

Other five-membered heterocyclic arynes have been postulated^{13,14} as intermediates, dating back to the dehydrobenzofuran suggested as an intermediate by Stoermer and Kahlert¹⁵ in 1902. Some evidence for dehydroferrocene has been adduced by Huffman,^{16a} and Wittig^{16b} has reported the trapping of dehydroindene.

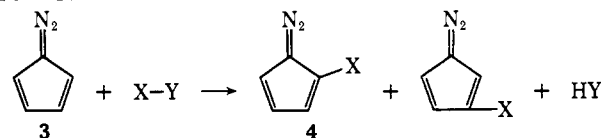
An attractive precursor to this new carbocyclic aryne (**2**) is the diazocyclopentadiene-2-carboxylate anion (**1**), which, by analogy to the well-known reaction

yielding benzyne from benzenediazonium-2-carboxylate, might be expected to lose carbon dioxide and nitrogen to give the desired aryne.



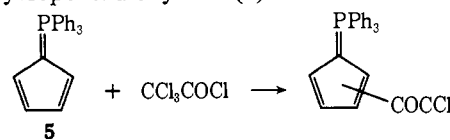
Results

Synthesis. One attractive approach to the synthesis of **1** is *via* acylation reactions carried out on diazocyclopentadiene¹⁷ (**3**). A variety of reagents have been reported¹⁸ to give electrophilic substitution products from **3**.



The treacherously explosive nature of **3** has been noted,¹⁹ but a modification of the Doering–DePuy synthesis¹⁷ has been suggested by Weil and Cais²⁰ to be safer, since it avoids the isolation of the material in the absence of solvent. We must report an explosion which occurred in one reaction mixture (cyclopentadiene, *p*-toluenesulfonyl azide and diethylamine), prepared in the prescribed²⁰ manner, after about 20 min at 3° in a refrigerator. The explosion showed enough force to break other containers in the refrigerator.

Trichloroacetyl chloride acylates triphenylphosphonium cyclopentadienylide (**5**) on the five-membered



(17) W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

(18) D. J. Cram and R. D. Partos, *ibid.*, **85**, 1273 (1963).

(19) F. Ramirez and S. Levy, *J. Org. Chem.*, **23**, 2036 (1958).

(20) T. Weil and M. Cais, *ibid.*, **28**, 2472 (1963).

(1) Abstracted from the Ph.D. Thesis of D. R. Bloch, University of Illinois, 1970. Presented in part at the IUPAC Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, Aug 1970, and at the National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(2) University of Illinois Fellow, 1967; USPH Trainee, 1967–1970 (USPH-2G-722).

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

(4) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Amer. Chem. Soc.*, **75**, 3290 (1953).

(5) R. W. Hoffmann, *Naturwissenschaften*, **52**, 655 (1965).

(6) M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, **82**, 3802 (1960); F. M. Logullo and L. Friedman, *ibid.*, **85**, 1549 (1963); B. H. Klanderman and T. R. Criswell, *ibid.*, **91**, 510 (1969).

(7) B. H. Klanderman, *ibid.*, **87**, 4649 (1965).

(8) L. Friedman and F. M. Logullo, *J. Org. Chem.*, **34**, 3089 (1969).

(9) L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965).

(10) G. Wittig and R. W. Hoffmann, *Chem. Ber.*, **95**, 2718 (1962).

(11) J. Sauer and G. Heinrichs, *Tetrahedron Lett.*, 4979 (1966).

(12) Reference 3, p 208.

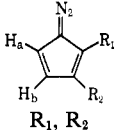
(13) G. Wittig and V. Wahl, *Angew. Chem.*, **73**, 492 (1961); G. Wittig, *Pure Appl. Chem.*, **7**, 180 (1963); T. Kauffmann, A. Risbert, J. Schultz, and R. Webber, *Tetrahedron Lett.*, 3563 (1964); G. Wittig, *Angew. Chem., Int. Ed. Engl.*, **1**, 415 (1962); T. Kauffmann, R. Nurnberg, J. Schultz, and R. Stabba, *Tetrahedron Lett.*, 4273 (1967).

(14) Reference 3, Chapter 6.

(15) R. Stoermer and B. Kahlert, *Chem. Ber.*, **35**, 1633 (1902).

(16) (a) J. W. Huffman, L. H. Keith, and R. L. Asbury, *J. Org. Chem.*, **30**, 1600 (1965); (b) G. Wittig and H. Heyn, *Chem. Ber.*, **97**, 1609 (1964).

Table I. Spectroscopic Parameters of Diazocyclopentadiene Derivatives

	Nmr							Infrared		Ultraviolet	
	Solvent	δ			J_{HH} , Hz			Solvent	cm^{-1}	Solvent	$m\mu$ (ϵ)
		H_a	H_b	H_c	ab	ac	bc				
CO_2H , H_c	<i>a</i>	7.05	6.08	6.90	4.6	2.0	3.3	<i>f</i>	1665	<i>i</i>	219 (11,300), 312 (16,200)
NO_2 , H_c^m	<i>b</i>	7.10	6.04	6.67							
	<i>c</i>	7.2	6.0	6.9	3.7	2.2	4.8	<i>f</i>		<i>j</i>	252 (13,000), 330 (7,000), 385 (6,000)
$\text{C}(\text{CN})=\text{C}(\text{CN})_2$, H_c^m	<i>c</i>	7.7	6.4	7.4	4.2	2.0	3.5			<i>k</i>	268 (14,100), 336 (2,700), 473 (16,800)
CO_2CH_3 , H_c	<i>a</i>	7.03	6.05	6.80	4.6	2.0	3.2	<i>f</i>	1690		
$\text{CO}_2\text{N}(\text{C}_2\text{H}_5)_4$, H_c	<i>a</i>	6.70	5.86	6.48	4.6	2.0	3.2	<i>g</i>	1580		
COCl , H_c	<i>d</i>	7.18	6.12	6.99	4.6	2.0	3.5	<i>g</i>	1728		
CO_2Na , H_c	<i>e</i>	7.05	6.02	6.63	4.8	2.2	3.2			<i>l</i>	214, 310
CO_2K , H_c	<i>b</i>	6.99	6.02	6.67				<i>h</i>	1540	<i>l</i>	215 (9,100), 309 (10,300)
CO_2K -crown ether, H_c	<i>d</i>	6.63	5.77	6.46	4.8	2.2	3.0	<i>f</i>	1570	<i>i</i>	212 (10,300), 310 (15,700)
H_c , CO_2H	<i>a</i>	6.72	6.50	7.57	5.2	2.3	2.1	<i>f</i>	1678		
H_c , NO_2^m	<i>c</i>	6.8	6.4	7.7	5.1	2.5	2.3				260 (10,000), 290 (9,000), 325 (17,000)
H_c , CO_2CH_3	<i>d</i>	6.63	6.34	7.38	5.3	2.3	2.1	<i>g</i>	1715		

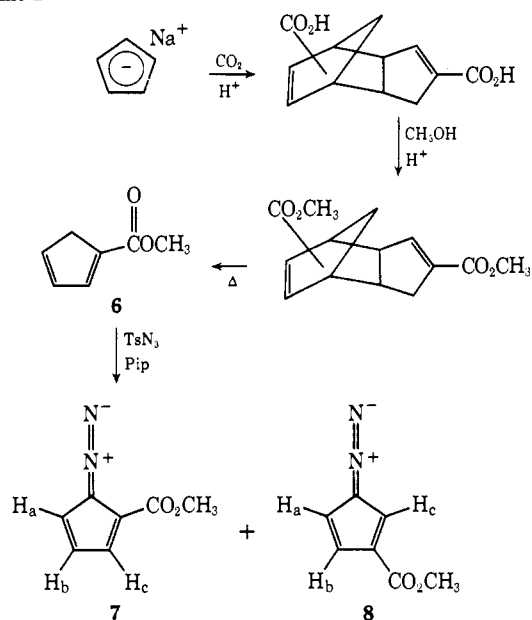
^a Solvent (internal standard), CDCl_3 (TMS). ^b CD_3OD (TMS). ^c CH_3COCH_3 (hexamethyldisiloxane). ^d CCl_4 (TMS). ^e D_2O (DSS). ^f CHCl_3 . ^g CCl_4 . ^h KBr . ⁱ C_6H_{12} . ^j 95% $\text{C}_2\text{H}_5\text{OH}$. ^k CH_3CN . ^l H_2O . ^m Reference 18.

ring.²¹ An analogous reaction to yield **4** ($X = \text{COCl}$) could possibly be followed by a haloform hydrolysis step to give the desired acid precursor to **1**. It was found, however, that reactions of **3** with trichloroacetyl chloride (or bromide), dichloroacetyl chloride, or ethyl chloroformate under a variety of conditions mild enough to preserve the diazo function, failed to give acylation products. Our awareness of the explosion hazard in the preparation of **3**, together with these initial failures to obtain acylation products, led us to explore other routes to **1**.

Modification of the Doering-DePuy synthesis of **3** has been successfully applied²² to substituted cyclopentadienes to prepare aryl-substituted analogs of **3**. Our first approach to **1** following this task was through the methyl ester of cyclopentadienylcarboxylic acid (**6**). The reactions of Scheme I led to the isolation, by chromatography, of **7** and **8** in 32 and 28% yields, respectively.

Structure proof was based primarily on infrared and nmr spectroscopy (Table I). Differentiation of the 2- and 3-substituted diazocyclopentadienes is most conveniently performed by considering nmr spin-spin coupling constants. In every case three-bond coupling constants were larger than four-bond coupling constants. For example, H_b in **7** shows two large (4.6 and 3.2 Hz) coupling constants (to H_a and H_c) whereas both H_a and H_c show one large and one small coupling constant. In **8**, H_c shows two small coupling constants (2.3 and 2.1 Hz). It is possible that the assignments for H_a and H_c should be reversed in **7** and its analogs but this would not invalidate the structure assignment differentiating **7** and **8**. Chemical-shift assignments form an internally consistent pattern in the data of Table I, with protons adjacent to an electro-

Scheme I



negative substituent being shifted to lower fields than those β to the same substituent.

Remaining ambiguities in chemical-shift assignments for the cyclopentadienyl ring protons could conceivably be removed by selective deuteration, if the reported¹⁸ preferential attack of electrophiles α to the diazo function is general. Attempts at acid-catalyzed deuterium exchange showed no evidence of success (by nmr) under conditions mild enough to preserve the diazo function. Heterogeneous catalysis, over palladium or Raney nickel, was also ineffective in promoting deuterium exchange.

The internal consistency seen in Table I for compounds prepared in this study, and for the nitro deriv-

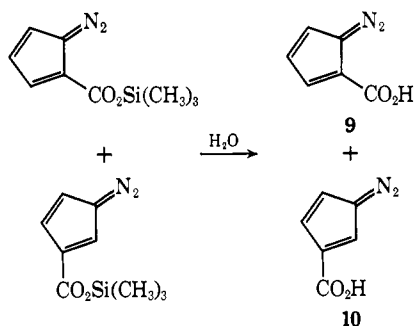
(21) Unpublished work from this laboratory.

(22) M. Regitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 733 (1967).

atives whose structure was established by Cram and Partos,¹⁸ gives us confidence in our structure assignments.

Numerous attempts to hydrolyze ester **7**, under acidic and basic conditions mild enough to preserve the diazo function, were unsuccessful in generating any detectable amount of the carboxylic acid. Conjugation of the carbonyl group with the electron-rich cyclopentadienyl ring of **7**, as evidenced in the low (1690 cm^{-1}) carbonyl stretching frequency in the infrared spectrum, would be expected to make saponification more difficult for **7** than is the case for most methyl esters. Acidic media promote rapid loss of the diazo function.

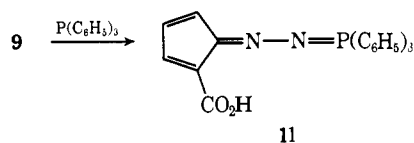
Failure to find conditions for hydrolysis of **7** by acyl-oxygen cleavage led us to consider other synthetic routes in which removal of the protective ester function might be effected by another process. The trimethylsilyl esters proved satisfactory in this respect in that their synthesis by a process analogous to that used for the methyl esters (Scheme I) gave a mixture of trimethylsilyl esters which was easily hydrolyzed to give a mixture of carboxylic acids **9** and **10**. These were



separated by chromatography. Despite evidence for some decomposition on the column, **9** was obtained in 34% yield, and the more slowly eluted **10** in 6% yield. (The nmr spectrum of the crude reaction mixture showed a **9**:**10** ratio of 1.7:1.) The order of elution from silica gel (**9** > **10**) is the same order seen for the 2- and 3-carbomethoxy and the 2- and 3-nitro analogs.

Mass spectrometry, nmr, and infrared evidence (Table I) are compatible with the structures assigned for **9** and **10**.

Further confirmation of the structure assignment for **9** is based on the characteristic reaction of diazocyclopentadienes with triphenylphosphine to give triphenylphosphoranes.^{19,20,22,23} Triphenylphosphine slowly reacts with diazo acid **9** at room temperature in ether-pentane to give **11**.

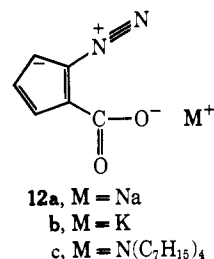


Sodium diazocyclopentadiene-2-carboxylate (**12a**) was prepared from **9** in methanol-sodium methoxide. The light-yellow crystalline sodium salt starts to decompose at *ca.* 170° . The potassium salt **12b** was prepared from **9** and methanol-potassium hydroxide. An nmr spectrum of the salt isolated by removal of the solvent *in vacuo* indicates no detectable amount of

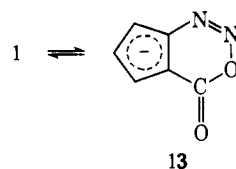
(23) M. Regitz and A. Liedhegener, *Tetrahedron*, **23**, 2701 (1967).

methanol or water of crystallization. The yellow needles of the potassium salt begin to darken at *ca.* 180° and do not melt below 230° .

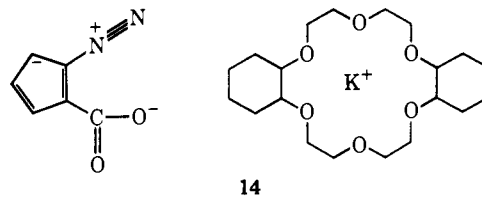
The thermal stability of **9** (mp 164° dec) was somewhat greater than anticipated. In particular the salts, by analogy with benzenediazonium-2-carboxylate, might have been expected to be explosive. We were unable to detonate **9** or its salts, **12**, by heating to 250° , striking with a hammer, treating with acid, or manipulating them during a number of chemical transformations. In one microanalytical combustion of **12b**, heating it in an oxygen atmosphere led to a rapid but nonexplosive evolution of gases. No other evidence for possible explosion hazards was noted. We would, however, in view of the explosive nature of closely analogous compounds, suggest cautious handling of **9** and its salts.



A choice between the zwitterionic open-chain structure **1** and ring-structure **13** for the anion derived from **9** might be based on the spectroscopic data of Table I. Only small changes in chemical shift are seen on going from acid **9** to salts **12a** and **12b** in methanol or water. Such polar solvents would be expected to favor the more polar **1** in the pictured equilibrium.



The complex (**14**) of potassium salt **12b** with dicyclohexyl-18-crown-6 ether²⁴ is soluble in nonpolar organic solvents where charge separation, as in **1**, is unfavored. The upfield shift (0.18–0.32 ppm) seen in the nmr of **14** (relative to **9**) would be consistent with an increased amount of **13** in equilibrium with **1** in chloroform. No convincing collateral evidence for the presence of **13** is discernible in the infrared or ultraviolet spectra, however, leaving us uncertain as to the importance of this isomer at equilibrium.

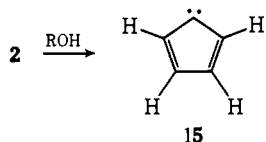


Decomposition and Trapping. The pyrolysis of the sodium salt **12a** in a number of protic media occurs smoothly at temperatures above *ca.* 140° to give nitrogen and, after acidification of the medium, carbon dioxide in approximately equal amounts. Photolysis of

(24) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

12a in water also gives equal amounts of nitrogen and carbon dioxide. This suggests the possibility of generating **2** by these processes.

The basicity of **2** is likely to be at least as great as that of the cyclopentadienyl anion. We might therefore expect rapid protonation in protic solvents, probably to yield cyclopentadienyliene (**15**). If this were rapid enough it would preclude the formation of Diels-Alder adducts of **2**. We therefore decided to avoid protic media for the generation of **2** in trapping



experiments. The solubility of salts **12a** and **12b** in suitable aprotic organic solvents was, however, too low to make them attractive as precursors to **2** in such media. The tetra-*n*-heptylammonium salt (**12c**) was found to be much more soluble.

Pyrolysis of **12c** at 170° in *o*-dichlorobenzene gave nitrogen and carbon dioxide in a ratio of 4:3. In the presence of tetraphenylcyclopentadienone (tetracyclone) (**16**), a small amount of carbon monoxide was also evolved. This could result from the decomposition of the adduct of **2** and tetracyclone. The nonvolatile products were mostly intractable, but were shown to contain tri-*n*-heptylamine. This evidence for destruction of the tetraalkylammonium ion suggests that **2** is sufficiently basic to promote elimination reactions in the ammonium ion to give **15**. This approach was therefore abandoned.

The potassium salt **12b** forms a stable complex, **14**, with dicyclohexyl-18-crown-6 ether. This complex is soluble in most organic solvents.²⁴⁻²⁶ Its pyrolysis, in solution or neat, in the range 140-200° gives approximately equal quantities of nitrogen and carbon dioxide.

Using crown ether complex **14**, we were successful in obtaining products which could have resulted from trapping of the dehydrocyclopentadienyl anion (**2**) with two different trapping agents. Several other trapping agents failed to give positive results.

Tetracyclone (**16**) has been extensively used in trapping benzyne^{8,9} and cycloalkynes.²⁷ The reaction of **2** would be expected to give the carbonyl-bridged adduct **17**. Only a few instances are known where a product of addition of **16** to a triple bond does not lose carbon monoxide upon reaction.^{28,29} Decarbonylation of adduct **17** gives the substituted indenyl anion, which on protonation gives 4,5,6,7-tetraphenylindene (**18**).

The product **18** was identified by comparison with an authentic sample prepared by the reactions of Scheme II. A related set of reactions had been reported earlier³⁰ to yield **18** but the compound had been characterized by its ultraviolet spectrum only. Our

(25) A similar use of crown ether complexes to increase the solubility of reagents has been noted.²⁶ We are grateful to Professor G. Fraenkel for communication of his results to us prior to publication.

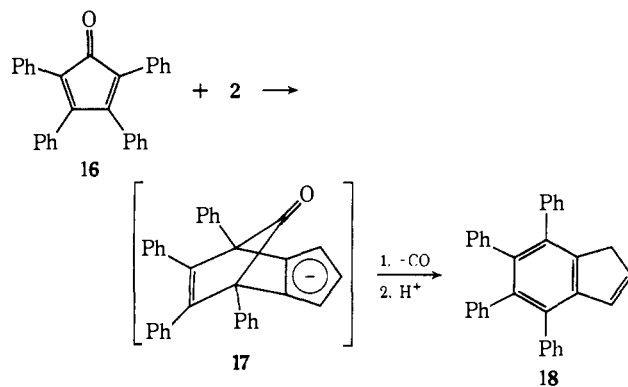
(26) G. Fraenkel and E. Pechhold, *Tetrahedron Lett.*, 153 (1970).

(27) G. Wittig, J. Weinlich, and E. R. Wilson, *Chem. Ber.*, **98**, 458 (1965); A. W. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 953 (1965).

(28) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

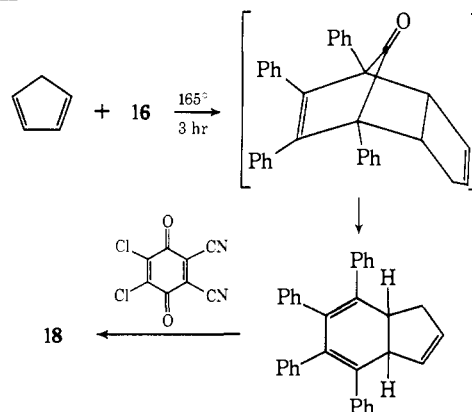
(29) K. MacKenzie, *J. Chem. Soc. C*, 1785 (1969).

(30) R. C. Cookson and D. W. Jones, *ibid.*, 1881 (1965).



nmr, infrared, and mass spectra are consistent with the assigned structure.

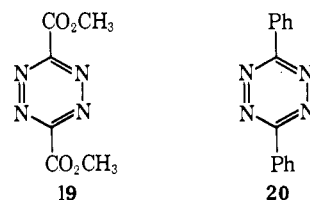
Scheme II



The reaction between **14** and **16** in boiling mesitylene also gave a second, unidentified product of molecular weight 830 (mass spectrum, 814 by osmometry), which contained the elements of two molecules of tetracyclone plus C₅H₂. The oxidation involved in forming this compound may have been carried out by tetracyclone since some 2,3-dihydro-tetracyclone was isolated from the reaction mixture. Further work will be required to establish the structure of this product.

A maximum yield (6.5%) of **18** was obtained by making a paste of **14** and **16** (in a 1.5:1 ratio) in isodurene. The viscous material was pyrolyzed for 1 min at 220°. The product was isolated and its nmr and mass spectra were compared to those of the authentic material. Decreasing the concentration of the reactants results in decreased yields of **18**, reflecting the high reactivity of **2**. Yields were accurately determined by glpc.

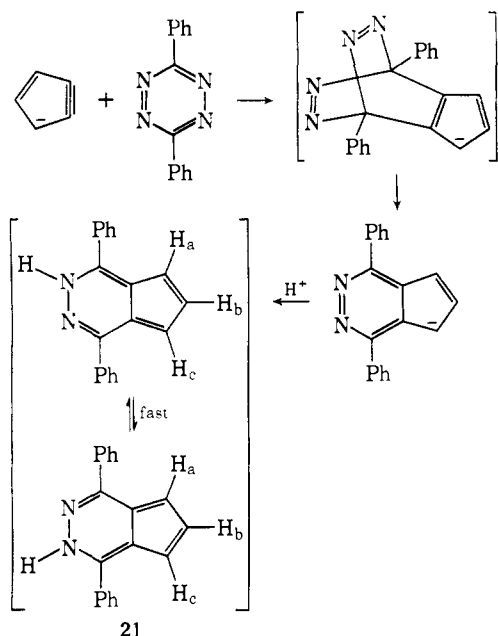
Derivatives of *sym*-tetrazine are less well known as trapping agents but give efficient trapping of arynes.¹¹ Both **19** and **20** have been used to trap benzyne.¹¹



In Diels-Alder reactions **19** and **20** show inverse electron demand,¹¹ reacting more rapidly with electron-rich dienophiles. 3,6-Diphenyl-*sym*-tetrazine (**20**), when present during the pyrolysis of **1**, gives up to 8.1% (of isolated material) of the expected pyridazine **21**

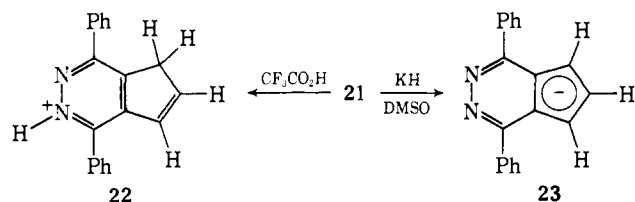
(Scheme III). This was identified by comparison with authentic material³¹ prepared by the addition of cyclopentadiene to **20** with oxidation of this resulting dihydropyridazine to **21**.

Scheme III



The nmr spectrum (in DMSO) of **21** is interesting in that H_b shows up as a clean triplet ($J = 3.5$ Hz) at δ 7.34 and H_a and H_c show up as a doublet at δ 6.86, perhaps reflecting the rapid tautomerization pictured. The doublet did not change with temperature, in deuteriochloroform solvent, over the range of $+44$ to -58° . Protons H_a and H_c are rapidly exchanged upon shaking the nmr sample with D_2O . This azulene analog **21** might be expected^{32,33} to show unusual basicity at these two positions of the aromatic ring, providing a mechanism for deuterium exchange through an intermediate such as **22**. In keeping with this, a solution of **21** in trifluoroacetic acid shows a new two-proton (methylene) doublet of doublets at δ 4.2 in a spectrum characteristic of **22**. A similar protonation has recently been reported³³ for another cyclopenta[*d*]-pyridazine.

The addition of potassium hydride to a DMSO solution of **21** gives anion **23**. The delocalization of the negative charge into the five-membered ring is suggested by the large (*ca.* 0.5 ppm) upfield shift



seen for H_b (δ 6.80) and for H_a and H_c (δ 6.35).

The very low-field chemical shift of the N-H proton (δ 13.9 in DMSO, δ 12.0 in chloroform) may be a reflection of the formation of H-bonded dimers of **21** similar to those formed by carboxylic acids.

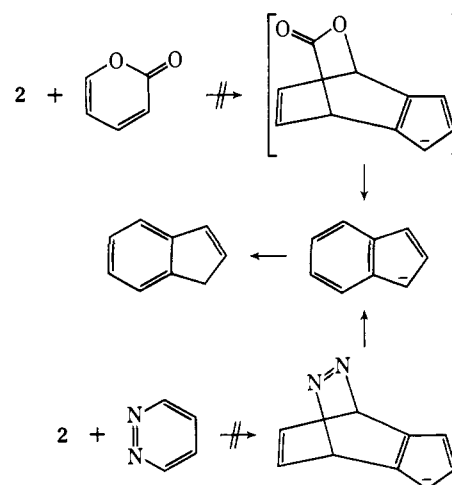
(31) W. J. Linn and W. H. Sharkey, *J. Amer. Chem. Soc.*, **79**, 4970 (1957).

(32) J. Schultz and F. A. Long, *ibid.*, **86**, 322 (1964), and references cited therein.

(33) A. G. Anderson, Jr., and D. M. Forkey, *ibid.*, **91**, 924 (1969).

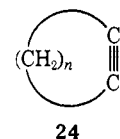
Unsuccessful attempts to trap **2** included the pyrolysis of **1** in the presence of anthracene,⁶⁻⁸ 1,2-diazine,³⁴ and α -pyrone. Small amounts of the expected cycloaddition products could have been missed in the first example. The low concentrations of anthracene which could be dissolved in the reaction medium make it seem unlikely, in view of our results with tetracyclone, that **2** would survive long enough to react with anthracene to give the triptycene analog.

Pyrolysis in α -pyrone and 1,2-diazine, which were employed as solvents for the reaction, gave no detectable (by glpc) trace of the expected product, indene. The decomposition in α -pyrone gave a very large amount of carbon dioxide under conditions at which α -pyrone is stable in the absence of **1**, possibly by some base-catalyzed decomposition. Carbonation of the indenyl anion gives a carboxylic acid which was shown to decarboxylate under the conditions of pyrolysis to give indene. We can therefore say with some certainty that these trapping agents are not successful in intercepting **2** before it reacts in some other way.



Discussion

The dehydrocyclopentadienyl anion might be expected to differ from benzyne in at least two important respects. It is more highly strained, and it bears a negative charge.



The chemistry of the cycloalkynes (**24**) clearly demonstrates the increase in reactivity seen with increased angle strain.³⁵⁻³⁹ Members of the series with $n > 7$ are stable. Cyclooctyne ($n = 6$) is isolable but reactive.³⁶ Cycloheptyne ($n = 5$) has a lifetime of only a few minutes³⁷ at -20° . The lower members

(34) R. H. Mizzoni and P. E. Spoerri, *ibid.*, **73**, 1873 (1951).

(35) W. Tochtermann, K. Oppenländer, and U. Walter, *Chem. Ber.*, **97**, 1318 (1964); R. Willstätter and W. V. Schmaedel, *ibid.*, **38**, 1992 (1905).

(36) A. T. Blomquist and L. H. Liu, *J. Amer. Chem. Soc.*, **75**, 2153 (1953).

(37) F. G. Willey, *Angew. Chem.*, **76**, 144 (1964).

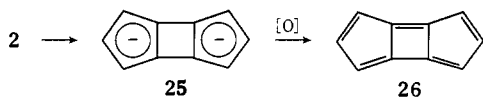
(38) G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3260 (1961); G. Wittig and R. Pohlke, *ibid.*, **94**, 3276 (1961); L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1917 (1965).

(39) L. K. Montgomery and L. E. Applegate, *ibid.*, **89**, 5305 (1967).

of the series ($n = 4$, $n = 3$) have only been demonstrated³⁸ to exist as transient reaction intermediates.

Selectivities, determined³⁹ from product studies of competitive reactions of an alkyne with a mixture of piperidyllithium and phenyllithium, go down as the angle strain increases. The factor by which phenyllithium is the more reactive varies with ring size: cycloheptyne, 21; cyclohexyne, 5.2; and cyclopentyne, 2.6 (with some uncertainty as to the latter value³⁹). Benzyne (4.4) is very similar in selectivity to the analogous six-membered ring alkyne, cyclohexyne.

One might therefore expect the dehydrocyclopentadienyl anion (**2**) to be very reactive, similar perhaps to cyclopentyne in selectivity. We observe that the yield of trapping product from **2** with **16** drops rapidly toward zero as solvent mesitylene is added to lower the concentration of the two reagents. This suggests that the intermediate is indeed very reactive and that it has available to it other reactions rapid enough to compete successfully in dilute solution with the addition to **16**. Attempts to isolate products resulting from such competing processes have so far been unsuccessful. An interesting possibility now being further investigated would involve a dimerization parallel to that by which benzyne gives biphenylene. In this case **25** would result, a compound which would be converted by a two-electron oxidation to **26**, a 10π -electron hydrocarbon of continuing interest.⁴⁰



Pyrolysis of a mixture of potassium salt **14** and anthracene, in the absence of added solvent, gives a residue which still contains 41.5% as much nitrogen as the starting material. This suggests an alternative mode of reaction of **2** involving nucleophilic attack by **2** at the terminal diazo nitrogen of **14** in a reaction analogous to that yielding **11**.

Although benzyne reacts with both nucleophiles and electrophiles^{11,41} there is much evidence that it reacts as an electrophilic dienophile, reacting more rapidly with more electron-rich dienes.^{7,42} The negative charge of **2** might be expected to decrease the electrophilic character of this reactive intermediate and our evidence suggests that this is the case.

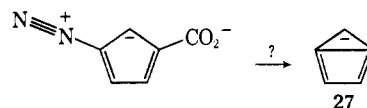
The two trapping agents used successfully in this work, **16** and **20**, differ in that **16** reacts more rapidly with electron-poor dienophiles,⁴³ while tetrazine **20** reacts more rapidly with electron-rich dienophiles.^{11,44,45} Tetracyclone **16** reacts, albeit slowly,^{28,38} with maleic anhydride while **20** does not react with maleic anhydride or tetracycanoethylene.⁴⁴ The opposite order of reactivities is seen toward the electron-rich di-

enophile **2**, if we may regard our yields of trapping product as an index to reaction rate. The yield (a maximum of 6.5%) of **18** in the reaction with **16** is accurately known by glpc studies. The yield (8.1%) of **21** from the reaction with tetrazine **20** was determined by isolation and therefore represents a lower limit. The order of trapping yields (**20** > **16**) is therefore in keeping with the idea that **2** behaves as a nucleophilic dienophile.

We cannot, of course, rule out mechanisms leading to **18** and **21** which do not involve **2**. Stepwise loss of carbon dioxide and nitrogen could possibly yield species capable of reacting with trapping agents in an "aryne" reaction,⁴⁶ giving an intermediate which on subsequent reaction would lead to the observed product. We have not, however, been able to suggest any such alternative to the intermediacy of **2** which seems plausible enough to advance here.

Direct evidence for a species with a high probability of having structure **2** is seen in the negative ion mass spectrum of carboxylic acid **9**. The m/e 63 peak expected for **2** is, however, only 0.4% as intense as the peak at 64, the base peak in the negative ion spectrum. Other peaks are seen at m/e 136 (M, 0.5%), 135 (M - 1, 3.2%), and 108 (M - 28, 3.6%). The decarboxylation leading to the m/e 64 peak must occur with rearrangement of the carboxyl proton to the ring. Neither methyl ester **7** nor the corresponding trimethylsilyl ester shows a peak at m/e 63.

It is interesting to note that diazocyclopentadiene-3-carboxylic acid also shows a peak at m/e 63. In one spectrum, obtained at an ionizing voltage of 25 eV, this peak has an intensity of 23%. It is interesting, in view of this observation, to speculate on the possible stability of the 1,3-dehydrocyclopentadienyl anion (**27**) which is related to 1,3-dehydrobenzene postulated by Berry, Clardy, and Schafer.⁴⁷ Both acids (**9** and **10**) show major peaks at m/e 63 in the positive ion spectra.



Experimental Section

Melting points were determined on a hot-stage apparatus using calibrated thermometers. Infrared spectra were taken with Perkin-Elmer Model 521, 237b, and 137 instruments. Ultraviolet spectra were taken with a Perkin-Elmer Model 202 spectrophotometer using 1.0-cm matched quartz cells. Nuclear magnetic resonance spectra were taken on Varian Associates A-60, A-60A, A-56/60, HA-100, and HA-220 instruments. Selected spectra were run by Mr. R. L. Thrift and staff. Chemical shifts are reported on the δ scale, parts per million downfield from tetramethylsilane as internal standard. Coupling constants, J , were determined from first-order analyses of the observed spectra. Gas chromatographic analyses were performed on Varian Aerograph 202B (thermal conductivity) and 204B (hydrogen flame ionization) gas chromatographs. Elemental analyses were performed by Mr. J. Nemeth and associates. Mass spectra were run on an Atlas CH4 mass spectrometer by Mr. J. Wrona. High-resolution mass spectra were run by Mr. R. L. Foltz, Battelle Memorial Institute, Columbus, Ohio.

Glassware was dried in an oven at 210° for a minimum of 5 hr and cooled in a nitrogen atmosphere. Solvents and reaction materials

(40) A. G. Anastassiou and G. W. Griffin, *J. Org. Chem.*, **33**, 3441 (1968); G. W. Griffin, A. G. Anastassiou, and F. L. Setliff, *ibid.*, **31**, 2705 (1966); P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962).

(41) Reference 3, Chapter 2.

(42) R. Huisgen and R. Knorr, *Tetrahedron Lett.*, 1017 (1963); F. M. Beringer and S. J. Haung, *J. Org. Chem.*, **29**, 445 (1964).

(43) J. J. Dudkowski and E. I. Becker, *ibid.*, **17**, 201 (1952); I. Benghiat and E. I. Becker, *ibid.*, **23**, 885 (1958); D. N. Matthews, Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., June 1961, quoted in ref 28.

(44) R. A. Carboni and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81**, 4342 (1959).

(45) J. Sauer, A. Mielert, D. Land, and D. Peter, *Chem. Ber.*, **98**, 1435 (1965).

(46) J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *Chem. Commun.*, 299 (1970).

(47) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1011 (1965).

were purified and dried by standard techniques immediately preceding their use.

Attempted Acylation of Diazocyclopentadiene (3). (A) A pentane solution of diazocyclopentadiene²⁰ (3) was treated with 1 equiv of trichloroacetyl chloride and triethylamine. Infrared and nmr spectra indicated no acylation on the cyclopentadiene ring. Acylation did not occur when triethylamine was used as the solvent. The addition of silver tetrafluoroborate to an acetonitrile solution of 3 and trichloroacetyl chloride gave no reaction at 0°, but when warmed to room temperature, the diazo function was destroyed (by infrared spectroscopy). Similar results were observed with acetyl chloride and ethyl chloroformate.

(B) A pentane solution of 3 was treated with dichloroacetyl chloride and triethylamine. No acylated product was detected.

Isomeric Methyl Diazocyclopentadienecarboxylates (7 and 8). To 1.255 g (10.1 mmol) of methyl cyclopentadiene-2-carboxylate⁴⁸ in 15 ml of dry methylene chloride was added 1.91 g (10.6 mmol) of *p*-toluenesulfonyl azide. The solution was cooled to -78° to 0.584 g (5.2 mmol) of triethylenediamine in 1 ml of methylene chloride was added dropwise under nitrogen. The resulting yellow solution was slowly warmed to 3°, during which time it turned dark red. After 15 hr, the solution was concentrated and chromatographed over 60 g of silica gel. Elution with 2.5% ether-petroleum ether (30-60°) was continued until the yellow 2 isomer (7) was removed from the column: 615 mg (32%); ir (CHCl₃) 2940, 2120 (=N=N), 1690 (C=O), 1525, 1445, 1395, 1360, 1290, 1265, and 1090 cm⁻¹; nmr (CDCl₃), δ 3.82 (s, 3.0, -CH₃), see Table I; mass spectrum, positive ion (70 eV) *m/e* (relative intensity) 151 (10), 150 (100), 119 (14), 107 (100), 92 (25), 91 (65), 64 (27), 63 (80); negative ion (70 eV) 150 (0.6), 122 (4.2), 64 (100).

Elution with 5% ether-petroleum ether removed the liquid yellow 3-isomer 8: 424 mg (28%, determined by nmr); ir (CCl₄) 2950, 2100 (=N=N), 1715 (C=O), 1530, 1442, 1430, 1345, 1230, 1175, 1115, and 930 cm⁻¹; nmr (CCl₄) δ 3.75 (s, 3.0, -CH₃), see Table I; mass spectrum (70 eV) *m/e* (relative intensity) 151 (10), 150 (100), 134 (17), 125 (21), 122 (42), 119 (58), 105 (41), 97 (48), 85 (73), 63 (52).

Attempted Hydrolysis of Methyl Diazocyclopentadiene-2-carboxylate (7). (A) Basic solvolysis media included aqueous sodium hydroxide, sodium hydroxide in diglyme, potassium *tert*-butoxide in DMSO, 5-30% potassium hydroxide in methanol, liquid ammonia, and benzene-Triton B. Under relatively mild conditions (5% potassium hydroxide-methanol, room temperature) no reaction occurred while under more strenuous conditions (30% potassium hydroxide-methanol) the 2120-cm⁻¹ peak (diazo function) was lost without formation of the desired acid.

(B) Acidic hydrolysis media included 90% acetic acid, acetic acid containing 0.01-1% sulfuric acid, 50-100% aqueous formic acid at various temperatures, and trifluoroacetic acid. Ester 7 was unaffected by 90% acetic acid at room temperature, but was slowly destroyed at 50° without formation of the desired acid. The ester was unaffected in formic acid at 0°, but rapid loss of the 2120-cm⁻¹ peak (the diazo function) occurred at room temperature. Varied amounts of sulfuric acid and trifluoroacetic acid resulted in destruction of the diazo function.

Diazocyclopentadienecarboxylic Acids (9 and 10). To 25.0 g (0.230 mol) of freshly distilled chlorotrimethylsilane, bp 58-59°, and a suspension of 25.0 g (0.114 mol) of isomeric dicyclopentadienedicarboxylic acids in 500 ml of dry benzene was added 18.6 ml (0.230 mol) of dry pyridine dropwise, under nitrogen with stirring. Pyridine hydrochloride began to precipitate upon addition of the base and stirring was continued for 5 hr. The reaction mixture was filtered under nitrogen and the solvent was removed to give 35.2 g (84.8%) of crude oily trimethylsilyl ester dimers: ir (benzene) 2920, 1685 (C=O), 1450, 1275, 1240, 1160, 1120, 1090, and 1075 cm⁻¹.

The crude trimethyl ester dimers were cracked at an oil bath temperature of 165°. The trimethylsilyl ester distilled between 75 and 78° (1.7 mm) to give 29.1 g (82.6%) of colorless material: ir (benzene) 2920, 1680 (C=O), 1590, 1470, 1360, 1310, 1250, 1090, and 950 cm⁻¹.

Anal. Calcd for C₉H₁₄O₂Si: C, 59.30; H, 7.74. Found: C, 59.33; H, 7.64.

To 1.59 g (8.73 mmol) of trimethylsilyl ester in 15 ml of dry ether was added 1.59 g (8.87 mmol) of *p*-toluenesulfonyl azide.

The solution was cooled to -78° under nitrogen and 0.86 ml (8.7 mmol) of piperidine was added dropwise. The resulting dark solution was transferred to an ice bath and stirred for 3 hr and then warmed to room temperature and stirred overnight. The reaction mixture stood 1 day at room temperature during which time a precipitate formed. The ether solution was decanted and extracted with 10- and 5-ml volumes of 5% NaHCO₃.

Ether extraction of the acidified (HCl) aqueous phase gave 673 mg of a yellow-red solid which was chromatographed over 20 g of silica gel. Elution with 25% ether-hexane gave 403 mg (34.2%) of the diazo-2-carboxylic acid (9); after recrystallization from ether mp 164.0-164.5°; ir (CHCl₃) 3100-2400 (acid O-H), 2120 (=N=N), 1665 (C=O), 1530, 1450, 1370, 1300, 1257, 1090, and 1055 cm⁻¹; nmr, see Table I; uv, see Table I; neut equiv 136.4 ± 1.0; mass spectrum, positive ion (70 eV) *m/e* (relative intensity) 137 (8), 136 (100), 103 (3) 91 (17), 63 (81); negative ion (70 eV) 136 (0.5), 135 (3.2), 108 (3.6), 64 (100), 63 (0.4).

Anal. Calcd for C₈H₄N₂O₂: C, 52.95; H, 2.96; N, 20.58. Found: C, 53.16; H, 2.97; N, 20.56.

Elution with 50% ether-hexane gave 168 mg of a mixture of the diazo-3-carboxylic acid and *p*-toluenesulfonamide. The solid was extracted with a small volume of ether, leaving white insoluble amide. Recrystallization from ether gave 74.5 mg (6.32%) of acid 10 as amber crystals: mp 171-172°; ir (CHCl₃) 3100-2400 (acid O-H), 2110 (=N⁺=N⁻), 1678 (C=O), 1530, 1445, 1250, 1185, and 933 cm⁻¹; nmr, see Table I; neut equiv 136.9 ± 1.0; mass spectrum, positive ion (70 eV) *m/e* (relative intensity) 137 (2), 136 (100), 108 (32), 91 (7), 64 (13), 63 (72); negative ion (70 eV) 136 (0.3), 135 (2.8), 108 (100), 64 (27.4), 63 (0.5), (25 eV) 135 (2.7), 108 (100), 64 (95), 63 (23).

Anal. Calcd for C₈H₄N₂O₂: C, 52.95; H, 2.96. Found: C, 53.17; H, 3.17.

Attempted Deuterium Exchange on Diazocyclopentadiene-2-carboxylic acid (9). Deuterium exchange attempts involved stirring acid 9 (a) for 24 hr with Raney nickel (W-2) in tetrahydrofuran (THF)-deuterium oxide (D₂O), (b) in THF-D₂O containing a small amount of 5% palladium on charcoal, (c) for 10 hr in acetic acid-*d* with 5% palladium on charcoal, and (d) for 4 weeks with acetic acid-*d*. For each reaction, the solvent was removed *in vacuo*. The nmr spectra of the residues were identical with that of undeuterated acid 9 and the three cyclopentadiene proton absorptions were of equal areas.

(2-Carboxycyclopentadienylhydrazono)triphenylphosphorane (11). A 5-ml ether solution of 200 mg (1.47 mmol) of diazo acid 9 and a 10-ml pentane solution of 400 mg (1.53 mmol) of triphenylphosphine were mixed and set aside in the dark at room temperature for 24 hr. The dark red product slowly crystallized, giving 535 mg of crude material. Two recrystallizations from *n*-hexane-tetrahydrofuran gave 297 mg (0.745 mmol, 50.7%) of orange-brown platelets: mp 122-123° dec; ir (CHCl₃) 3000, 2550, 1717 (C=O), 1512, 1440, 1343, 1170, 1012, and 835 cm⁻¹; nmr (CDCl₃) δ 6.55 (d of d, 1.0, *J* = 5.3 Hz, *J'* = 2.7 Hz), 6.90 (d of d, 1.0, *J* = 5.3 Hz, *J''* = 1.7 Hz), 7.2-7.9 (m, 16.0), and 10.75 (broad, 0.7, CO₂H).

Anal. Calcd for C₂₄H₁₉N₂O₂P: C, 72.36; H, 4.81. Found: C, 72.67; H, 4.84.

Sodium Diazocyclopentadiene-2-carboxylate (12a). To 524 mg (3.85 mmol) of diazo acid 9 was added 3.5 mmol of sodium methoxide in methanol. The methanol was removed *in vacuo* and the light yellow residue was washed with dry ether to remove the excess acid. The salt begins to darken at 170° and steadily turns darker up to 230°. No liquification is observed; nmr and uv, see Table I.

Decomposition of Sodium Diazocyclopentadiene-2-carboxylate (12a). A flask, containing sodium salt 12a dissolved in diglyme, was flushed with helium and sealed with a serum stopper. The solution was heated to 160° and gas samples were periodically removed and analyzed by glpc (8 ft × 1/8 in., Porapak Q, Waters Association, Inc.). The ratio of nitrogen to carbon dioxide remained >1. After 30 min, the solution was acidified and glpc analysis indicated approximately equal amounts of nitrogen and carbon dioxide.

A sample of 12a in water was photolyzed with two G.E. Sunlamps in a Vycor test tube. The tube was flushed with helium and sealed. Periodic removal of a gas sample indicated only nitrogen was present (glpc). After 50 min, the solution was acidified and the nitrogen-carbon dioxide ratio was 1:1. No acid 9 was present after photolysis.

Tetra-*n*-heptylammonium Diazocyclopentadiene-2-carboxylate (12c). Tetra-*n*-heptylammonium iodide (860 mg, 1.60 mmol) was stirred magnetically with silver oxide (523 mg, 2.26 mmol) in 5 ml

(48) W. E. Franklin, C. H. Mack, and S. P. Rowland, *J. Org. Chem.*, **33**, 626 (1968).

of anhydrous methanol for 2 hr. The mixture was filtered and the solvent was removed *in vacuo*. The residue was taken up in 25 ml of dry benzene and diazo acid **9** (218 mg, 1.60 mmol) was added. The solution was concentrated to 10 ml, diluted to 25 ml with benzene, and again concentrated to 10 ml. The remainder of the benzene was removed *in vacuo*, leaving a brown oil. Several attempted crystallizations were unsuccessful: ir (CCl₄) 2120 (=N=N), 1580 (C=O), 1460, 1395, 1385, 1330, 1285, 1095, and 1045 cm⁻¹; nmr (CDCl₃), 3.0–3.5 (m, 8.0, -CH₂(CH₂)₂CH₃), and 0.7–1.9 (m, 52.0, -CH₂(CH₂)₂CH₃), and see Table I.

Pyrolysis of Tetra-*n*-heptylammonium Diazocyclopentadiene-2-carboxylate (12c). An *o*-dichlorobenzene solution of ammonium salt **12c**, prepared from 30 mg of diazo acid **9**, was heated at 170° for 30 min in the presence of an equivalent amount of tetracyclone. Gas samples, removed periodically and subjected to glpc analysis (6 ft × 1/4 in., Porapak Q, 44°), indicated the presence of nitrogen, carbon dioxide, and carbon monoxide.

Chromatography over alumina with ether eluent gave tri-*n*-heptylamine.

4,5,6,7-Tetraphenylindene (18). To 20 g (0.052 mol) of **16** in 150 ml of mesitylene was added 5.0 ml (0.056 mol) of freshly prepared cyclopentadiene. The solution was heated under reflux for 3 hr. The solvent was removed *in vacuo* giving a light red powder. Five grams of this material was chromatographed over 200 g of silica gel, eluting with 25% benzene–hexane. The first fraction gave 1.29 g of a white solid, mp 158–163°, with no carbonyl absorption. A portion was recrystallized from ethanol to give 3a,7a-dihydro-4,5,6,7-tetraphenylindene: mp 182–185° (lit.³⁰ 184–187°); ir (CHCl₃) 3070, 3010, 1600, 1485, 1440, 1065, 1025, and 910 cm⁻¹; nmr (CDCl₃) δ 7.08 (m, 10.0), 6.75 (m, 10.0), 5.85 (m, 1.0), 5.60 (m, 1.0), 4.25 (m, 1.0), 3.45 (m, 1.0), and 2.85 (m, 2.0); mass spectrum (70 eV) 422.

A 10-ml benzene solution of dihydroindene (200 mg, 0.474 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (108 mg, 0.474 mmol) was boiled for 30 min. The solution was chromatographed over 43 g of alumina (Merck, neutral) with benzene to give 198 mg of **18**, mp 197–203°. Recrystallization from ethanol gave 170 mg (85.5%): mp 208–210° (lit.³⁰ 208–210°); ir (CHCl₃) 3045, 2990, 1595, 1490, 1435, 1380, 1070, 1024, 910, 695, and 590 cm⁻¹; nmr (CDCl₃) δ 3.36 (t, 2.0, *J* = 2 Hz, *J'* = 2 Hz, -CH₂-), 6.46 (t of t, 1.2, *J* = 2 Hz, *J'* = 5.5 Hz, -CH=), 6.74 (m, shoulder, =CH-), 6.80 (m, 11.2, aromatic and vinyl), and 7.12 (m, 10.0, aromatic); mass spectrum (70 eV) *m/e* (relative intensity) 421 (37), 420 (100), 343 (13), and 265 (17).

Anal. Calcd for C₃₃H₂₄: C, 94.28; H, 5.71. Found: C, 94.10; H, 5.62.

1,4-Diphenyl-2*H*-cyclopenta[*d*]pyridazine (21). A solution of freshly prepared cyclopentadiene (2.8 g, 43 mmol) and diphenyl-tetrazine **20**^{44,49} (1.0 g, 4.3 mmol) in 100 ml of carbon tetrachloride was heated for 3 hr at 60°. The initial red solution turned orange during this period. The solvent was removed leaving a yellow-orange residue. Recrystallization from ether–hexane gave 770 mg of yellow solid with an orange coloration. This material was chromatographed over 50 g of silica gel, eluting with 25% ether–hexane. The yellow fraction, preceded by red diphenyltetrazine, was collected and repeatedly recrystallized from benzene to give yellow crystals of analytically pure **21**: mp 210–211° (lit.³¹ 211–212°); ir (CHCl₃) 3400 (N–H), 3000, 1595, 1495, 1460, 1405, 1365, and 1067 cm⁻¹; nmr (DMSO-*d*₆) δ 6.86 (d, 1.8, *J* = 3.5 Hz), 7.34 (t, 1.1, *J* = 3.5 Hz and *J'* = 3.5 Hz), 7.59 (m, 5.9), 8.18 (m, 4.1), and 13.9 (broad, 0.6); uv-visible max (hexane) 211 (ε 3.73 × 10⁴), 250 (ε 5.90 × 10⁴), 280 (ε 3.93 × 10⁴), 320 (ε 9.50 × 10³), and 435 mμ (ε 9.21 × 10³).

Anal. Calcd for C₁₉H₁₄N₂: C, 84.44; H, 5.18; N, 10.37. Found: C, 84.27; H, 5.20; N, 10.36.

Potassium Diazocyclopentadiene-2-carboxylate–Crown Ether Complex. Potassium diazocyclopentadiene-2-carboxylate (**12b**) was prepared by dissolving a slight excess of acid **9** in a methanol solution containing potassium hydroxide. The solvent was removed *in vacuo* and the residue was washed with anhydrous ether to remove excess acid **9**, leaving the potassium salt **12b**: darkens at 180°; ir (KBr) 2120 (=N=N), 1540 (C=O), 1430, 1395, 1370, 1335, 1280, 775, and 683; nmr and uv, see Table I.

Treatment of **12b** with the cyclic ether 3,5,8,15,18,21-hexaoxatri-cyclo[20.4.0.0.0^{9,14}]hexacosane²⁴ gave potassium salt complex **14**: ir (CHCl₃) 2950, 2110 (=N=N), 1570 (C=O), 1395, 1365, 1290, 1090, and 990 cm⁻¹; nmr and uv, see Table I.

Pyrolysis of Potassium Diazocyclopentadiene-2-carboxylate–Crown Ether Complex (14). (a) **In the Presence of Tetracyclone (16).** Dry isodurene (0.4 ml) was added to 4.00 g (10.9 mmol) of dicyclohexyl-18-crown-6 ether and 1.37 g (0.78 mmol) of potassium salt **12b**. The mixture was ground to a paste under nitrogen and 588 mg (1.52 mmol) of **16** was added and thoroughly mixed. The paste was pyrolyzed for 1 min in a bath at 220°. The reaction mixture was cooled rapidly, acidified, diluted to 100 ml with benzene, and boiled for 30 min.

Aliquots were subjected to glpc analysis (5 ft × 1/8 in., 5% FFAP on Chromosorb W, 275°) which indicated a final yield of 213 mg (0.507 mmol) of tetraphenylindene (**18**). The solution was chromatographed over 500 g of alumina (Merck, acid-washed). Elution with hexane gave 190 mg (0.450 mmol) of **18**, confirmed by nmr and mass spectral data.

Elution with 50% benzene–hexane gave 134 mg of unreacted **16** and 100% benzene gave 431 mg of a material that was recrystallized from ether–hexane giving dark purple crystals: mp 285.5–286.5°; ir (CCl₄) 1710 (C=O), 1600, 1580, 1490, 1465, 1442, 1345, 1325, 1165, 1075, and 1010 cm⁻¹; nmr (CDCl₃) δ 5.5 (d, 1.0, *J* = 7.5 Hz), 6.4–6.8 (m, 16), 6.9–7.3 (m, 24), and 7.4 (d, 1.1, *J* = 4 Hz); uv max (dioxane) 266 (ε 562,000), 302 (ε 415,000), 355 (sh) (ε 89,600), 390 (sh) (ε 23,600), and 590 mμ (ε 9440); mass spectrum (70 eV) *m/e* (relative intensity) 832 (24), 831 (68), 830 (100), 802 (16), 774 (15), 753 (2), 725 (8), and 697 (17).

A subsequent fraction yielded 60 mg of *trans*-2,3-dihydro-tetracyclone: mp 161–162.5° (lit.⁵⁰ 160–161°). The ir and nmr were compatible with reported values.⁵⁰

(b) **In the Presence of 1,4-Diphenyl-*sym*-tetrazine (20).** To 200 mg (1.15 mmol) of potassium salt **12b** was added 732 mg (1.98 mmol) of dicyclohexyl-18-crown-6 ether and 2 ml of isodurene. The mixture was stirred until homogeneous and 450 mg (1.92 mmol) of tetrazine **20** was added. The mixture was pyrolyzed under nitrogen for 2.5 min in a bath maintained at 220°. The reaction mixture was cooled, acidified with acetic acid, and chromatographed over alumina (neutral, Merck), eluting with ether. The fraction containing the crude pyridazine **21** was rechromatographed on a 20 × 20-cm precoated preparative tlc plate (silica gel F-258, Brinkmann) with 5% ether–benzene, using known **21** as a standard. An nmr of the desired fraction was identical with that of **21**. Compound **21** was recrystallized from ether–hexane to give 25 mg (8.1%) of material with an infrared spectrum and mass spectrum identical with those of **21**.

(c) **In the Presence of Anthracene.** The pyrolysis was carried out in a drybox under a nitrogen atmosphere. To 45 ml of dry isodurene was added 1.00 g (7.35 mmol) of diazo acid **9** and 4.00 g (10.9 mmol) of dicyclohexyl-18-crown-6 ether. Then 338 mg (8.45 mmol) of potassium hydride was cautiously added and the reaction flask was swirled until bubbling ceased. This solution was added dropwise to 1.90 g (10.6 mmol) of anthracene in 15 ml of isodurene in a three-necked round-bottom flask equipped with a thermometer, dropping funnel, and Vigreux column. The flask was heated in a bath at 220° and the temperature of the reaction medium was maintained above 185°. The addition took 20 min. The reaction solution was cooled overnight and filtered.

The filtrate was concentrated and chromatographed over silica gel with benzene–hexane yielding 1.80 g (94.7% recovered) of anthracene and 4.0 g (100%) of crown ether.

The isodurene insoluble material was heated on the steam bath with 100 ml of water for 1.5 hr. The water-soluble portion (540 mg) contained 65% C, 5.2% H, and 6.9% N (about 18% of the available nitrogen remained). The water-insoluble material (702 mg) did not melt up to 350° and did not sublime at 200° and 0.1 mm. Heating 100 mg of this material overnight in 5 ml of DMSO at 100° dissolved 12 mg, while heating 100 mg in DMF at 150° dissolved 40 mg. The infrared spectrum of each soluble fraction had very broad absorption bands. No further characterization was attempted. In a related run, analysis of the benzene-soluble product fraction showed retention of 41.5% of the total available nitrogen.

(d) **In the Presence of α-Pyrone.** (A) To 10 ml of dry benzene was added 105 mg (0.77 mmol) of **9** followed by 30.8 mg (0.77 mmol) of potassium hydride. The addition was carried out under nitrogen in a glove bag. The mixture was stirred until bubbling ceased and 512 mg (1.39 mmol) of 18-crown-6 ether was added. The solution was filtered and the solvent was removed *in vacuo*. The dark oil

(49) J. Allegretti, J. Hancock, and R. S. Knutson, *J. Org. Chem.*, **27**, 1463 (1962).

(50) J. Ciabattini and G. A. Berchtold, *ibid.*, **31**, 1336 (1966).

was taken up in 2 ml of freshly distilled α -pyrone (110°, 26 mm).⁵¹ The flask was protected from the atmosphere (Drierite-KOH) and pyrolyzed for 75 min in an oil bath maintained at 145°. Aliquots were removed periodically, acidified, and subjected to analysis on a 6 ft \times 1/4 in. column of 10% DEGS on Chromosorb W. No indene was observed.

(B) The above procedure was repeated and aliquots of the gases from the reaction vessel were removed periodically during a 20-min period and analyzed (Porapak Q) indicating a nitrogen-carbon dioxide ratio of 1:120.

In the Presence of 1,2-Diazine. To 28 mg (0.21 mmol) of **9** and 160 mg (0.43 mmol) of 18-crown-6 ether in 2 ml of dry benzene was added 35 mg (0.88 mmol) of potassium hydride. The addition was carried out under nitrogen. After the bubbling ceased, the

(51) H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

solution was filtered. The solvent was removed *in vacuo* and the dark residue was taken up in 2 ml of dry diazine in a 5-ml flask. The flask was fitted with a serum stopper and flushed with helium. The solution was pyrolyzed in an oil bath at 190°. Gas evolution ceased after 7 min. Gas samples removed through the serum cap showed the nitrogen-carbon dioxide ratio to be 1:1 by glpc (5 ft \times 1/4 in., Porapak Q). Trapping the carbon dioxide with Ascarite gave 32% of the theoretical yield.

A portion of the solution was acidified with 5% HCl. No indene was observed by glpc (10% DEGS on Chromosorb W). Another portion was acidified with 1 equiv of HCl and treated with an ether solution containing an excess of diazomethane. No methyl ester was observed by glpc.

Acknowledgment. This research was supported by a grant from the National Science Foundation (NSF-GP 13331).

Stable Carbonium Ions. LXXXV.¹ Laser Raman and Infrared Spectroscopic Study of Alkylcarbonium Ions²

George A. Olah,* John R. DeMember, Auguste Commeyras, and Jean Luc Bribes

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and Faculté des Sciences, Université de Montpellier, Montpellier, France. Received May 13, 1970

Abstract: Raman and infrared spectroscopic data of the *tert*-butyl cation (**1**) and their correlation with those of isoelectronic model trimethylboron provide direct spectroscopic evidence for the planarity of the $^+CC_3$ carbon skeleton. The nearly identical character of the Raman spectra of ion **1** and those of the *tert*-amyl cation (**3**), the dimethylisopropylcarbonium ion (**4**), and the pentamethylethyl cation (**5**) reflects the generally classical nature of these ions.

The first nmr (1H and ^{13}C) and infrared spectroscopic study of stable alkylcarbonium ions generated from ionization of alkyl fluorides in SbF_5 was reported in 1962.³ This was followed by detailed studies of generation of the ions from other precursors in related superacid systems.⁴ Pmr data observed for the *tert*-butyl cation (**1**) as well as *tert*-amyl² and isopropyl^{3,4} cations were consistent with but not conclusive evidence for the planarity of the $^+CC_3$ (or $^+CHC_2$) carbon skeletons. For the dimethylisopropyl- (**4**) and dimethyl-*tert*-butyl- (**5**) carbonium ions, where the possibility exists for degenerate rearrangements (equilibrium I) and/or for a static bridged species (II, III), no clear differentiation was available on the basis of pmr data.

The high-energy (600–3100 cm^{-1}) ir spectra of *tert*-butyl and perdeuterio-*tert*-butyl cation have been reported.^{4a} However, rigorous interpretation of these ir data was not possible since the low-energy ir and the Raman spectra of cation **1** were not available.

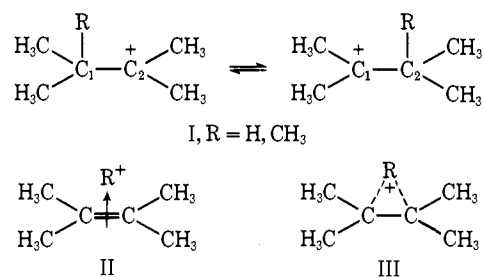
* Address correspondence to this author at Case Western Reserve University.

(1) Part LXXIV: G. A. Olah, J. A. Olah, and R. H. Schlosberg, *J. Org. Chem.*, **35**, 328 (1970).

(2) Presented in part at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 23–25, 1968.

(3) G. A. Olah, Plenary Lecture, 9th Reaction Mechanisms Conference, Brookhaven National Laboratories, Upton, N. Y., Aug 1962.

(4) (a) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964); (b) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).



Recently, we⁵ have reported a cmr investigation of alkylcarbonium ions. On the basis of estimated average shifts and coupling constants, cmr results were indicative of an equilibrating classical pair of carbonium ions for both **4** and **5**, as shown in equilibrium I. Interestingly, although correlations between hybridization and long-range coupling constants are somewhat questionable,^{6,7} the low values of $J_{^{13}CCH}$ obtained for the *tert*-butyl cation could raise the question of the planarity of this ion.⁵ ("Planar," of course, refers always only to the arrangement of bonds at the positive carbon center and not to the overall geometry.)

(5) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(6) G. M. Karabatsos and C. E. Orzech, *ibid.*, **86**, 3574 (1964).

(7) K. A. McLauchlan and T. Schaeffer, *Can. J. Chem.*, **44**, 321 (1966).