

Figure 1. Epr spectrum of Cl_2^+ .

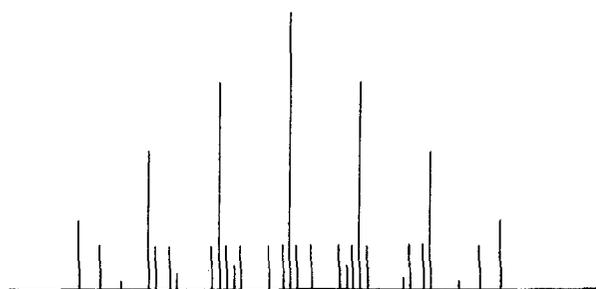


Figure 2. Theoretical spectrum for Cl_2^+ with natural isotopic abundances (see text).

to -60° , no change in the spectra is observed except that the hyperfine pattern disappears as viscosity broadening of the signal takes place. The same behavior of the antimony pentafluoride solution is observed, except that the viscosity broadening sets in at around 0° instead of -60° .

The stoichiometry of the formation of Cl_2^+ from ClF is not yet known with certainty, but the following reaction is the most plausible.



To our knowledge, Cl_2^+ is the first simple diatomic radical ion observed by epr in solution. Other diatomic radical ions, like Cl_2^- , O_2^+ , and O_2^- , have been observed in rigid media.^{5,6}

When the solutions of Cl_2^+ are heated to 60° , a second paramagnetic species (II) is formed ($g = 2.006$) which is in equilibrium with Cl_2^+ . When a solution containing I and II is cooled from 60° to lower temperatures, the relative amounts of I and II change reversibly, with I predominating at lower temperatures. Investigation of the system is still in progress, and at the present time we cannot yet unequivocally state the nature of species II, although it may be the radical cation ClF_3^+ .

(6) For a review, see J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

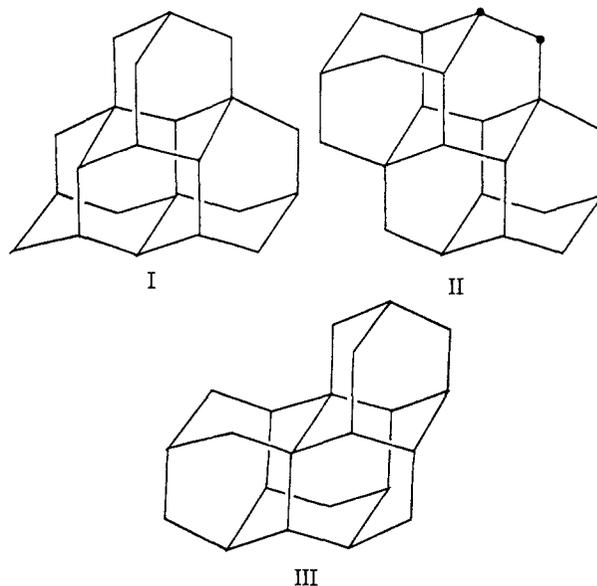
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George A. Olah, Melvin B. Comisarow
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
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Nonacyclo[11.7.1.1^{2,18}.0^{3,16}.0^{4,13}.0^{5,10}.0^{6,14}.0^{7,11}.0^{15,20}]-docosane,¹ a Bastard² Tetramantane

Sir:

There exists a close formal similarity between the simple aliphatic hydrocarbons and the homologous series of adamantane compounds based on the diamond structure. Methane, ethane, and propane correspond to adamantane,³ diamantane ("congressane"),⁴ and triamantane.⁵ Just as ethane can be thought of as two tetrahedral methane units joined together, so can diamantane be regarded as a similar combination of two tetrahedral adamantane units. Propane and triamantane bear the same relationship. The point groups of corresponding alkane and diamondoid hydrocarbons are the same, provided the alkanes adopt staggered conformations. A further analogy exists in the number of possible isomeric forms of corresponding members of the two homologous series. Such isomers first appear with the fourth member of each series. Two structural isomers of C_4H_{10} are possible, isobutane and *n*-butane, and the latter can exist in two minimum energy conformations, *anti* and *skew*. The carbon skeletons of these three forms correspond in arrange-



(1) IUPAC name kindly supplied by D. R. Eckroth, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. E-18. *Cf. J. Org. Chem.*, **32**, 3362 (1967).

(2) "Webster's New Collegiate Dictionary," G. and C. Merriam, Co., Springfield, Mass., 1953: "... of an unusual, abnormal, or non-standard form, shape, or size... Of a kind similar to, but inferior to, or less typical than, the standard..."

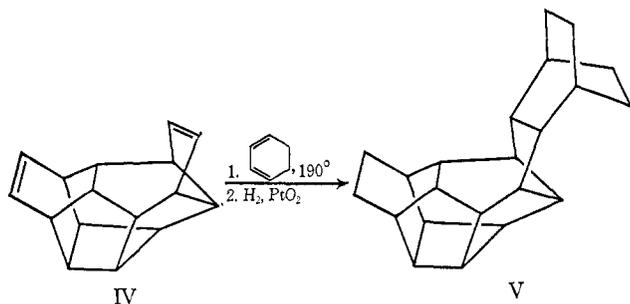
(3) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

(4) C. Cupas, P. von R. Schleyer and D. J. Trecker, *ibid.*, **87**, 917 (1965); I. L. Karle and J. Karle, *ibid.*, **87**, 918 (1965).

(5) V. Z. Williams, Jr., P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *ibid.*, **88**, 3862 (1966).

ment to the three possible isomeric tetramantanes: *iso*-tetramantane, C_{3v} (I), *anti*-tetramantane, C_{2h} (II), and *skew*-tetramantane, C_2 (III). We have attempted to prepare one or more of these tetramantanes by the same Lewis acid rearrangement approach successful for the lower members of the series.³⁻⁵

Cyclooctatetraene dimer (IV)⁶ was elaborated to the desired C and H level by Diels-Alder reaction with cyclohexadiene followed by hydrogenation; the structure of the product obtained is believed to be V, on the basis of the mode of synthesis and nmr and ir evidence. The exact structure of this compound, mp 147-149°, is not important for our purposes, since any nonacyclic $C_{22}H_{28}$ isomer was desired as starting material. Rearrangement of V with a twofold weight excess of $AlBr_3$ -



sludge catalyst^{5,7} in CS_2 at 100° under an HBr atmosphere was complete in 2-9 hr, as followed by gas chromatography. The oily product from the reaction mixture gave crystals in 5-8% yield after cooling at -78° for several days. This crystalline substance corresponded to the major peak in the gas chromatograph of the crude product.

The same substance could be obtained by allowing IV to react with methylcyclopentadiene, followed by reduction and rearrangement, but a much longer contact time with the sludge catalyst was required.

The new compound, after recrystallization from acetone-hexane, had mp 144.5-146.5°, somewhat lower than would be expected for a tetramantane. *Anal.* Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.60; H, 9.79. The mass spectrum indicated a highly intertwined polycyclic structure. The molecular ion peak at m/e 292 is by far the most prominent (38% Σ_i) and confirms the empirical formula assigned. The most intense fragmentation peak at m/e 91 (possibly the tropylium ion) has only 5.6% of the base peak intensity. The 100-MHz nmr spectrum (Figure 1) shows four groups of resonance signals. The complicated upfield multiplet integrates for two protons. This feature is incompatible with structures I or II.^{5,8} The information provided by these methods was otherwise not very revealing.

Therefore, we used single-crystal X-ray diffraction techniques to determine the structure. Lattice dimensions and diffraction intensities were measured with a General Electric XRD-5 diffractometer equipped with a goniostat and scintillation counter, with molybdenum radiation, $Mo\ K\alpha_1$ 0.70926 Å. The crystals are mono-

(6) Review: G. Schröder, "Cyclooctatetraen," Verlag Chemie GmbH, Weinheim, Germany, p 60.

(7) M. Nomura, P. von R. Schleyer, and A. A. Arz, *J. Am. Chem. Soc.*, **89**, 3657 (1967).

(8) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

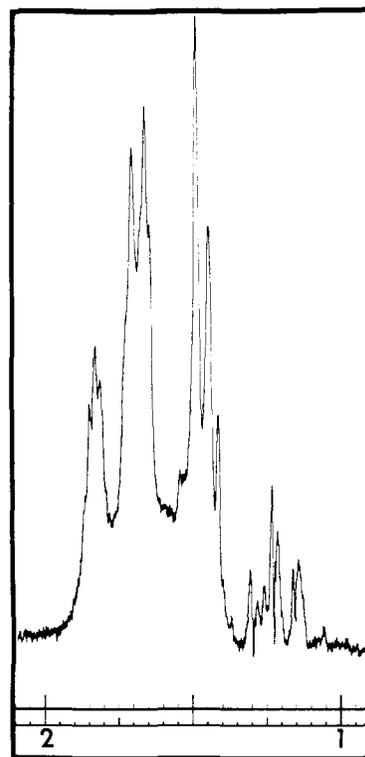
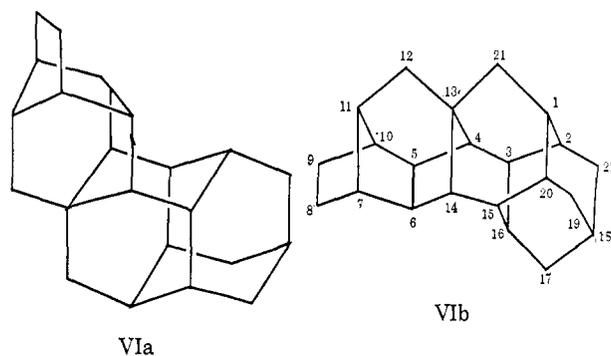


Figure 1. The 100-MHz nmr spectrum of VI; solvent CCl_4 , δ in ppm from tetramethylsilane.

clinic, space group $P2_1/c$, $Z = 4$, with cell dimensions $a = 6.328 \pm 0.004$, $b = 22.544 \pm 0.010$, $c = 12.656 \pm 0.007$ Å and $\beta = 122.56 \pm 0.05^\circ$. Intensities of 1979 reflections (with $2\theta < 45^\circ$) were measured by the stationary-crystal-stationary-counter technique. The structure was determined by application of the symbolic addition procedure.⁹ An E map showed the positions of the carbon atoms, and these were refined first with isotropic and then with anisotropic thermal parameters. A difference Fourier was then calculated, and the positions of the 28 hydrogen atoms were located. The present R value ($R = \Sigma|\Delta F|/\Sigma|F_o|$), after refinement of 311 parameters (carbon atoms anisotropic and hydrogen atoms isotropic), is 0.08. Figure 2 shows a stereoscopic view of the structure. The representation VIa facilitates comparison with the structure of *anti*-tetramantane (II), and VIb shows still another perspective.



Nonacyclo[11.7.1.1^{2,18}.0^{3,16}.0^{4,13}.0^{5,10}.0^{6,14}.0^{7,11}.0^{15,20}]-dodecosane^{1,10} (VI) has a truly unusual structure. Nor-

(9) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

(10) We are wont to call this compound "bastardane."²

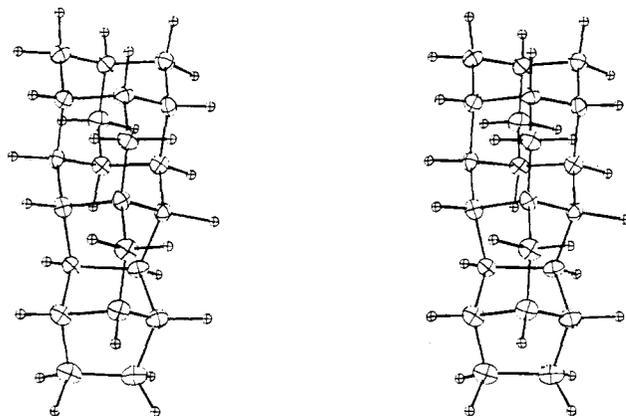


Figure 2. Stereopair representation of nonacyclo[11.7.1.12..18.-03.16.04.13.05.10.06.14.07.11.015.20]docosane (VI).

bornane, noradamantane,¹¹ bicyclo[3.2.1]octane, and diamantane units are all interconnected. In effect, the two carbon atoms shown by heavy dots in II have been moved to the extreme upper left in VIa to make an ethylene bridge (C₈ and C₉) of the norbornane moiety.

I, II, and III must be considerably more stable than VI. Despite this, none of the regular tetramantanes are formed, at least from V. We have also heated VI with the catalyst at 150° but, besides loss of material,⁷ no further isomerization could be observed. This result shows that, at least in the higher members of the series, the usual thermodynamic considerations^{8-5,7,11,12} do not alone control the nature of the product obtained. Not only diamondoid molecules but also polycyclic cage systems of irregular structure can be prepared by the rearrangement route.

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(11) Noradamantane can also be prepared by rearrangement: P. von R. Schleyer and E. Wiskott, *Tetrahedron Letters*, 2845 (1967).

(12) A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966).

Paul von Ragué Schleyer, Eiji Osawa
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Michael G. B. Drew
Department of Chemistry and Lawrence Radiation Laboratory
University of California, Berkeley, California 94720

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Reactions of Olefins and Palladium Chloride in the Presence of Fluoride Salts

Sir:

The dimerization of ethylene to an isomeric mixture of butenes catalyzed by palladium salts in organic sol-

vents has been reported.^{1,2} We have discovered an unusual effect of fluoride salts, most notably sodium fluoride, on the course of this reaction. For example, the reaction of ethylene, palladium chloride, and sodium fluoride in benzonitrile at 160° resulted in the formation of propylene as the major hydrocarbon product.

In a typical experiment, a mixture of 0.010 mol of palladium chloride, 0.10 mol of sodium fluoride, and 40 ml of benzonitrile was heated under vacuum to 160° in a shaking autoclave with a capacity of 75 ml. Ethylene was then added to a pressure of 20 psig. After 4 hr (11 psig) the gas was transferred to an evacuated sample bulb and then examined with gas chromatography using a supported dibutyl maleate column at 45° and a silica gel column programmed from 50 to 200°. The gas sample had the following analysis: ethylene (56.6%), propylene (15.1%), 1-butene (0.98%), *trans*-2-butene (2.7%), *cis*-2-butene (0.96%), methane (2.9%), ethane (1.6%), vinyl fluoride (0.21%), acetaldehyde (1.4%), carbon monoxide (1.0%), and carbon dioxide (21.5%).³ In the absence of sodium fluoride, there occurred a similar pressure drop, but in this case the product gas mixture contained very little propylene (<0.3%). The addition of potassium fluoride resulted in a slight increase in the amount of propylene formed, whereas lithium fluoride and cesium fluoride inhibited propylene formation. The results of the experiments performed in benzonitrile are summarized in Table I.⁴

Table I. The Reaction of Ethylene and Palladium Chloride in Benzonitrile^a

Salt	Percentages in product gas mixture					
	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈ ^b	CH ₄	C ₂ H ₆	C ₂ H ₃ F
NaF	56.6	15.1	3.7	2.9	1.6	0.21
None	68.0	0.28	1.2	0.57	20.8	^c
KF	85.0	0.66	1.1	0.70	0.81	0.12
LiF	85.6	0.047	0.30	0.13	13.7	
CsF	96.3	0.062	0.13	0.28	2.5	0.29
NaF ^d	99.9					

^a 40 ml of solvent, 0.010 mol of PdCl₂, 0.10 mol of salt, 160° for 4 hr. ^b Mixture of isomers. ^c 0.61% C₂H₃Cl found. ^d No PdCl₂ present.

Similar results were obtained with adiponitrile and nitrobenzene as solvents (Table II). Again, the addition of sodium fluoride catalyzed the formation of propylene from ethylene. However, in nitrobenzene this effect is not as pronounced as in the nitrilic solvents. Using adiponitrile as the solvent, sodium chloride was shown to cause a slight increase in the amount of propylene.

All of the reactions are complicated by a concurrent reaction of solvent with palladium chloride which resulted in formation of palladium metal. The organic products of these reactions have not been investigated thoroughly. It has been determined, however, that

(1) A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).

(2) J. T. Van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964).

(3) All products were identified by comparisons of gas chromatographic retention times and mass spectra with those of authentic samples.

(4) The amounts of acetaldehyde, carbon monoxide, and carbon dioxide formed in these reactions were not reproducible and are not given in the tables. The formation of these products is probably due to small amounts of water and oxygen in the reaction system.