Table II. Some Bond Distances and Angles for $ffarsCo_2(CO)_6$[a]

Bond	Distance, Å
Co(1)–As(1)	2.339 (4)
Co(2)–As(2)	2.336 (4)
Co(1)–Co(2)	2.482 (4)
Mean Co–C	1.81 (2)
Mean Co–C (bridging)	1.94 (2)
Mean As–C	1.95 (2)
Mean As–CH_3	1.97 (3)
Mean C–O	1.14 (3)
Mean C–F	1.32 (3)
C(1)=C(2)	1.34 (3)
C(1)–C(4)	1.54 (3)
C(2)–C(3)	1.48 (4)
C(3)–C(4)	1.57 (4)

Bond	Angle, deg
As(1)–Co(1)–Co(2)	110.1
As(1)–Co(1)–C(6)	92.3
As(1)–Co(1)–C(7)	104.1
As(1)–Co(1)–C(9)	85.7
As(1)–Co(1)–C(10)	157.7
As(2)–Co(2)–Co(1)	109.3
As(2)–Co(2)–C(5)	90.6
As(2)–Co(2)–C(8)	101.5
As(2)–Co(2)–C(9)	86.6
As(2)–Co(2)–C(10)	157.1
Co(1)–As(1)–C(2)	114.8
Co(1)–As(1)–C(11)	117.9
Co(1)–As(1)–C(12)	119.0
Co(2)–As(2)–C(1)	115.5
Co(2)–As(2)–C(13)	117.3
Co(2)–As(2)–C(14)	119.0
Co(1)–C(9)–Co(2)	78.6
Co(1)–C(10)–Co(2)	80.3
As(2)–C(10)–C(2)	134.9
C(2)–C(1)–C(4)	94.8
As(1)–C(2)–C(1)	133.3
C(1)–C(2)–C(3)	93.4
Mean Co–C–O (nonbridging)	177.5 (2.2)
Mean Co–C–O (bridging)	140.0 (1.9)

[a] Standard deviations for bond distances are given in parentheses. The standard deviations for angles lie in the range 0.5–2.5°.

Table III. Atomic Coordinates of the Nonhydrogen Atoms in $ffarsCo_2(CO)_6$[a]

Atom	*x*	*y*	*z*
As(1)	0.4383 (1)	0.2919 (2)	0.3103 (1)
As(2)	0.3124 (1)	0.4330 (2)	0.4678 (1)
Co(1)	0.3509 (2)	0.4045 (2)	0.2571 (1)
Co(2)	0.2760 (2)	0.4932 (2)	0.3533 (1)
F(1)	0.4305 (13)	0.1037 (12)	0.4518 (10)
F(2)	0.5320 (11)	0.1942 (15)	0.4782 (10)
F(3)	0.4436 (12)	0.2823 (14)	0.5829 (9)
F(4)	0.3443 (13)	0.1957 (13)	0.5539 (9)
O(1)	0.4380 (13)	0.4794 (16)	0.1290 (10)
O(2)	0.2438 (12)	0.2506 (14)	0.2030 (10)
O(3)	0.4505 (11)	0.5265 (14)	0.3537 (10)
O(4)	0.2172 (11)	0.5188 (14)	0.2044 (9)
O(5)	0.2669 (16)	0.7015 (14)	0.3839 (12)
O(6)	0.1152 (12)	0.4065 (17)	0.3665 (11)
C(1)	0.3813 (14)	0.3188 (16)	0.4667 (11)
C(2)	0.4222 (14)	0.2704 (16)	0.4149 (12)
C(3)	0.4523 (17)	0.1963 (21)	0.4667 (15)
C(4)	0.4011 (18)	0.2459 (20)	0.5279 (14)
C(5)	0.1774 (16)	0.4364 (21)	0.3614 (13)
C(6)	0.2860 (14)	0.3089 (17)	0.2230 (11)
C(7)	0.4050 (15)	0.4505 (19)	0.1796 (13)
C(8)	0.2693 (16)	0.6209 (20)	0.3710 (12)
C(9)	0.3904 (17)	0.4958 (17)	0.3306 (12)
C(10)	0.2602 (17)	0.4917 (18)	0.2501 (11)
C(11)	0.5527 (16)	0.3218 (25)	0.3092 (16)
C(12)	0.4363 (21)	0.1543 (18)	0.2760 (17)
C(13)	0.3757 (20)	0.5194 (21)	0.5317 (14)
C(14)	0.2285 (17)	0.3871 (26)	0.5346 (14)

[a] Estimated standard deviations are given in parentheses and refer to the least significant digits.

Acknowledgment. We are grateful to the National Research Council of Canada for financial assistance.

* Address correspondence to this author.

J. P. Crow, W. R. Cullen*
W. Harrison, J. Trotter
Department of Chemistry, University of British Columbia
Vancouver 8, British Columbia, Canada

Received June 17, 1970

Monodehydro[22]annulene[1]

Sir:

It has been calculated that annulenes (monocyclic conjugated polyenes) containing ($4n + 2$) π electrons and a reasonably planar carbon skeleton will be aromatic up to and including [22]annulene, but that [26]annulene will no longer be aromatic.[2] The theoretical considerations apply equally to the dehydroannulenes (monocyclic conjugated polyenynes) as regards the out-of-plane π electrons, and it is probable that the limit for aromaticity in this series will also lie between the 22- and the 26-membered ring compounds. Nmr spectroscopy represents the simplest method for determining whether a given conjugated macrocyclic system is aromatic, and dehydroannulenes are preferred to the annulenes since the nmr spectra of the dehydro compounds are less prone to be temperature dependent than those of the more "mobile" annulenes.[3]

Annulenes and/or dehydroannulenes of all ring sizes up to and including the 30-membered, except for the 22-membered,[4] have been prepared up to now.[3,6] In agreement with expectation, the nmr spectra of the various 14- and 18-membered ring compounds all exhibited a pronounced diamagnetic ring current,[3] showing them to be aromatic, while those of the 26- and 30-membered ring compounds did not.[3,7] We now describe the synthesis of monodehydro[22]annulene (*e.g.*, **5**), the first 22-membered monocyclic conjugated system to be obtained,[8] and present evidence that in fact it is aromatic. Dehydroannulenes containing ($4n + 2$) out-of-plane π electrons are therefore aromatic when $n \leqslant 5$, and nonaromatic when $n \geqslant 6$, in agreement with theory.

trans-4-Octene-1,7-diyne (**1**)[9] was treated with 1.2 mol equiv of ethylmagnesium bromide in tetrade-

---

[1] Unsaturated Macrocyclic Compounds. LXXII. For part LXXI, see A. B. Holmes and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 5284 (1970).

[2] M. J. S. Dewar and G. J. Gleicher, *ibid.*, 87, 685 (1965). See also H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc., Ser. A*, **251**, 172 (1959); 257, 445 (1960); C. A. Coulson and W. T. Dixon, *Tetrahedron*, 17, 215 (1962).

[3] See F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc., Spec. Publ.*, No. 21, 75 (1967).

[4] The statement by Dewar and Gleicher[2] that Jackman, *et al.*,[5] had found [22]annulene to be aromatic is in error.

[5] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **84**, 4307 (1962).

[6] See F. Sondheimer, *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967); *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 125 (1968).

[7] C. C. Leznoff and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 4247 (1967).

[8] For the synthesis of polycyclic systems which may be considered bridged aza[22]annulene derivatives, see R. B. Woodward, *Proc. Robert A. Welch Found. Conf. Chem., Res.*, **12**, 167 (1968); M. J. Broadhurst, R. Grigg and A. W. Johnson, *Chem. Commun.*, 23, 1080, 1480 (1969); 807 (1970).

[9] Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 4940 (1968).

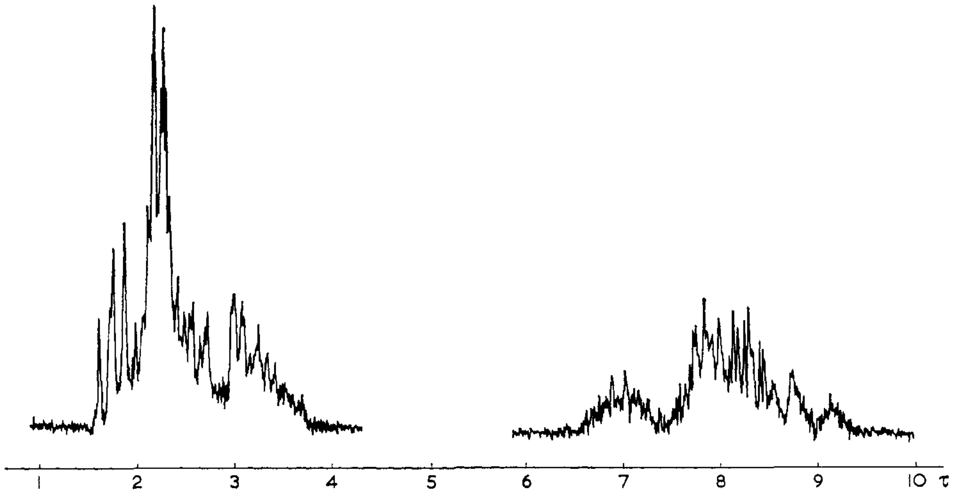
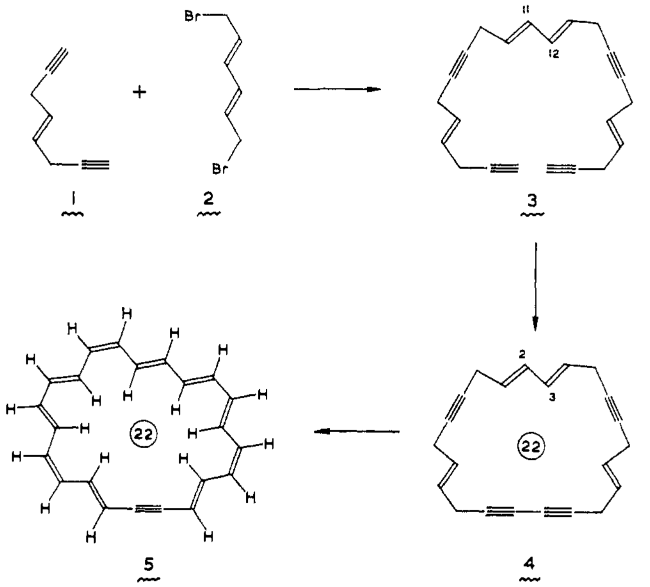


Figure 1. Nmr spectrum of monodehydro[22]annulene (*e.g.*, **5**), measured in CD_2Cl_2 at 100 MHz (peak positions measured from CH_2Cl_2, taken as τ 4.68).

hydrofuran at room temperature, and then with 0.5 mol equiv of *trans,trans*-1,6-dibromo-2,4-hexadiene (**2**)[10] in the presence of cuprous chloride[12] (boiling 1 hr). The resulting all-*trans*-4,10,12,18-docosatetraene-1,7,15,21-tetrayne (**3**), obtained as colorless crystals in $\sim$25% yield after chromatography on silica gel, showed: mp 88.5–89.5°; λ_{max}^{EtOH} 223 sh nm (ϵ 24,200), 229 (26,500), and 237 sh (17,800); $\nu_{max}^{CCl_4}$ (cm^{-1}) 3320 s (HC≡), 2130 w (C≡C), 995 s, and 975 s (trans C=C); nmr spectrum ($CDCl_3$, 100 MHz) τ 3.65–3.95 (m, 2, olefinic H^{11}, H^{12}), 4.15–4.55 (m, 6, other olefinic), 7.06 (broad s, 12, methylene), and 7.92 (t, 2, acetylenic).



Oxidative coupling of **3** by dropwise addition of a solution in pyridine and tetrahydrofuran during 4 hr to cupric acetate monohydrate in pyridine at 70°[13] gave the corresponding cyclic "monomer," all-*trans*-1,3,9,17-cyclodocosatetraene-6,12,14,20-tetrayne (**4**), in 12% yield after chromatography on silica gel. Substance **4** formed colorless crystals: mp 100–101°; mass spectrum, *m/e* 284; λ_{max}^{EtOH} 223 sh nm (ϵ 22,700), 229 (25,300), and 237 sh (15,800); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2280 w, 2180 w (C≡C), 995 s, and 975 s (trans C=C); nmr ($CDCl_3$, 100 MHz), τ 3.65–3.95 (m, 2, olefinic H^2, H^3), 4.10–4.60 (m, 6, other olefinic), and 7.07 (m, 12, methylene).

Compound **4** was rearranged with a saturated solution of potassium *tert*-butoxide in *tert*-butyl alcohol at 30° for 3 min. Chromatography on alumina then gave monodehydro[22]annulene (*e.g.*, **5**) in $\sim$10% yield as sole highly colored product. The substance formed red-purple crystals from benzene–pentane (red in concentrated solution), which decomposed at $\sim$220° on attempted melting point determination; mass spectrum, *m/e* 284.158 (calcd for $^{12}C_{22}{}^{1}H_{20}$: 284.157); $\lambda_{max}^{Et_2O}$ 280 nm (ϵ 28,800), 372 (132,000), 438 sh (11,900), 452 (12,200), and $\sim$495 sh (3600); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2135 w (C≡C), 995 s, and 970 s (trans C=C). The monodehydro[22]annulene appeared to be homogeneous (*e.g.*, no separation occurred on silver nitrate coated Kieselgel tlc plates[14]). The monocyclic nature of the substance was confirmed by catalytic hydrogenation in ethyl acetate over platinum, which led to cyclodocosane (*m/e* 308).

The nmr spectrum of the monodehydro[22]annulene (Figure 1) consisted of very complex multiplets at τ 1.55–3.75 and 6.55–9.30, due to the outer and inner protons, respectively.[15] The integrated areas were $\sim$13:7 (found, 12.6:7.4, 12.7:7.3, 13.3:6.7), indicating the molecule to contain 13 outer and seven inner protons, and therefore to be made up of seven trans double bonds, three cis double bonds, and one acetylene. The exact sequence of double bonds is unknown, and structure **5** is one of many possibilities. The appearance of the outer proton band at relatively low field and the inner proton band at high field clearly demonstrates the existence of a magnetically induced diamagnetic ring current, showing the substance to be aromatic.[3] The

---

[10] Prepared by treatment of 1,5-hexadiene-3,4-diol[11] with phosphorus tribromide in chloroform at $\sim$0–30° (see E. H. Farmer, B. D. Laroia, T. M. Switz, and J. F. Thorpe, *J. Chem. Soc.*, 2937 (1927)).

[11] R. A. Braun, *J. Org. Chem.*, **28**, 1383 (1963); U. S. Patent 3,240,822 (1966) [*Chem. Abstr.*, **64**, 15,743*f* (1966)].

[12] See J. P. Danehy, D. B. Killian, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **58**, 611 (1936).

[13] The conditions were essentially identical with those used for the coupling of all-*trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne to the corresponding cyclic "monomer." [9]

[14] See R. Wolovsky, *J. Amer. Chem. Soc.*, 87, 3638 (1965).

[15] The spectrum (in tetrahydrofuran-d_8) determined at −60° was essentially unchanged.

spectrum is in clear contrast to those of tridehydro[26]annulene,[7] tridehydro[30]annulene,[3] and pentadehydro[30]annulene,[3] in which all the protons appear as a very broad band at $\sim\tau$ 2.0–4.5.

Acknowledgments. We are indebted to the Science Research Council and to the Royal Society for generous financial support.

* Address correspondence to this author.

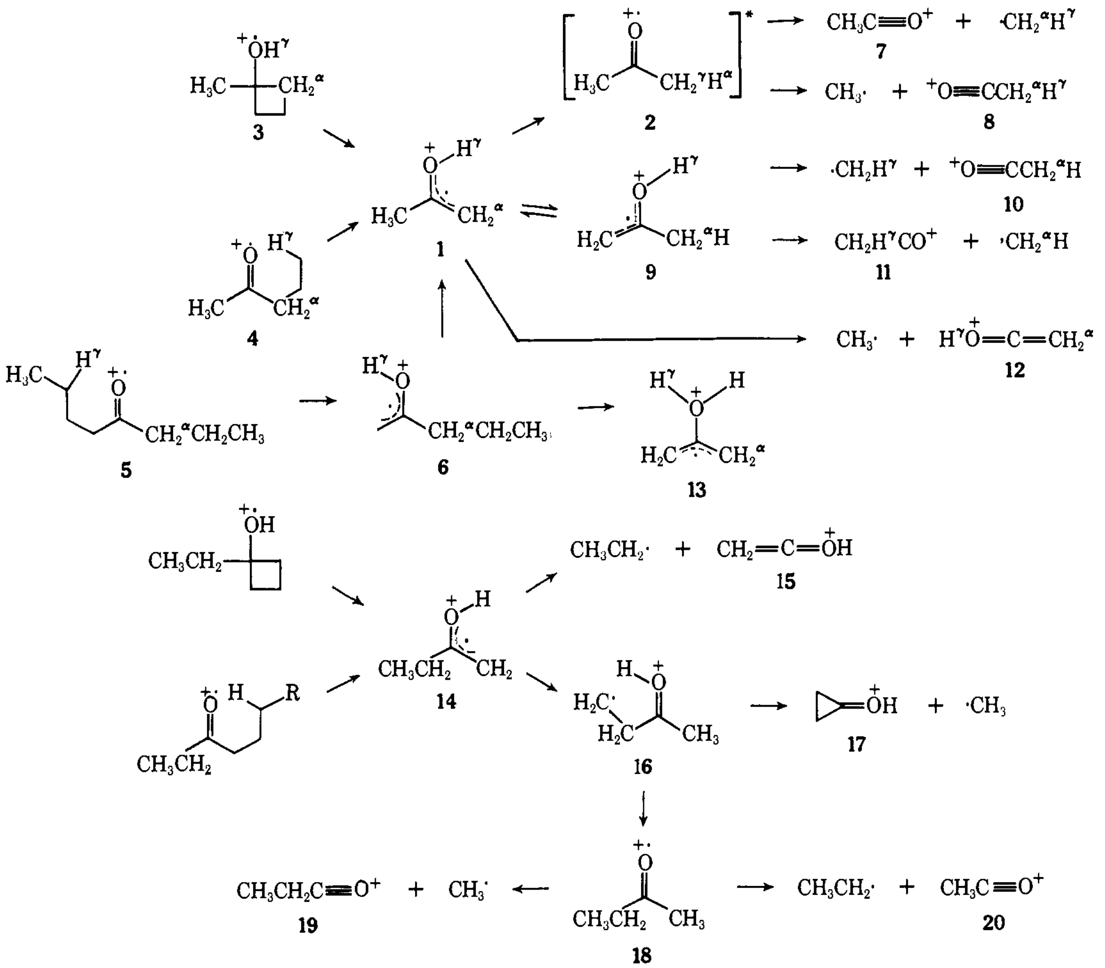
R. M. McQuilkin, F. Sondheimer*
Chemistry Department, University College
London W.C.1, England

Received August 10, 1970

Ketonization of Gaseous Enol Ions[1]

Sir:

In the mass spectra of aliphatic ketones abundant ions can be formed in both the keto and enol forms, but interconversion between such tautomers has not been reported.[2-4] Considerable evidence[3] has been presented to show that the keto tautomer is of higher energy, and that the enol ion does not ketonize prior to fragmentation.[5] We report evidence from the metastable ion abundances of labeled compounds that the major decomposition pathways of three simple enol ions appear to involve initial ketonization.



In ion cyclotron resonance studies[3,4] of $C_3H_6O^+$ ions no appreciable tautomerism between the keto and enol forms was observed despite the relatively long (millisecond) ion lifetimes involved. However, we find that the predominant product, $C_2H_3O^+$, arising from decomposition of the enolic $C_3H_6O^+$ (**1**) in the mass spectrometer appears to be formed through rearrangement to an unstable keto intermediate, **2**, not through the simple cleavage **1** → **12** (Table I).[7] Direct losses of CH_2^α and H^γ from **1** to form CH_3CO^+ (**7**), especially in greater abundance than $C_2H_2^\alpha H^\gamma O^+$ (**8** or **12**), as observed, appear improbable. However, formation of **7** and **8** through the common intermediate **2** is consistent with the identity (±0.2 eV) found for the appearance potentials of **7** and **8**. Also **1** → **12** is a simple cleavage reaction, and so should be favored over the rearrangement **1** → **2** in decomposition of the higher energy normal ions;[8] the data of Table I are

---

(1) (a) Metastable Ion Characteristics. XVI. Paper XV: I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **92**, 3797 (1970); (b) reported in part at the International Mass Spectroscopy Conference, Kyoto, Japan, Sept 1969, Preprints, p 217.

(2) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 18.

(3) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969), and references therein.

(4) G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91**, 3986 (1969); submitted for publication. We are indebted to Professor Djerassi for preprints of these manuscripts.

(5) For example, the reactions **6** → $\mathbf{1}^{1b,3,4}$ and **14** → **15** + **17**.[6]

(6) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 160 (1968).

(7) The full papers will include data on nine different labeling patterns of enolic $C_3(H,D)_6O^+$ ions and six of $C_4(H,D)_8O^+$ ions. Except where noted, the normal spectra indicated that the isotopic enolic ions were formed in good purity.

(8) F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, **90**, 5915 (1968).