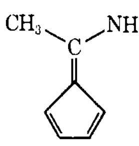
mass spectrum (70 eV) m/e (relative intensity) 128 (45), 103 (7), 90 (100), 89 (96), 75 (55), 63 (50), 50 (20), 38 (35), and 27 (20).



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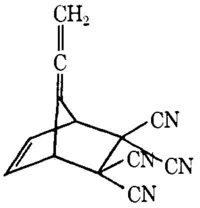


9

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

Table I. Flash Vacuum Pyrolysis of Phenyldiazomethane[a]

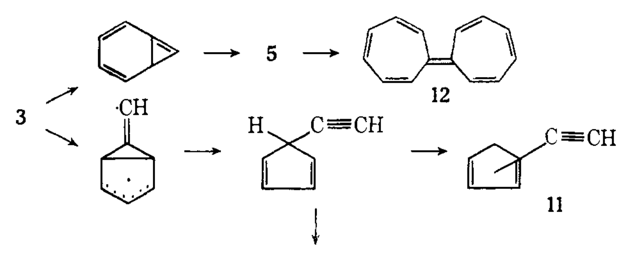
T, °C	Product distribution[b] C_6H_6	4	11	Residue
600	5	Trace		54
800	4	10	4	31
900	10	30	14	16
1000	9	25	19	12

[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 data indicate that phenylcarbene (**3**) undergoes *ring expansion* at lower temperatures (≤600°)[12] to cycloheptatrienylidene (**5**) and *ring contraction* at temperatures >600°, 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]

$C_6H_5CHN_2 \longrightarrow 3$

10



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(8) (a) R. F. Pottie 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).

(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]

(13) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969).

(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 report[1] 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

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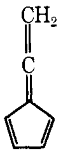
(1) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970).

(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).



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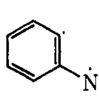

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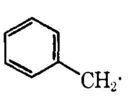

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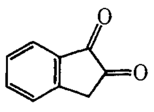
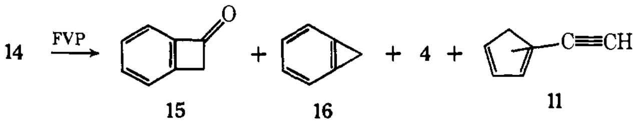


14

pyrolysate on the surface of a large dewar at liquid nitrogen temperatures gave a product mixture consisting of benzocyclobutenone (**15**), benzocyclopropene (**16**), fulvenallene (**4**), and ethynylcyclopentadiene (**11**). Benzocyclobutenone (**15**) showed the following characteristics: mp 203–205° (2,4-dinitrophenylhydrazone derivative); ir (neat) 1785 and 1764 (C=O) cm^{-1}; uv max (C_2H_5OH) 290 (ϵ 2900), 282 (ϵ 2900), and 238 (ϵ 10,900) nm; nmr ($CDCl_3$) δ 7.1–7.6 (m, 2), 3.95 (s, 1) [lit.[4] mp 204° (2,4-dinitrophenylhydrazone derivative); ir 1773 and 1756 cm^{-1}; uv max (C_2H_5OH) 293 (ϵ 3980), 285 (ϵ 3980), and 242 (ϵ 14,700) nm]. Benzocyclopropene (**16**) exhibited the following: uv max (~0.1 Torr) 274, 267, 261, 255, and 249 nm; nmr ($CDCl_3$) δ 7.28 (s, 2), 3.2 (s, 1) [lit.[5] uv max (C_6H_{12}) 278, 270, 263, 258, and 250 nm; nmr δ 7.12 (s, 2), 3.11 (s, 1)]. Fulvenallene (**4**) showed: uv max (~0.1 Torr) 242 (strong), 288 (weak), and 335 (weak); partial ir (~0.2 Torr) 3135, 3092, 1935 (C=C=C), and 1073 (C=C=C) cm^{-1}; nmr, as before;[1] partial mass spectrum (50 eV) *m/e* (relative intensity) 90 (100), 89 (93), 88 (2), 87 (3), 86 (5), 85 (3), 78 (4), 64 (17), 63 (51), 62 (24), 61 (9), 51 (13), 50 (10), 39 (20), 38 (11), 37 (5), 28 (25). Ethynylcyclopentadiene (**11**) had the following characteristics:[6] nmr ($CDCl_3$)[7] δ 6.2–6.9 (m), 3.2 (s), 3.0–3.16 (m); partial ir (~0.5 Torr)[8] 3340 (H—C≡C), 2110 (-C≡C-), 1375 (CH_2), 892 (C—C≡CH), and 625 cm^{-1} (H—C≡C).



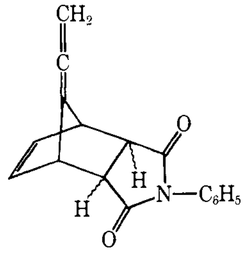
The yields of the various products were found to be temperature dependent (Table I). These data vividly illustrate the efficiency of this FVP process. Benzocyclobutenone was readily separated from the C_7H_6 isomers by distillation on the vacuum line. Complete separation of the C_7H_6 isomers, however, proved to be especially difficult.[6] Nevertheless, relatively pure fulvenallene (**4**) could be readily obtained in convenient quantities which allowed a more complete characterization[1] of this novel molecule. **4** is quite stable in the vapor at low pressures (<0.5 Torr) and this has made possible a detailed vibrational and band-shape analysis of the gas-phase ir spectrum.[9] Its gas uv spectrum was close to that of fulvene (uv max 241, 244, and 362 nm).[10]

Table I. Flash Vacuum Pyrolysis of 1,2-Indandione[a]

	Product distribution, %[b]				
Temp, °C	14	15	16	4	11
600	91	2			
700	37	41	1	2	
750	32	54	3	7	
850		28	8	55	
900		16	4	63	2–5
950		9	3	68	2–5
1000			~0.5	72	5–10

[a] Average oven pressure was about 0.05 Torr; rate of sample introduction was about 1.5 mg/min. [b] Mole %.

Dilute nmr solutions of **4** in chloroform or methanol had random stabilities with some surviving for as long as 2 hr at room temperature. No dimers of **4** have been obtained as yet. Reduction of **4** over Adams catalyst gave ethylcyclopentane (~70%). Besides the tetracyanoethylene adduct, **9**,[1] we have also obtained the adduct **17**[11] from N-phenylmaleimide: mp 166–168°; parent mass 263.09778 (calcd for $C_{17}H_{13}NO_2$: 263.0946); partial mass spectrum (70 eV) *m/e* (relative intensity) 263 (8.3), 173 (40), 129 (6.8), 116 (25), 90 (100), 63 (20); ir (KBr) 5.05 (C=C=C) and 5.66 (C=O) μ; nmr ($CDCl_3$) δ 7.0–7.5 (m, 5), 6.47 (t, 2), 4.90 (s, 2), 3.80–3.95 (m, 2), and 3.40–3.60 (m, 2). An adduct from ethynylcyclopentadiene (**11**) and N-phenylmaleimide was also obtained for which structure **18** was assigned:[11] mp 150° dec; parent mass 263.09560; partial mass spectrum (70 eV) *m/e* (relative intensity) 263 (11), 173 (35), 129 (4.4), 116 (13), 90 (100), 63 (10); ir (KBr) 3.09 (H—C≡C), 5.64, and 5.85 (C=O) μ; nmr ($CDCl_3$) δ 7.1–7.6 (m, 5), 6.34 (m, 2), 3.48 (m, 2), 2.50 (m, 1), 2.0 (m, 2), and 1.6 (m, 1). The chemistry of **4** is being further explored.



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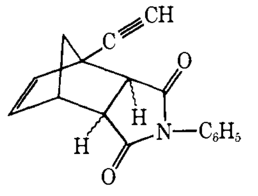

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A scheme which satisfactorily accounts for the products and their temperature dependence is given below. A number of points require verification. First, it is not certain which carbonyl is extruded in the primary step, or even if formation of **19** precedes benzocyclobutenone (**15**). Similarly, decarbonylation of the latter could be concerted. Recently, however, the pyrolysis of 3,3-dimethylindan-1,2-dione at 600° has been reported[12] to give *o*-isopropenylbenzaldehyde as a major product; the intermediacy of **19** is consistent with this result. Also, methyl and cyano or carboalkoxy substituted analogs of the biradical **13** have been detected chemically[13a] and have been assigned a triplet

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(4) (a) M. P. Cava and K. Muth, *J. Amer. Chem. Soc.*, **83**, 652 (1960); (b) M. P. Cava, D. Mangold, and K. Muth, *J. Org. Chem.*, **29**, 2947 (1964).

(5) E. Vogel, W. Grimme, and S. Korti, *Tetrahedron Lett.*, 3625 (1965).

(6) **11** and **4** could not be separated and, consequently, we were not able to completely characterize this product.

(7) The complexity of the nmr absorption at δ 3 indicates the presence of more than one isomer. The ratio of high-field absorption (δ 3) to low field absorption (δ 6–7) is about 1.

(8) The ir data for **11** were obtained from a mixture with **4**. The bands for the latter could be clearly distinguished.

(9) C. L. Angell, unpublished results.

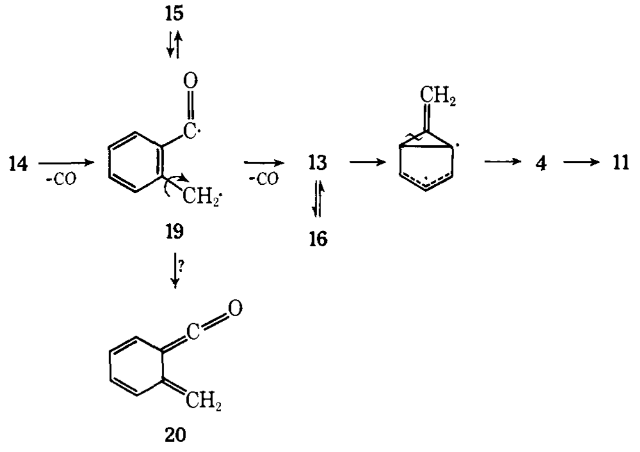
(10) H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

(11) The stereochemistry of **17** and **18** was not determined, nor was any attempt made to isolate isomers. Of course, the *endo* geometry is favored.

(12) R. F. C. Brown and M. Butcher, *Aust. J. Chem.*, **22**, 1457 (1969).

(13) (a) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967); (b) G. L. Closs and L. R. Kaplan, *ibid.*, **91**, 2168 (1969).

ground state on the basis of esr spectroscopy;[13a,b] the corresponding benzocyclopropenes have been obtained and decompose at room temperature to styrenes most likely through the 1,3-biradical intermediate.[13a] In our case the multiplicity of the various biradical intermediates remains to be determined. Significantly, no evidence for the singlet species **20**, which has been postulated as a photochemical intermediate from benzocyclobutenones,[12,14] was obtained. Finally, we have found that benzocyclobutenone (**15**) undergoes FVP to the triad of C_7H_6 products (**4**, **16**, and **11**) as implied by the scheme; similarly **4** is converted to **11** at temperatures ≥1000°.



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(14) M. P. Cava and R. J. Spangler, *J. Amer. Chem. Soc.*, **89**, 4550 (1967).

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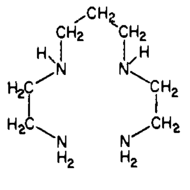
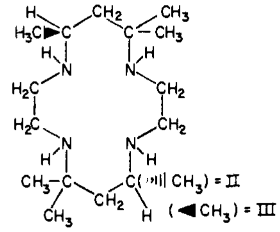
Effect of Macrocyclic Structures on the Rate of Formation and Dissociation of Copper(II) Complexes

Sir:

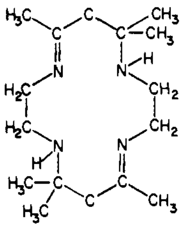
The kinetics of formation of copper(II) complexes with ligands containing four nitrogen donor groups are measured for the somewhat flexible 14-membered macrocyclic ligands[1-4] shown in structures II, III, and IV as well as for an open-chain polyamine, 2,3,2-tet (I), and a porphyrin ligand (V). In acid solutions the aliphatic macrocyclic ligands react much slower with Cu(aquo)$^{2+}$ than do the porphyrins. Furthermore, with tet *a* (II) and tet *b* (III) the initial products have a different structure than the final products, and the rearrangements to give their more stable products are very slow. Because acid has such a large effect on the kinetics, the formation reactions with the unprotonated ligands also are examined in 0.5 *M* NaOH where copper is present in the form of the soluble hydroxide complexes, Cu(OH)$_3^-$ and Cu(OH)$_4^{2-}$.[5] Under these conditions the 14-membered macrocycles II, III, IV react more slowly than the open-chain ligand I by factors of 10^3–10^4 (Table I).



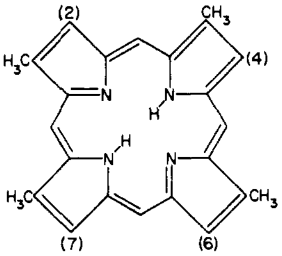
I, 2,3,2-tet



II, tet *a* or *meso*-1,7-CTH
III, tet *b* or *rac*-1,7-CTH



IV, *trans* [14]diene or 1,7-CT



V, hemotoporphyrin IX
(2),(4) = $CHOHCH_3$
(6),(7) = CH_2CH_2COOH
VI, deuteroporphyrin-2,4-disulfonic acid dimethylester
(2),(4) = SO_3H
(6),(7) = $CH_2CH_2COOCH_3$

The more rigid porphyrin V is less reactive than I by a factor of 10^9. All the reactions are second order and the products are believed to be square-planar complexes of copper. However, the microscopic mechanisms of formation must differ greatly. The porphyrin structure has the greatest tendency to force a mechanism of simultaneous multiple desolvation of the metal ion while the open-chain polyamine can readily react by the stepwise replacement of coordinated solvent (H_2O and OH^-). In the case of the 14-membered macrocycles both paths must be considered. It is difficult for these ligands to twist and fold in order to maintain a stepwise desolvation path. Models indicate that some degree of multiple desolvation is necessary in the coordination of the third and fourth nitrogens. However, the rate-determining steps may be earlier in the coordination process. Three factors which suggest that twisting or folding of these cyclic ligands is important are (1) their much greater reactivity compared to the porphyrin molecule, (2) the formation of intermediate structural isomers, and (3) the fact that subtle changes in structure, as in tet *a* compared to tet *b*, cause noticeable changes in the rate constants.

Table I also gives the observed rate constants for the reaction of Cu(aquo)$^{2+}$ with tet *a*, tet *b*, and the *trans*-[14]-diene at pH 4.7 in comparison to data recently available for a sulfonated deuteroporphyrin (VI)[6] and for an open-chain pentadentate polyamine, tetraethylenepentamine (tetren).[7] The hematoporphyrin (V) was not used because of its limited solubility in acidic solutions. At pH 4.7 copper(II) is incorporated into the porphyrin ring more rapidly by several orders of

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(1) The macrocyclic ligands in structures II, III, and IV were prepared by the procedures of Curtis,[2,3] and his abbreviations are given along with those of Busch and coworkers.[4]

(2) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

(3) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(4) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969).

(5) L. A. McDowell and H. L. Johnston, *ibid.*, **58**, 2009 (1936).

(6) J. Weaver and P. Hambright, *Inorg. Chem.*, **8**, 167 (1969).

(7) R. E. Shephard, G. M. Hodgson, and D. W. Margerum, to be submitted for publication.