than that of the *trans* isomer as anticipated,[2,5] but agreed perfectly with a *cis* configuration of the 3,5-anisyl groups. Since the two methylenic protons H_m and H_x are no longer equivalent, a more complex spectrum should be observed. Indeed, while the aromatic protons appeared as a quartet centered at τ 2.92 and the methoxyl protons showed a singlet at τ 6.19, the remaining protons exhibited the splitting expected of structure II. The benzylic protons H_a appeared as a quartet at τ 4.80, being split by the nonequivalent protons H_m and H_x. Proton H_m, *trans* to the aryl groups, exhibited a sextet at a lower field than the methylene protons of the *trans* isomer (deshielded), τ 7.66 (J_{AM} = 7.9 c.p.s. and J_{MX} = 12.4 c.p.s.) compared to τ 7.95. The splitting was also in agreement with *cis* structure II, H_m being split first into a doublet by H_x, then into two triplets by the two benzylic protons H_a. The same analysis applies for H_x (*cis* to the aryl groups) which appeared as a sextet at τ 8.63 (J_{AM} = 11.5 c.p.s. and J_{MX} = 12.4 c.p.s.). The shift to higher field is undoubtedly caused by the shielding due to the 3,5-substituents.

Both *cis*- and *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazolines were isomerized to 3,5-bis(*p*-methoxyphenyl)-2-pyrazoline[6] (IV), isolated as its N-acetyl derivative V, m.p. 91–92.5° (identified by infrared spectrum and mixture melting point comparisons). This, along with the acid-catalyzed isomerization of both isomers to the 2-pyrazoline IV (by n.m.r. spectra), confirms the 3,5-position of the substituents. Correct combustion analyses were obtained on all new compounds reported.

The thermal and photolytic decompositions of II and III to the corresponding cyclopropanes failed to show the expected stereospecificity.[1,2] The results are summarized in Table I.

TABLE I

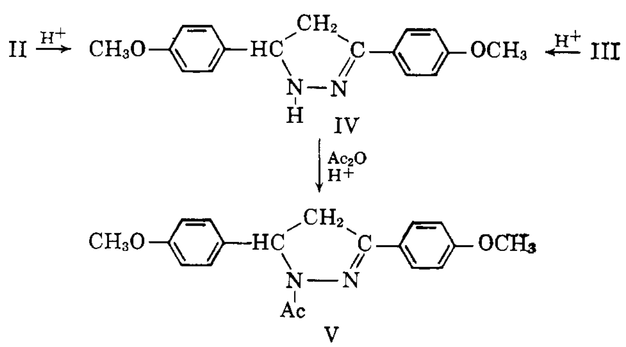
DECOMPOSITIONS OF II AND III

	% of cyclopropanes[c,d]			
	Thermal[a]		Photolytic[b]	
	cis	*trans*	*cis*	*trans*
II (*cis*)	43.0	57.0	57.2	42.8
III (*trans*)	6.7	93.3	0.7	99.3

[a] In toluene at 100°. [b] In THF at 13°; a second set was carried out in benzene with comparable results. Corrections were made for isomerization of the cyclopropanes[7] under the reaction conditions. [c] In all cases quantitative yields of cyclopropanes were obtained; no olefins were found. [d] Percentages were calculated by comparison of the areas under the methoxy peaks in the n.m.r. spectra of the resulting cyclopropanes (*cis* τ 6.52; *trans* 6.39[8]). These values are averages of two separate decompositions and are accurate to within ±1.5%.

Samples of the *cis*- and *trans*-1,2-bis(*p*-methoxyphenyl)cyclopropanes were obtained by the base-catalyzed decomposition of 3,5-bis(*p*-methoxyphenyl)-2-pyrazoline (III), a reaction that had previously been reported to produce only the *trans* isomer.[9] Assignment of structure was made by comparison of the n.m.r. spectra with those of other *cis*- and *trans*-1,2-diarylcyclopropanes.[2,10]

While a small increase in stereospecificity was observed in the photolytic decompositions, the *cis*-1-pyrazoline gave a considerable amount of *trans*-cyclopropane V. It is apparent from these results



that, in the biradical generated from the *cis*-1-pyrazoline (both thermally and photolytically), rotation around a single bond is faster than coupling. This may be due to steric or electronic factors or a combination thereof. Further work directed to shed some light on this question is in progress. Mechanistic considerations and details of these and other studies will be the subject of a future publication.

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(5) J-P. Anselme, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1964, p. 13.

(6) Prepared from the chalcone and hydrazine.

(7) There have been several recent reports concerning the photolytic isomerization of cyclopropanes in solution: G. W. Griffins, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963); W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, **No. 12**, 791 (1963); R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *Proc. Chem. Soc.*, 144, 1964; G. S. Hammond, P. Wyatt, C. D. DeBeor, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

(8) Relative to TMS at 60 Mc. in Spectrograde CCl_4.

(9) M. Hamada, *Botyu-Kagaku*, **21**, 22 (1956).

(10) D. Y. Curtin, *et al.*, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

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RECEIVED OCTOBER 16, 1964

Formation of Perhydrophenalenes and Polyalkyladamantanes by Isomerization of Tricyclic Perhydroaromatics

Sir:

Adamantane[1] and its methyl and dimethyl[2] homologs have been prepared by aluminum halide catalyzed isomerizations of tricyclic saturated hydrocarbons having from 10 to 12 carbon atoms. In each case, two of the rings in the saturated hydrocarbon consisted of the [2.2.1]bicycloheptyl or the [2.2.2]bicyclooctyl systems and it has been assumed that these strained moieties are required for the conversions to adamantanes. We have recently found that polymethyladamantanes are formed in good yields as end products in the aluminum halide catalyzed isomerizations of perhydrogenated (Raney nickel) acenaphthene, fluorene, anthracene, and phenanthrene.[3] This communication deals with the characterization and identification of a number of intermediate as well as final products of isomerization.

The mixture of at least four isomeric perhydroacenaphthenes (by v.p.c.) rapidly and exothermically formed 1-ethyladamantane in high yield on treatment with aluminum bromide–olefin complex at 0°; continued reaction at 25° resulted in an almost quantitative yield of 1,3-dimethyladamantane. 1-Ethyladamantane, b.p. 219°, m.p. −60°, $n^{20}D$ 1.4931,

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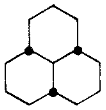
(1) P. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

(2) P. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, **9**, 305 (1961).

(3) U. S. Patent 3,128,316.

d^{20}_{4} 0.935 (lit.[4] b.p. 218–219°, m.p. −57.7°, n^{20}_{D} 1.4950, d^{20} 0.9378), displayed an n.m.r. spectrum a portion of which was superimposable on the theoretically derived A_2B_3 pattern with a coupling constant of $J = 8$,[5] and the relative area of this portion accounted for the five protons of the ethyl group. 1,3-Dimethyladamantane, b.p. 204°, m.p. −30°, n^{20}_{D} 1.4783, d^{20}_{4} 0.9016 (lit.[6] b.p. 201.2–201.4 (742 mm.), n^{20}_{D} 1.4783), gave an n.m.r. spectrum entirely consistent with the assigned structure and an infrared spectrum identical with that published for the synthesized compound.[6] This compound was identical with the C_{12} product of isomerization of hydrogenated methylcyclopentadiene dimer.[2] Recently the aluminum chloride catalyzed isomerization of 1-ethyl- to 1,3-dimethyladamantane has been demonstrated.[7]

Perhydrofluorene, a mixture of at least three isomers (by v.p.c.), rapidly isomerized at 0° forming a single compound, I, perhydrophenalene with *trans*-ring fusions. Continuing the reaction at around 25° converted I to 1-ethyl-3-methyladamantane, and this finally rearranged to 1,3,5-trimethyladamantane in high yield. Compound I, trapped by v.p.c., melted slightly below 0°, displayed no methyl absorption at 1379 cm.$^{-1}$ in the infrared, and gave an n.m.r. spectrum consisting of two broad, relatively symmetrical peaks centered on 0.98 and 1.57 p.p.m., presumably due to axial and equatorial hydrogens. Vapor-phase dehydrogenation of I at 380° over a lithium carbonate doped platinum-on-alumina catalyst formed considerable catalyst "coke" and a yellow solution containing perinaphthane contaminated by small amounts of hexahydroperinaphthene and dibenzo[*c,d*:*l,m*]perylene[8] (ultraviolet absorption at 436, 412, 408, 392, 372, and 263 mμ). A v.p.c.-trapped sample of perinaphthane, m.p. 58.0–64.5° (lit.[9] m.p. 68–69°), gave a "clean" mass of 168 by low-voltage mass spectrometry and its n.m.r. spectrum displayed six aromatic protons at 7.1–7.7 p.p.m., four α-hydrogens in a triplet at 2.97, 3.07, and 3.17 p.p.m., and two β-hydrogens as a quintet at 1.83, 1.95, 2.04, 2.13, and 2.24 p.p.m. The ultraviolet spectrum was similar to that published for perinaphthane[10] and the infrared showed bands due to aromatic absorption at 12.2, 12.6, and 12.87 μ resembling those found in the cases of 1,8-dimethylnaphthalene[11a] and acenaphthene.[11b] The first-formed adamantane, 1-ethyl-3-methyladamantane (v.p.c.-trapped), in low-voltage mass spectrometry gave major masses of 178, 163, and 149 in the proportion of 3:1:30, corresponding to the parent ion and losses of a methyl and ethyl group; the n.m.r. spectrum displayed the A_2B_3 pattern of the ethyl group superimposed on the spectrum typical of bridgehead methyladamantane, and all the different types of protons can be accounted for quantitatively. The final product of isomerization, 1,3,5-trimethyladamantane, had the expected n.m.r. spectrum and an infrared spectrum identical with that recently published for the synthesized compound.[12]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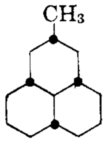
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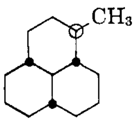
III

Perhydroanthracene, a mixture of at least four isomers (by v.p.c.), on short contacting with aluminum bromide–olefin complex at 0° rearranged almost quantitatively to *trans,syn,trans*-tetradecahydroanthracene, m.p. 86.2–88.0° (lit.[13] m.p. 90°). Additional contacting at 0° resulted in liquefaction and conversion of the solid to a mixture of at least two methylperhydroperinaphthenes (II and III). At 25° the mixture of II and III rearranged relatively rapidly to 1,3-dimethyl-5-ethyladamantane in almost quantitative yield and this further isomerized very slowly to 1,3,5,7-tetramethyladamantane. A small amount of 1-methyladamantane always accompanied the tetramethyladamantane. The mixture of II and III, b.p. 125–128 (14 mm.), n^{20}_{D} 1.4927, crystallized at −5° and filtration and recrystallization gave II, m.p. 31.5–32.5°. High-resolution infrared spectrometry established the presence of 0.95 methyl group per molecule of II[14]; the n.m.r. spectrum of II resembled that of *trans,syn*-2-methyldecalin[15] except that triple instead of double spikes projected from the two broad absorption bands characteristic of the *trans*-decalin structure. Although III was not isolated and characterized, its structure is surmised to be that illustrated on the basis of a study of the equilibrium between *trans,anti*-1- and *trans,syn*-2-methyldecalin[16] in that the concentration of III relative to that of II during isomerization is close to that predicted for equilibrium between the two isomers. Low-voltage mass spectrometry of the first-formed adamantane, 1,3-dimethyl-5-ethyladamantane, b.p. 235.2°, m.p. <−80°, n^{20}_{D} 1.4811, d^{20}_{4} 0.8986, produced ions with masses of 192, 177, and 163 in the proportion of 1:1:10, respectively, corresponding to the parent ion and loss of a methyl and an ethyl group. Again, the n.m.r. spectrum of this compound displayed the typical A_2B_3 pattern for the ethyl group superimposed on the spectrum typical of bridgehead methyladamantanes, and the different types of protons are accounted for quantitatively. The final product of isomerization, 1,3,5,7-tetramethyladamantane, m.p. 65–66.5° (lit.[17] 66–67°), gave the simple, predicted n.m.r. spectrum, two sharp peaks of equal area, and the infrared spectrum was identical with that published for the synthesized compound.[17]

On treatment with aluminum bromide–olefin com-

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(4) S. Hala and S. Landa, *Collection Czech. Chem. Commun.*, **25**, 2692 (1960).

(5) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 585.

(6) S. Landa and Z. Kamycek, *Collection Czech. Chem. Commun.*, **24**, 1320 (1959).

(7) S. Hala and S. Landa, *ibid.*, **29**, 1319 (1964).

(8) E. Clar, *Ber.*, **76**, 458 (1943).

(9) E. Langstein, *Monatsh.*, **31**, 861 (1910).

(10) R. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Serial No. 213.

(11) (a) "Sadtler Standard Spectra," The Sadtler Research Laboratory, Philadelphia, Pa., 1963, Serial No. 7458; (b) Infrared Spectral Data, American Petroleum Institute Research Project 44, Serial No. 772.

(12) H. Koch and J. Franken, *Ber.*, **96**, 213 (1963).

(13) R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Am. Chem. Soc.*, **83**, 4006 (1961).

(14) J. M. Duswalt, unpublished results from this laboratory.

(15) A. W. Weitkamp, E. M. Banas, and G. O. Johnson, paper presented before the Division of Petroleum Chemistry, 143rd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962.

(16) A. Schneider, G. Suld, and E. J. Janoski, paper presented before the Division of Petroleum Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964.

(17) S. Landa and Z. Kamycek, *Collection Czech. Chem. Commun.*, **24**, 4004 (1959).

plex at 0°, perhydrophenanthrene, a mixture of at least four isomers (by v.p.c.), very rapidly rearranged to *trans,syn,trans*-tetradecahydroanthracene. The course of subsequent isomerization was identical with that described above for the rearrangement of *trans,-syn,trans*-tetradecahydroanthracene.

In forthcoming papers, the thermodynamics and probable mechanism of formation of adamantanes from tricyclic saturated hydrocarbons will be discussed; in addition, the detailed infrared, n.m.r., and mass spectrometry of the various intermediate and final products will be presented.

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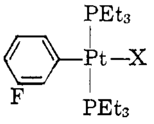
RECEIVED OCTOBER 1, 1964

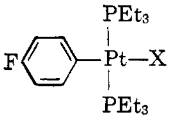
Electronic Factors in the *trans* Effect

Sir:

I wish to report a technique for discriminating between two electronic factors which contribute to the *trans* effect in the nucleophilic substitution of metal complexes.[1] The F^{19} n.m.r. shielding parameters of the *m*- and *p*-fluorophenylplatinum complexes **1** and **2** measure the ability of the fluorophenyl group to compete with the anionic ligand X for the electron density of the central platinum atom. The *meta* parameter varies with the σ-donor character of X as transmitted by the platinum atom while the *para* parameter varies with the π-acceptor nature of X. Since both properties are believed to contribute to the *trans*-activating effect of X, this criterion of electronic character is a useful tool for studies of inorganic reaction mechanisms.



1



2

The F^{19} n.m.r. shielding parameters of substituted fluorobenzenes are a sensitive probe for electronic effects in aromatic compounds.[2] Application of this probe to the *m*- and *p*-fluorophenylplatinum complexes **1** and **2** (X = CH_3) shows that there is a strong flow of electron density from the platinum atom to the fluorobenzene ring (see Table I). The positive shielding parameter of 11.7 p.p.m. for **2** puts the bis(phosphine)platinum substituent in a class with strong resonant donors such as hydroxyl and alkoxyl. The +4.06-p.p.m. shift for the *meta* compound is much larger than that which would be obtained if the methyl group were attached directly to the ring (+1.15 p.p.m.). The strong shielding effect in both compounds can be ascribed to interaction between the filled platinum d-orbitals and the benzenoid π-orbitals. This interaction enhances the electron density throughout the ring and at the *ortho* and *para* positions in particular.

The shielding parameters of the *m*-fluorophenyl complexes **1** are quite sensitive to changes in the *trans* ligand. The shifts presumably represent variations in electron density in the σ-bond system of the complexes induced by the σ-donor effect of the *trans* ligand X. The shielding parameter sequence parallels the basicity[3] sequence of X as measured in a nonpolar solvent, *e.g.*, $CH_3^- > C_6H_5^- > FC_6H_4^-$, and $CN^- > Cl^- > Br^- > I^-$.

TABLE I

PARAMETERS FOR COMPOUNDS 1 AND 2

Ligand X	F^{19} Shielding parameter[a] ($\int$) 1	2	π-Bond criterion[b] (*Z*)
CH_3	+4.06	11.70	7.64
C_6H_5	3.5	10.92	7.4
m-FC_6H_4	3.42	10.65	7.23
p-FC_6H_4	3.30	10.79	7.49
CN	2.27	9.32	7.05
Cl	2.13	10.11	7.98
Br	1.97	9.86	7.89
NCS	1.75	9.29	7.54
I	1.56	9.54	7.98

[a] The chemical shift in p.p.m. relative to fluorobenzene as an internal standard in an 8–10% solution of the complex in acetone-d_6. [b] $Z = \int_2 - \int_1$.

The major resonance structure which enhances the electron density in the *para* position of the benzene ring in compound **2** involves overlap of the filled platinum $5d_{xy}$-orbital with the adjacent carbon p_π-orbital. The same d-orbital may also take part in π-bonding with vacant orbitals on the *trans* ligand X. Hence, the F^{19} shielding parameter of **2**, after correction for inductive effects, provides a criterion of the ability of X to compete with the *p*-fluorophenyl ring for electron density in the d_{xy}-orbital. This criterion, *Z* (the difference between the parameters of **1** and **2**), takes values ranging from 7.05 for the strongly π-bonding cyanide ion to almost 8 for the halide ions which have little or no π-acceptor capacity.[4] The aryl ligands seem to form substantial π-bonds to the platinum as proposed by Chatt and Shaw.[5] The fact that halide ions give higher *Z* values than does methyl, which should be an ideal example of a non-π-bonding ligand, suggests that the halides may actually be weak π-donors.[4]

These experimental results support the postulate that the *trans* effect is, in reality, at least two effects and that either of two types of ligands can produce *trans* activation.[1] Strong donor ligands such as methyl and phenyl weaken the *trans*-metal–ligand bond by polarization of the platinum atom while strong π-acceptor ligands can facilitate nucleophilic substitution in the *trans* position by stabilizing the transition state during the reaction. This combination of effects accounts for the powerful *trans* activation produced by ligands such as cyanide (and probably R_3P) which are both σ-donors and π-acceptors.

The compounds used in this study were prepared by the procedures of Chatt and Shaw.[5,6] *trans*-Dichlorobis(triethylphosphine)platinum(II) was treated with *p*-fluorophenylmagnesium bromide to give *trans*-di-*p*-fluorophenylbis(triethylphosphine)platinum(II), m.p. 199–200°. A benzene solution of the di-*p*-fluorophenyl

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[1] The topic of the *trans* effect has been reviewed by F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[2] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

[3] J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962), and references cited therein.

[4] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[5] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

[6] Satisfactory elemental analyses were obtained for all new compounds.