

Proton H_8 (τ 2.82) appears as a triplet which collapses into a singlet on irradiation of H_7 and H_9 . Protons H_3 and H_4 (τ 2.33), which accidentally have the same chemical shift, appear as a complex multiplet. On irradiation of H_2 or H_5 , protons H_3 and H_4 collapse into a doublet with some further fine structure. Irradiation of H_6 causes a slight change in the center of the H_3 - H_4 multiplet. Proton H_2 appears as a complex multiplet which is somewhat simplified on irradiation of H_7 and H_9 . Irradiation of H_6 gives no detectable simplification of the H_2 multiplet. Irradiation of H_3 and H_4 changes H_2 into a singlet; however, H_7 and H_9 probably were irradiated at the same time. On irradiation of H_6 or protons H_7 and H_9 , the H_5 complex multiplet collapses somewhat, and on irradiation of H_3 and H_4 , the H_5 multiplet collapses into a doublet.

In view of the complexity of the nmr spectrum, a computer simulation was carried out in order to obtain some of the coupling constants. From the decoupling experiments described above, it is clear that the group of four protons (H_2 - H_5) are coupled only slightly to the group of three protons (H_7 - H_9). Therefore, the two groups can be treated separately, with H_6 decoupled, in order to simplify the calculation. The four-spin system was simulated using the computer program LAME⁸ (LACON3 with magnetic equivalence), and the results are given in Table I.

Table I

J	2,3	2,4	2,5	2,9	3,4	3,5	3,6
Hz	8.9 ^a	0.1 ^a	0.0 ^a	Small ^b	6.7 ^a	1.7 ^a	Small ^b
J	4,5	4,6	5,6	5,7	6,7	7,8	8,9
Hz	7.7 ^a	Small ^b	4.9 ^b	Small ^b	2.0 ^b	4.0 ^b	4.0 ^b

^a Calculated. ^b Measured.

The coupling constants in Table I clearly indicate the structure of ion III. Hence, $J_{7,8}$ and $J_{8,9}$ are both 4.0 Hz, which, when compared to $J_{1,2} = 3.8$ Hz in cyclopentenyl cation,⁹ indicates that carbons C_7 - C_9 are part of a five-membered ring. Furthermore, the coupling constants observed in the four-spin group, H_2 - H_5 , closely resemble those of naphthalene¹⁰ ($J_{1,2} = 8.3$, $J_{1,3} = 1.3$, $J_{2,3} = 6.5$ Hz) and those of 1,3-cyclohexadiene¹¹ ($J_{1,2} = 9.42$, $J_{1,3} = 1.06$, $J_{1,4} = 0.91$, $J_{2,3} = 5.14$ Hz), which indicates that C_2 - C_5 comprise part of a six-membered ring.

Delocalization of charge is indicated by the proton chemical shifts in ion III. The protons H_7 - H_9 in III are shifted considerably upfield relative to H_3 (τ 1.54) and H_4 (τ -1.10) in cyclopentenyl cation.⁹ This demonstrates that C_7 - C_9 in III are not part of an isolated allylic ion. The average shift of protons H_2 - H_5 in III is τ 2.95, whereas that of the olefinic protons in 1,3-cyclohexadiene is τ 4.22 and that of naphthalene is τ 2.45. The deshielding of H_2 - H_5 in III compared to H_1 - H_4 in 1,3-cyclohexadiene indicates delocalization of positive charge onto C_2 - C_5 . This evidence for charge delocalization over the seven carbons C_2 - C_5 and C_7 - C_9 suggests the presence of homointeraction between C_2 and C_9 , and between C_5 and C_7 . In the

(8) Private communication from Dr. B. Kaptein to Dr. F. A. L. Anet.

(9) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968).

(10) N. Jonathan, S. Gordon, and B. P. Daily, *J. Chem. Phys.*, **36**, 2443 (1962).

(11) C. Ganter and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 741 (1966).

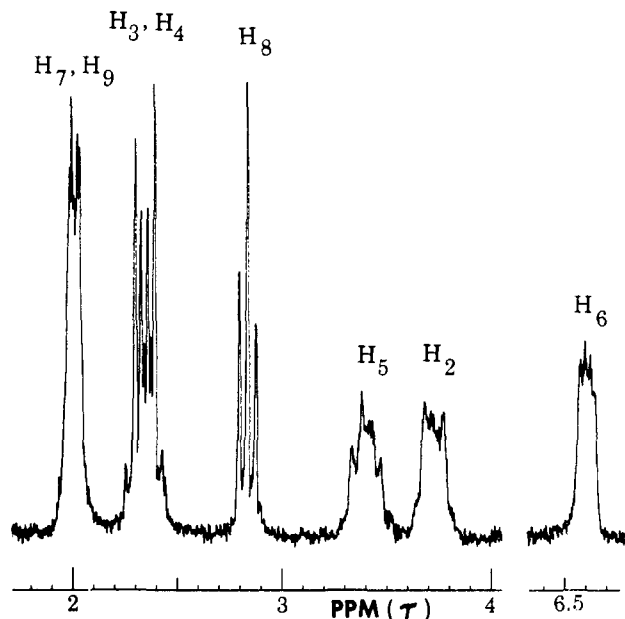


Figure 1. Nmr spectrum (100 MHz) of 1-methylbicyclo[4.3.0]nonatrienyl cation(III) in $\text{FSO}_3\text{H-SO}_2\text{ClF}$ (1:3 v/v) at -85° (the methyl absorption is not shown). CDHCl_2 was used as an internal standard, τ 4.70.

transformation of ion II to ion III, four protons including the bridgehead, H_6 , and the methyl protons are shifted upfield a total of *ca.* 13.1 ppm, and the other seven downfield *ca.* 16.6 ppm. The deshielding of the seven peripheral protons indicates the presence of a ring current in a seven-membered ring in analogy to that observed in monohomotropylium ion IV.² This, together with the evidence for charge delocalization, demonstrates substantial homoaromatic character in cation III.

Work on the generation and observation of other bishomotropylium ions is in progress in these laboratories.

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Flash Vacuum Pyrolysis. VII.¹ Fulvenallene. The Ring Contraction and Expansion of Phenylcarbene Sir:

It now appears that the high-temperature fragmentation of aromatic intermediates such as **1a-c** to cyclo-

(1) Part VI: E. Hedaya, I. S. Krull, R. D. Miller, M. E. Kent,

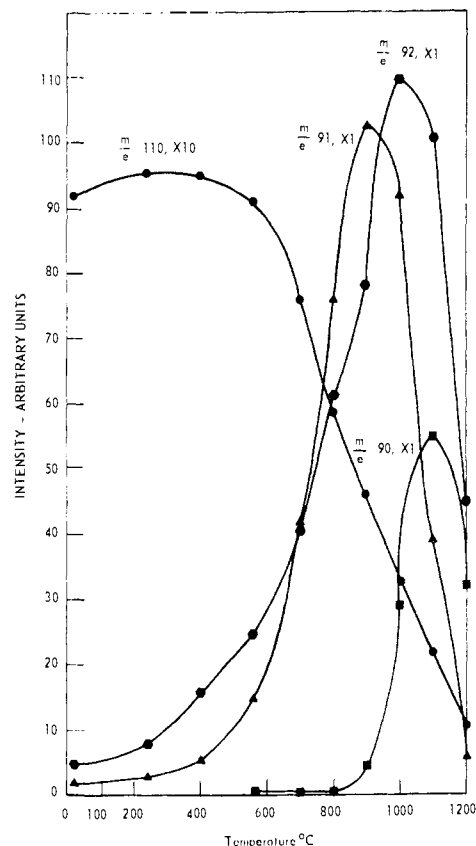
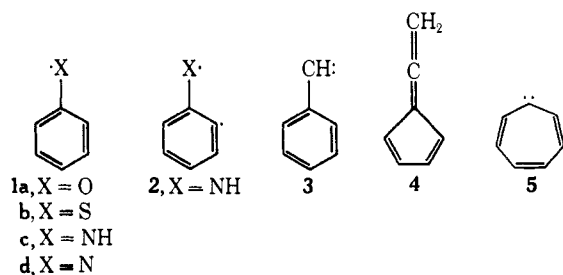


Figure 1. Flash vacuum pyrolysis of benzyl fluoride; attenuation factors are noted.

pentadienyl radicals² and the similar rearrangement of phenylnitrene (**1d**) or its isomer **2** to cyanocyclopentadienes³ has significant generality. Here we report the first example of the ring contraction of an analogous intermediate, phenylcarbene (**3**), to the isolable isomer, 5-vinylidencyclopentadiene⁴ (fulvenallene, **4**). Furthermore, a competing reaction of **3** is its ring expansion to cycloheptatrienylidene (**5**).



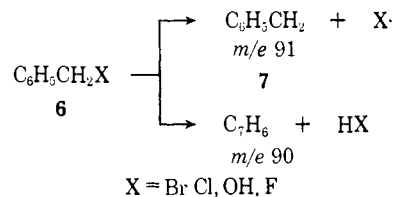
Evidence for formation of **4** was initially obtained in a survey of the flash vacuum pyrolysis (FVP) of benzylic P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 6880 (1969); Part V: E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 1875 (1969).

(2) (a) A. G. Harrison, F. R. Horner, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **85**, 5593 (1963); (b) R. F. Pottie and F. P. Lossing, *ibid.*, **85**, 269 (1963); (c) I. P. Fisher, F. F. Palmer, and F. P. Lossing, *ibid.*, **86**, 2741 (1964); (d) E. Hedaya and D. W. McNeil, *ibid.*, **89**, 4213 (1967).

(3) (a) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967); (b) E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, *ibid.*, 3415 (1968); (c) W. D. Crow and C. Wentrup, *ibid.*, 5569 (1968); (d) W. D. Crow and C. Wentrup, *Chem. Commun.*, 1026 (1968); (e) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6419 (1968).

(4) Some tetraphenyl-substituted derivatives of **4** have been previously reported: (a) H. Prinzbach, U. Fishcher, and R. Cruse, *Angew. Chem.*, **5**, 602 (1966); (b) G. Rio and G. Sanz, *Bull. Soc. Chim. Fr.*, 3367 (1966).

derivatives (**6**) using mass spectroscopy. These were pyrolyzed at low pressures ($\sim 1 \mu$) and short contact times (1 msec) in an oven directly coupled to the ionization chamber of a mass spectrometer.^{5a} We observed that **6** gave both the expected benzyl radical (m/e 91) and a thermal species having m/e 90 (C_7H_6) whose ionization potential (IP (90) 8.65 eV) did not vary with the precursor.



A more detailed study of the fluoride was carried out since the m/e 90: m/e 91 ratio was the largest compared to the other derivatives. The major products had m/e 92, 91, and 90 (Figure 1) while a minor product (not shown) had m/e 182. The presence of benzyl radicals was confirmed by titration with methyl radicals generated by the copyrolysis of ethyl nitrite.^{1,5,6} However, the complexity of the appearance potential curve for m/e 91 at elevated temperatures showed that this results from a superposition of signals of parent and fragment ions from benzyl radicals and toluene, respectively. No new signals were observed which could be associated with the reaction of methyl radicals with m/e 90.

Chemical identification of the m/e 90 thermal species was achieved by pyrolysis of benzyl fluoride at 1050° and *ca.* 100 μ in the apparatus previously described^{5b} where the pyrolysate was rapidly quenched in an ammonia matrix on the surface of a dewar at liquid nitrogen temperatures. Subsequent vacuum distillation of the volatiles and removal of the ammonia gave a brown residue from which a reactive yellow liquid could be obtained. This could, in general, be distilled on the vacuum line at -60 to -30° .

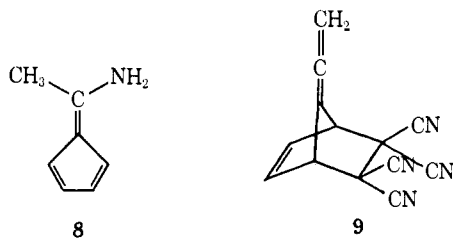
The low-temperature nmr and the reaction products with ammonia and tetracyanoethylene provided evidence for the structure of the yellow product (**4**): nmr ($CDCl_3$, -30°) δ 6.45 (s, 2), 5.35 (s, 1). The nmr solution also contained undecomposed benzyl fluoride and traces of ammonia. The yield of **4** at an oven temperature of 1060° was about 15% on the basis of quantitative nmr analysis using cyclohexane as an internal standard. The reaction of ammonia with **4** was best observed in the nmr solution itself. On warming to temperatures at or above 0° the adduct **8** was obtained: nmr ($CDCl_3$) δ 6.2–6.6 (m, 4), 2.21 (s, 3); mp 81°; partial ir (KBr) 3410, 3320, 3215, 3090, 2940, 2920, 1630, and 1570 cm^{-1} ; uv max (hexane) 316 $m\mu$ (log ϵ 4.3); mass spectrum (70 eV) m/e 107; [lit.⁷ mp 79–81°, uv max (hexane) 316 $m\mu$ (log ϵ 4.3)]. Addition of a dilute solution of tetracyanoethylene in tetrahydrofuran to **4** on the vacuum line at -30° gave the adduct **9**: mp 115° dec; partial ir (KBr) 3090, 2990, 2910, 2300, 2215, 1990, 1432, 1303, 895, 880, 870, and 818 cm^{-1} ; nmr ($(CD_3)_2C=O$) δ 6.90 (t, 1), 5.4 (s, 1), 4.85 (t, 1); partial

(5) (a) P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, **49**, 506 (1968); (b) E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969).

(6) S. Pignataro, A. Cassuto, and F. P. Lossing, *J. Amer. Chem. Soc.*, **89**, 3693 (1967).

(7) K. Hafner, G. Schulz, and K. Wagner, *Ann.*, **678**, 34 (1964).

mass spectrum (70 eV) m/e (relative intensity) 128 (45), 103 (7), 90 (100), 89 (96), 75 (55), 63 (50), 50 (20), 38 (35), and 27 (20).



The mode of formation of **4** can involve a benzyl radical or phenylcarbene precursor which is converted to a bicyclic intermediate. We favor the phenylcarbene route because: (1) the trend in the m/e 90:91 ratio from different benzylic derivatives suggests an α -elimination process rather than stepwise elimination of HX (Br < Cl < OH < F). (2) No evidence for **4** was observed from benzyl radicals generated by pyrolysis of benzyl nitrite or bibenzyl in the temperature range 400–1100°. (3) The FVP of phenyldiazomethane also gave fulvenallene in substantial yields at >900°.

In the latter experiments phenyldiazomethane (**10**), which was prepared by pyrolysis of the sodium salt of benzaldehyde tosylhydrazone and purified by distillation *in vacuo*,⁹ was subjected to flash vacuum pyrolysis (FVP) using the apparatus designed for the isolation of products.^{5b} Rapid quenching of the pyrolysate at liquid nitrogen temperatures and subsequent distillation gave a volatile fraction and a residue. The volatile fraction was characterized by nmr and was found to contain benzene, fulvenallene (**4**), and ethynylcyclopentadiene (**11**)¹⁰ as major products; toluene was a minor product. The yields of **4** and **11** increased dramatically with increasing temperature (Table I). In contrast,

Table I. Flash Vacuum Pyrolysis of Phenyldiazomethane^a

T , °C	Product distribution ^b			
	C_6H_6	4	11	Residue
600	5	Trace		54
800	4	10	4	31
900	10	30	14	16
1000	9	25	19	12

^a Average oven pressure was about 0.05 Torr; rate of sample introduction was about 1.5 mg/min. ^b Mole %, except for residue which is weight %.

the weight per cent yield of the residue decreased. Analysis of the residue obtained at 600° by nmr showed that heptafulvalene (**12**)¹¹ was the major component (39% yield based on **10**). On the other hand, the residue formed at 900° consisted of *cis*- and *trans*-stilbene (3.0 and 4.0%, respectively on the basis of nmr and glpc analysis). Anthracene was another major

(8) (a) R. F. Pottier and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 2634 (1960); (b) F. P. Lossing, private communication.

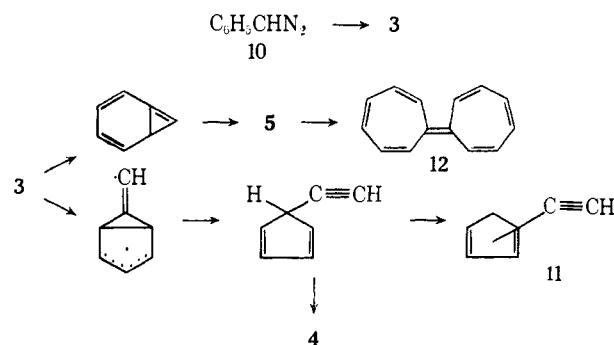
(9) G. M. Kaufman, J. A. Smith, G. G. Vendor Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

(10) The characterization of this isomer is described in the accompanying report: E. Hedaya and M. E. Kent, *ibid.*, **92**, 2149 (1970).

(11) (a) W. von E. Doering, "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworth Scientific Publications, London, 1959, p 35; (b) J. R. Mayer, Ph.D. Dissertation, Yale University, 1955; (c) D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Amer. Chem. Soc.*, **86**, 3329 (1964).

component. These products were also formed by the FVP of heptafulvalene (**13**) itself at 900°.

The data indicate that phenylcarbene (**3**) undergoes ring expansion at lower temperatures ($\leq 600^\circ$)¹² to cycloheptatrienylidene (**5**) and ring contraction at temperatures $> 600^\circ$, as summarized by the scheme postulated below. Thus, thermally generated phenylcarbene in the gas phase appears to have very different properties compared to **3** generated in solution by photolysis or base-induced α elimination.¹⁴



(12) Professor W. M. Jones has informed us that they have also observed the formation of heptafulvalene when the sodium salt of benzaldehyde tosylhydrazone is pyrolyzed over glass beads at 250° and 40 Torr in a rapid stream of nitrogen. The intermediacy of cycloheptatrienylidene was invoked to rationalize their data.¹³

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(14) (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964; (c) H. Dietrich and G. W. Griffin, *Tetrahedron Lett.*, 153 (1968); (d) G. L. Closs and K. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964); C. D. Gutsche, G. L. Bachman, and R. J. Coffey, *Tetrahedron*, **18**, 617 (1962).

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Flash Vacuum Pyrolysis. VIII.¹ 1,2-Indandione. A Source of Fulvenallene and Some of Its Isomers

Sir:

In the previous report¹ we described the isolation and characterization of fulvenallene (**4**) which was obtained by the flash vacuum pyrolysis (FVP) of benzyl fluoride or phenyldiazomethane. Evidence was also presented which implied a phenylcarbene primary intermediate (**3**). An alternate approach to **4** was suggested by the rearrangement of **2** (a phenylnitrene isomer generated from benzotriazole) to cyanocyclopentadienes.² Analogously, the phenylcarbene isomer **13** could be a fulvenallene (**4**) source. Here we report the FVP of 1,2-indanedione (**14**)³ which efficiently undergoes sequential thermal decarbonylation most likely to **13** and ultimately **4**.

The FVP of **14** was not studied using mass spectroscopy owing to its involatility. Rapid quenching of the

(1) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970).

(2) (a) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967); (b) W. D. Crow and C. Wentrup, *Chem. Commun.*, 1026 (1968); (c) E. Hedaya and M. E. Kent, unpublished results.

(3) M. P. Cava, R. L. Little, and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2257 (1958).