

out introducing strong non-bonding interactions into the system. Thus, the *trans* isomers will react through energetically unfavorable transition state I. The *trans* isomers would react more slowly than the *cis* isomers in this situation.

As can be seen from Table IV, for each *cis-trans* pair studied, the *trans* isomer rearranges more rapidly than its *cis* isomer. This indicates that case II or case III (above) describes the mechanistic situation. In each of these cases conformation I, the "elbowed-out" or "chair-form" conformation, is the preferred one for Claisen rearrangement.

In the case of the 3,5-dimethylphenyl ethers, an isomerization of the terminal double bond into conjugation with the aromatic ring is apparently occurring at the temperatures necessary for measurable rates. However, even for these pairs of isomers which apparently represent a more complicated kinetic situation, the rate relationship

of *trans* and *cis* isomers is maintained (the *trans* isomers rearrange faster than the *cis* isomers).

These results indicate that of the four theoretical possibilities initially discussed, only those two involving conformation I as the preferred one for the transition state of the Claisen rearrangement may be considered. The data cannot be interpreted so as to differentiate between the possibility that all compounds react by conformation I (case II) and the alternative possibility that in an highly hindered environment, the transition state may be forced to take on the unpreferred conformation II (case III).

Thus, the rate data on the rearrangement of *cis*- and *trans*- $\gamma$ -substituted allyl aryl ethers support acceptance of conformation I, the "elbowed-out" or "chair-form" conformation, as the preferred representation of the transition state of the Claisen rearrangement.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

## Some Chemistry of [2.2]Metacyclophane. A Transannular Electrophilic Aromatic Substitution Reaction<sup>1</sup>

BY NORMAN L. ALLINGER, MARGARET A. DA ROOGE AND ROBERT B. HERMANN

RECEIVED JULY 5, 1960

The position at which an aromatic ring of [2.2]metacyclophane would be expected to undergo nitration was calculated using the method of partial rate factors to account for the effect of the side chains, and using the molecular orbital method to account for the effect of the other ring. Instead of the predicted product, there was isolated from the reaction a pyrene derivative which resulted from a simultaneous nitration and transannular ring closure of the forming aromatic carbonium ion. Other physical and chemical properties of the [2.2]metacyclophane are reported.

[2.2]Metacyclophane (I) was first prepared in 1899,<sup>2</sup> and its structure has been established beyond doubt, both by classical methods of organic chemistry,<sup>2,3</sup> and by X-ray crystallography.<sup>4</sup> Since the latter work has revealed the exact molecular structure, the compound furnishes an excellent case for the study of transannular resonance effects. These effects lead to results which can be both calculated theoretically and determined experimentally. A number of theoretical and experimental studies have been carried out in the past which were directed at the detection of transannular resonance.<sup>5</sup> In the present work the goal has been: first, by applications of the available theory, to reach some conclusions concerning the properties of [2.2]-metacyclophane; second to test these conclusions experimentally; and third, as it turns out, to reconcile the results.

The synthesis of [2.2]metacyclophane (I) has been improved considerably over that described in the literature.<sup>3</sup> Upon treating *m*-xylidene dibromide with phenyllithium under conditions of moderate dilution, a mixture of reaction products was obtained from which it was possible to isolate I in a yield of 39%.<sup>6</sup>

The theoretical studies were made in part on the basis of the simple molecular orbital theory, using certain approximations. Only the twelve  $\pi$ -electron system was considered initially. The resonance integrals were taken as equal to  $\beta$  for adjacent atoms in the same ring, and zero otherwise except for the one between carbons 8 and 16.<sup>7</sup> From the crystal structure<sup>4</sup> it is known that the benzene rings are approximately planar, and carbons 8 and 16 are separated by 2.689 Å. and have the axes of their *p*-orbitals colinear (from scale drawings). The magnitudes of both the  $2p\sigma$  Slater and SCF overlap integrals for the system were estimated. Using the formula<sup>8</sup>  $H_{ij} = 0.773 \beta (S_{ij}/1 + S_{ij})/(S/1 + S)$ , where *i* and *j* refer to the pair of atoms in question, and *S* and  $\beta$  are the values for benzene, the numerical value for the  $2p\sigma$  exchange integral between carbons 8 and 16 was found to be 0.308  $\beta$  (SCF) or 0.221  $\beta$  (Slater). The other inter-ring exchange integrals were taken as equal to zero. The overlap integrals were neglected, as were the effects of the side chains. The matrix corresponding to the secular equations of the twelve  $\pi$ -electron system was diagonalized with the aid of

(1) Supported by a research grant from the National Science Foundation.

(2) M. Pellegrini, *Rec. trav. chim.*, **18**, 457 (1899).

(3) W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

(4) C. J. Brown, *ibid.*, 3278 (1953).

(5) For leading references, see (a) D. J. Cram and R. H. Bauer, *THIS JOURNAL*, **81**, 5971 (1959).

(6) While this kind of a "Wurtz" reaction is well known (see for example C. S. Marvel and B. D. Wilson, *J. Org. Chem.*, **23**, 1483 (1958), and references therein) it has been stated<sup>4</sup> that Compound I was not to be obtained by this method.

(7) The numbering system shown for I follows the suggestions of D. J. Cram and J. Abell, *THIS JOURNAL*, **77**, 1179 (1955).

(8) (a) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952); *Rec. Chem. Prog.*, **13**, 67 (1952); (b) M. Simonetta and S. Winstein, *THIS JOURNAL*, **76**, 18 (1954).

an IBM 650 computer. The resulting energy levels are given in Table I, both for SCF and for Slater overlaps. Unless otherwise stated, the SCF values are employed in the calculations. The  $\pi$ -bond orders were also found, but except for the 8,16-bond were essentially those of isolated benzene rings. Since the hydrocarbon is alternant, the charge densities are all unity.

TABLE I  
ENERGY LEVELS OF [2,2]METACYCLOPHANE ( $\beta$ )

SCF		Slater	
$\pm 2.060$	$\pm 1.000$	$\pm 2.041$	$\pm 1.000$
$\pm 1.956$	$\pm 1.000$	$\pm 1.967$	$\pm 1.000$
$\pm 1.104$	$\pm 0.900$	$\pm 1.074$	$\pm 0.928$

Although the interaction of the two rings leads to a splitting of the energy levels, the total  $\pi$ -energy of the compound is seen to be  $16.038 \beta$ , which gives a resonance energy beyond that of two isolated benzene rings of only  $0.038 \beta$  or  $0.75$  kcal./mole.

From these energy levels, predictions can be made concerning the ultraviolet spectrum of the compound. The treatment is analogous to that given by Ingraham for [2,2]paracyclophane.<sup>9</sup> From the parity of the wave functions it was found that only four transitions in the  $260 \text{ m}\mu$  region were allowed, from and to energy levels as follows: (1)  $+1.104 \rightarrow -1.104$ ; (2)  $+1.104 \rightarrow -1.000$ ; (3)  $+1.000 \rightarrow -1.000$ ; (4)  $+0.900 \rightarrow -0.900$ . The ultraviolet spectrum of benzene shows an electronic transition at  $260 \text{ m}\mu$  which corresponds to a transition energy of  $2\beta$ . In the present case, when  $2\beta$  is set equal to the transition energy at  $260 \text{ m}\mu$ , the allowed transitions have energies of  $2.208$ ,  $2.104$ ,  $2.000$  and  $1.800\beta$ . The spectrum in this region is therefore predicted to consist of four bands having wave lengths of  $235$ ,  $247$ ,  $260$  and  $288 \text{ m}\mu$ . If the energy levels derived from the Slater overlap integrals were used instead of those from the SCF overlap integrals, the predicted wave lengths are  $242$ ,  $251$ ,  $260$  and  $280 \text{ m}\mu$ .

The observed spectrum (Fig. 1) shows strong absorption in the  $225$ – $250 \text{ m}\mu$  region. There is weak absorption above  $280 \text{ m}\mu$ , and relative to the model compound, the general absorption band has shifted to longer wave length and the extinction has been reduced. The shift to lower intensity and longer wave length is typical of bent benzene rings,<sup>10</sup> and an interpretation for the phenomenon has been given.<sup>9</sup> The remaining aspects of the spectrum are in fair agreement with the predictions, and this is perhaps as good as can be expected in view of the approximations.

The molecular orbital theory is quite well suited to predicting the position at which aromatic substitution will occur under various conditions. There are various simplifications that may be used to make the theory easier to apply. In the present work the perturbation method of Dewar,<sup>11</sup> rather

(9) L. L. Ingraham, *J. Chem. Phys.*, **18**, 988 (1950); **27**, 1228 (1957).

(10) (a) D. J. Cram, N. L. Allinger and H. Steinberg, *THIS JOURNAL*, **76**, 6132 (1954); (b) W. Baker, K. M. Buggle, J. F. W. McOmie and D. A. Watkins, *J. Chem. Soc.*, 3594 (1958); (c) H. Rapoport and G. Smolinsky, *THIS JOURNAL*, **82**, 1171 (1960).

(11) M. J. S. Dewar, *J. Chem. Soc.*, 3532 (1952); *Rec. Chem. Prog.*, **19**, 1 (1958).

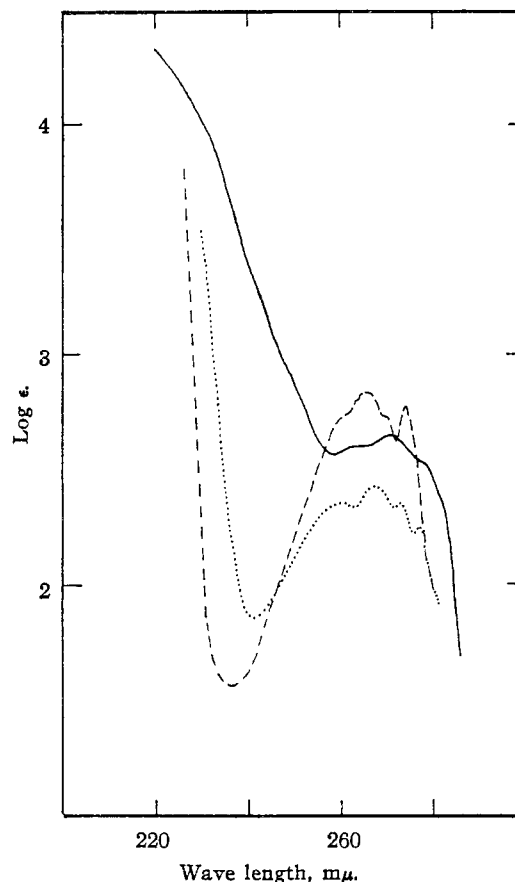
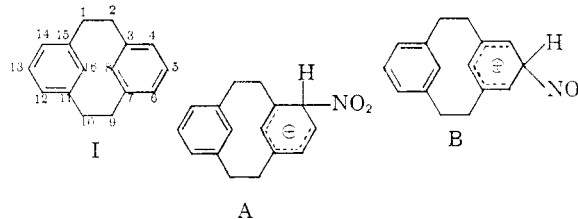


Fig. 1.—Ultraviolet spectra in ethanol: I, —; V, ·····; 1,2-bis-(3-methylphenyl)-ethane, ----.

than the more accurate but more laborious standard treatment has been used to take into account the effect of one ring on the other. The method of partial rate factors<sup>12</sup> has been used to account for the effect of the side chains, and the final predictions then have been based on a combination of these effects. The strain and distortion present in the system has been neglected at this stage.



To apply Dewar's method to I, the geometries of the possible transition states must be assumed. If substitutions at positions 4 and 5 lead, respectively, to the Wheland intermediates A and B, and the transition states are assumed to have some intermediate geometry similar to that for other aromatic nitrations, the method can be applied in a straightforward way.

For substitution at the 5-position the carbons 4, 6, 8, 11, 13 and 15 are starred. The coefficients of the non-bonding orbital ( $a_{oi}$ ) are equal zero if  $i$  is unstarred. The relative coefficients of the nonbond-

(12) F. E. Condon, *THIS JOURNAL*, **70**, 1963 (1948).

ing orbital at the starred atoms are found from the relationship  $\sum_k a_{ok} H_{ki} = 0$ , the sum being over atoms  $k$  attached to a given unstarred atom  $i$ . These relative coefficients are normalized by the relationship  $\sum_j a_{jo}^2 = 1$ , summed over all the atoms over which the non-bonding orbital extends. When the coefficients are normalized it is found that  $a = (3.071)^{-1/2}$ . If atoms 4 and 6, respectively, are  $r$  and  $s$ ,  $\Delta E^\ddagger = 2\beta_x (a_{or} + a_{os})$ , where  $\Delta E^\ddagger$  is the change in  $\pi$ -energy in going to the transition state. Dewar has shown that  $\beta_x = 6.0$  kcal./mole in nitrations,<sup>11</sup> and hence the activation energy for the 5-position is 13.71 kcal./mole. The activation energy in the 4-position is found to be the same as a position in benzene, 13.86 kcal./mole. The calculated ratio of the rates of substitution in I at positions 5 and 4 is then

$$\frac{k_5}{k_4} = e^{-(\Delta E_5^\ddagger - \Delta E_4^\ddagger)/RT} = 1.29$$

Qualitatively then, there is exceptionally little difference in reactivity in positions 4 and 5 due to transannular resonance. The value 1.29 was taken for the partial rate factor attributable to the other phenyl.

The effect of the side chains can be estimated using *m*-xylene as a model compound. The partial rate factors for the nitrations of toluene are:  $o_f = 42$ ,  $m_f = 2.5$ ,  $p_f = 58$ .<sup>13</sup> Although no quantitative studies of the nitration of *m*-xylene in the 4- and 5-positions appear to have been reported, it has been shown for mercuration<sup>14</sup> that partial rate factors for substitution in these positions can be calculated quite accurately from those of toluene. For substitution in the 4- and 5-positions of *m*-xylene, respectively, the partial rate factors calculated from the data on toluene are  $o_f p_f = 2436$  and  $m_f^2 = 6.25$ . As an approximation these values will be used for the side chains in I.

Using these quantities then, the ratio of the relative rates of substitution in I at positions 4 and 5, taking into account the other phenyl and the side chains, is

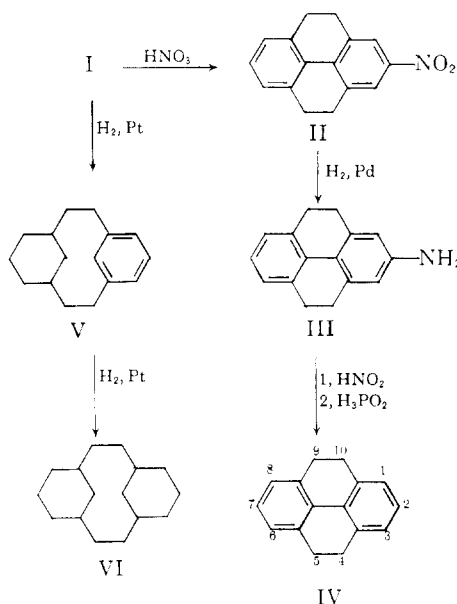
$$\frac{k_4}{k_5} = \frac{(0.78)(2436)}{(6.25)} = 302$$

When the statistical factors are taken into account the ratio of 4-nitro- to 5-nitro[2.2]metacyclophane formed is calculated to be 604.

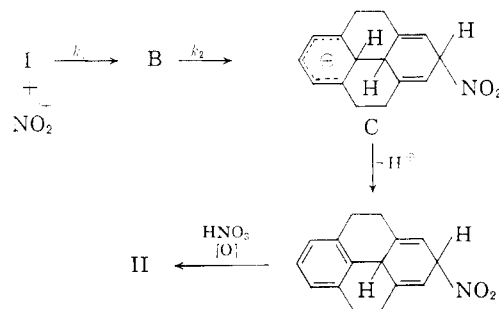
Nitration of I was consequently carried out with the expectation of isolating 4-nitro[2.2]metacyclophane, in line with the above calculations. Under very mild conditions (dilute nitric acid in acetic acid at room temperature for one minute) a mono-nitro compound was formed in good yield. It was shown from the n.m.r. spectrum and by chemical transformations of this compound that it in fact had structure II. Earlier studies have shown<sup>15</sup> that when a proton is pushed into the  $\pi$ -electron cloud of an aromatic ring, its nuclear magnetic resonance absorption occurs at a higher field than

otherwise. With compound I, the proton at carbon 8 is found to be at  $\tau = +5.73$ , which is extremely high for an aromatic proton. In II, this absorption band is gone. Since the elemental analysis of II shows that it contains 2 less hydrogens than the expected 4-nitro-[2.2]metacyclophane, a structure for II is indicated in which the hydrogens at 8 and 16 in I have been lost by cyclization. The remainder of the n.m.r. spectrum also supports the structure II assigned to this product.

Chemical evidence for the structure of II was obtained by reduction of the nitro group to an amino group with hydrogen and palladium. The resulting amine III was diazotized, and the diazonium salt was reduced with hypophosphorus acid. The hydrocarbon obtained (IV) was identified by direct comparison with an authentic sample.



The bridged structure II is unusual and the mechanism of its formation is of interest. The following scheme can be considered



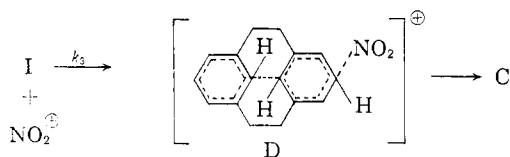
If  $k_1$  were rate determining, the transition states for substitution at 4 and 5 should be as assumed earlier and substitution at C-5 is not consistent with such an assumption. If  $k_2$  were rate determining,  $k_2$  would be even smaller than  $k_1$ , and certainly C-5 substitution would not occur.

An alternative mechanism would be an attack by the nitronium ion on one ring, and a simultaneous attack by the developing phenonium ion on the

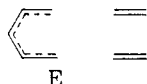
(13) H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature*, **169**, 291 (1952).

(14) H. C. Brown and C. W. McGary, Jr., *THIS JOURNAL*, **77**, 2310 (1955).

(15) J. S. Waugh and R. W. Fessenden, *ibid.*, **79**, 846 (1957).



other ring, *via* a transition state such as D. The  $\Delta H^\ddagger$  for formation of this transition state can be estimated by a modification of Dewar's method. If the transition state (actually the Wheland intermediate) is represented by figure E



a benzene ring has been substituted, another benzene ring has been converted to two isolated double bonds, and a carbon-carbon  $\sigma$  bond has been formed. The latter lowers the energy of the system by 83 kcal./mole<sup>16</sup> while conversion of the benzene ring to the diene costs 43, or 80 kcal./mole.<sup>17</sup> These two energies nearly cancel in the intermediate, and if it is assumed that they will also cancel in the transition state a  $\Delta H^\ddagger$  corresponding to that of benzene (13 kcal./mole.)<sup>11</sup> is calculated. This value of  $\Delta H^\ddagger$  is based on an unstrained ground state though, and any change in strain in going from I to D must also be taken into account. Clearly there is strain in I, and this strain is largely relieved by allowing the  $\sigma$ -bond formation. Qualitatively the effect is in the proper direction to explain the product formed, and requires that the overall rate be accelerated (relative to *m*-xylene) by the release of strain. In line with this conclusion it was noted that *m*-xylene did not react at all under the conditions used to nitrate I, and it was calculated from the data that the reaction of I was faster than that of *m*-xylene by a factor of at least 10,000.

A rough estimate of the strain in I was made from a consideration of the van der Waals interaction between carbons 8 and 16, and the bond angle bending. The distance between the two carbons in question is 2.7 Å., and it is known that in crystals the interplanar van der Waals separation of aromatic rings is 3.4 Å.<sup>18</sup> Since the rings in adjacent planes do not lie directly above one another, this corresponds to an average van der Waals separation of 3.54 Å. between the carbons. Hill has shown<sup>19</sup> that an approximate van der Waals energy can be calculated for any pair of atoms in terms of two parameters,  $\alpha$  and  $\epsilon$ . The first of these is the ratio of the actual distance between atomic centers to the sum of the van der Waals radii, in this case, 0.76, and the second is a measure of the amount of energy required to push the atoms in question together. The value of  $\epsilon$  varies quite a bit; some typical values<sup>19</sup> are 2.92 for two hydrogens (bound to carbons), 4.89 for two neon atoms, and 7.77 for two oxygen atoms<sup>20</sup> (all in units of  $10^{-15}$

erg/molecule). A value of 6.0 for the two carbon atoms in the present case ought to be accurate within a factor of two. These numbers yield a van der Waals repulsion of 2.2 kcal./mole.

The bond angle bending is roughly estimated from the fact that each of the four bonds which join the methylenes to the rings is bent from the plane of the ring by some 15°. Taking the force constant for such bending as  $0.8 \times 10^{-11}$  erg/radian<sup>2</sup>, the strain energy from bending all four of these bonds<sup>21</sup> amounts to 15.8 kcal./mole. This gives a total strain energy of 18 kcal./mole. Although this calculation is very rough, it does indicate that the strain energy is indeed large, and  $\Delta H^\ddagger$  should therefore be rather small. The entropy of activation will also be more favorable here than it would be in a bimolecular case where the aromatic rings were not held together.

The conclusion that the reaction proceeds through a transition state D which involves two simultaneous aromatic substitutions seems inescapable. Such a reaction is quite unusual in aromatic systems, but has an analogy in olefinic systems, where squalene, for example, is known to cyclize enzymatically in a concerted process.<sup>22</sup>

The hydrogenation of I was unexceptional. With a platinum catalyst in acetic acid it took up six molar equivalents of hydrogen and gave the perhydroderivative VI, m.p. 174.3°, in 91% yield. The first benzene ring hydrogenated slightly faster than the second, so that when the reaction was stopped after approximately three molar equivalents of hydrogen had been absorbed, the hexahydroderivative V, m.p. 121.5°, was isolated in a yield of 11%, while VI and I were isolated in yields of 30 and 51%, respectively. Judging from models the hexahydroderivative is comparatively free from strain, and the ultraviolet spectrum (Fig. 1) is more normal, in agreement with this conclusion.

### Experimental

[2,2]Metacyclophane (I).—Phenyllithium was prepared by adding 6.8 g. (0.043 mole) of bromobenzene in 100 ml. of dry benzene to 0.7 g. (0.1 mole) of pieces of lithium ribbon in 150 ml. of anhydrous ether during one hour while keeping the solution under reflux under a nitrogen atmosphere. A solution of 10.0 g. (0.039 mole) of *m*-xylene dibromide<sup>23</sup> in 600 ml. of dry benzene was then added during 6 hours to the phenyllithium solution. After 1–2 hours an orange color was obtained in the reaction mixture. On occasion no color was obtained, and in these cases no I could be isolated. After the addition was complete, refluxing was continued for 2 hours, and the solution was cooled and water was carefully added. The organic phase was separated, washed with water, dried, and the solvent was removed under vacuum until approximately 50 cc. of material remained. The residual oil was allowed to stand in the refrigerator for 2–3 days, and the crystals were collected; 1.4 g., m.p. 128–131° (39%). Recrystallization from ethanol gave 1.5 g., plates, m.p. 132–133°, reported<sup>8</sup> m.p. 132–133°.

The infrared spectrum of the compound in carbon disulfide appeared to be unexceptional. The ultraviolet spectrum is recorded in Fig. 1. The n.m.r. spectrum was obtained at 40 megacycles in carbon tetrachloride with tetramethylsilane as an internal standard.<sup>24</sup> The hydrogens on carbons 4, 5 and

(16) L. Pauling, "The Nature of the Chemical Bond," third edition, Cornell University Press, Ithaca, N. Y., 1960, p. 85.

(17) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 669. The quantity referred to as  $\beta$  in the present work is called  $\gamma$  by Wheland.

(18) For a number of examples and references see ref. 10a.

(19) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(20) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja and N. A. LeBel, *THIS JOURNAL*, **82**, 5876 (1960).

(21) F. H. Westheimer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 533.

(22) T. T. Tchen and K. Bloch, *J. Biol. Chem.*, **226**, 931 (1957).

(23) P. Ruggli, B. B. Bussemaker and W. Müller, *Helv. Chim. Acta*, **18**, 613 (1935).

(24) We are indebted to Dr. A. Bothner-By of the Mellon Institute for determining and interpreting the n.m.r. spectra described in this paper.

6 form the characteristic pattern<sup>25</sup> of an AB<sub>2</sub> system with A at +2.76 and B at +3.03  $\tau$ , with  $J/\delta = 0.65$ . The proton at carbon 8 was seen at +5.73  $\tau$ . The methylene hydrogens were seen as a pair of doublets with  $\tau = +6.80, 6.95, 7.83$  and  $7.98$ . The peak areas were consistent with the interpretation given.

**2-Nitro-4,5,9,10-tetrahydropyrene (II).**—Nine milliliters of 6 *N* nitric acid was added in one portion to a solution of 20 mg. of I in 15 ml. of acetic acid. After 1 minute the solution was poured onto excess ice and water. After the ice had melted the precipitate was collected and washed with water. Crystallization of this material from ethanol gave yellow needles, m.p. 110–111°, wt. 205 mg. (88%).

*Anal.* Calcd. for C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub>: C, 76.47; H, 5.21; N, 5.58; Found: C, 76.52, 76.50; H, 5.24, 5.37; N, 5.59.

**2-Amino-4,5,9,10-tetrahydropyrene (III).**—Hydrogenation of nitro compound II was carried out at room temperature in methanol with a palladium-on-charcoal catalyst. The theoretical amount of hydrogen was taken up, the solution was filtered, the solvent was removed under vacuum, and the residue was crystallized from ethanol. The product was obtained as colorless needles, m.p. 165–166.5°, yield 84%.

*Anal.* Calcd. for C<sub>16</sub>H<sub>13</sub>N: C, 86.88; H, 6.83. Found: C, 86.72; H, 6.81.

The infrared spectrum in chloroform showed the strong bands characteristic of a nitro group at 6.60 and 7.50  $\mu$ . The n.m.r. spectrum<sup>24</sup> in carbon tetrachloride showed peaks at +2.11, 2.91 and 6.60 $\tau$ . The first of these was assigned to protons 1 and 3; the second to protons 6, 7 and 8; and the third, which showed no splitting, was assigned to the methylene protons. The band areas were consistent with this assignment.

The acetyl derivative, prepared by allowing III to stand for several hours with excess acetic anhydride and pyridine, was obtained as a white powder from ethanol, m.p. 201–201.5°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>17</sub>NO: C, 82.10; H, 6.51. Found: C, 81.51; H, 6.31.

**4,5,9,10-Tetrahydropyrene (IV).**—Nitro compound II, 250 mg., was reduced in ethanol solution with palladium-on-carbon. The solution was acidified with hydrochloric acid, filtered and evaporated to dryness at 40° to give the amine hydrochloride. The hydrochloride was added to a solution of 1 ml. of water in 6 ml. of acetic acid, and the suspension was stirred at 50°. Hydrochloric acid (0.5 ml.) was added and some of the hydrochloride remained undissolved. After dropwise addition of a solution of 0.37 g. of sodium

nitrite in 2 ml. of water, a clear yellow solution resulted. After 5 min., 6 ml. of hypophosphorus acid was added to the solution. The reaction mixture was allowed to stand for 18 hours at room temperature. Brownish-yellow plates resulted, which were recrystallized (charcoal) once from ethanol and melted at 133–136°. A second recrystallization brought the m.p. up to 137–138°. The mixture melting point with an authentic sample<sup>26</sup> showed no depression, and the two samples had identical ultraviolet spectra.

**Perhydro[2.2]metacyclophane (VI).**—Compound I, 100 mg., was hydrogenated using 500 mg. of platinum oxide in 20 ml. of acetic acid. Six moles of hydrogen was taken up in 24 hours. Ether was added to the solution to dissolve the crystals which had separated, the solution was filtered, and the solvent was evaporated. The residue, recrystallized from ethanol, yielded needles, wt. 97 mg. (91%), m.p. 174.0–174.3°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>28</sub>: C, 87.27; H, 12.72. Found: C, 87.30; H, 12.69.

**Hexahydro[2.2]metacyclophane (V).**—Compound I, 350 mg., was hydrogenated with 500 mg. of platinum oxide in 30 ml. of acetic acid. The reaction was stopped after 3 moles of hydrogen had been taken up. Ether was added to the solution to dissolve the solid which had precipitated, the catalyst was removed by filtering the solution, and the solvent was evaporated. The residual white solid was dissolved in pentane and chromatographed with pentane on a column of 12 g. of neutral alumina of activity I.<sup>27</sup> The first 30 ml. of eluate contained 110 mg. of VI. The next 40 ml. of eluate contained no solid, while the following 30 ml. yielded 40 mg. of V. The column was then washed with pentane-ether, and 180 mg. of I was obtained. Crystallization of V from ethanol yielded needles, m.p. 121–121.5°. The mixture melting point of V with I was depressed.

*Anal.* Calcd. for C<sub>16</sub>H<sub>22</sub>: C, 89.72; H, 10.27. Found: C, 89.86; H, 10.04.

**1,2-Bis-(3-methylphenyl)-ethane.**—Fifteen grams of  $\alpha$ -bromo-*m*-xylene in 25 ml. of ether was added dropwise to 6 g. of magnesium in 10 ml. of ether. The reaction mixture was then diluted with water and the aqueous phase was extracted with ether. The ether extracts were combined and dried and the ether was evaporated. The product was distilled, b.p. 110–114° (0.1 mm.). A center cut was redistilled for analysis,  $n_D^{20}$  1.5546.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>: C, 91.42; H, 8.56. Found: C, 91.09; H, 8.45.

(26) E. D. Bergmann and Z. Pelchowicz, *Bull. Res. Council Israel*, **3**, 91 (1953). We are indebted to Dr. Bergmann for furnishing us with the authentic material.

(27) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

## The Nuclear Magnetic Resonance Spectra of Monosubstituted Acetylenes

BY MAURICE M. KREEVOY, HUGH B. CHARMAN AND DANIEL R. VINARD

RECEIVED DECEMBER 14, 1960

N.m.r. and infrared spectroscopic methods were used to obtain a formation constant of 0.1–0.2 for the hydrogen bonded complex of phenylacetylene with pyridine. This hydrogen bonding results in a downfield shift of about one p.p.m. in the resonance line of the acetylenic proton of phenylacetylene and other monosubstituted acetylenes in pyridine solution. Monosubstituted acetylenes show long-range spin-spin coupling constants of 2–3 c. sec.<sup>-1</sup> if the substituents are saturated. Spin-spin coupling is undetectable in vinylacetylene and propynal, however. This is interpreted in terms of two mechanisms for transmission of coupling. The data also support the hypothesis that the Baker-Nathan effect and inductive effects are approximately independent.

The nuclear magnetic resonance (n.m.r.) spectra of monosubstituted acetylenes are interesting both for theoretical and practical reasons. They give some new insight into the electronic structure of such compounds and the nature of their solutions. They provide an additional tool for the identification of this structural element in molecules of unknown structure. In the present paper salient

features of the n.m.r. spectra of a number of monosubstituted acetylenes are described and interpreted. To aid in the interpretation, n.m.r. spectra and also infrared spectra were obtained for a series of pyridine-carbon tetrachloride-phenylacetylene mixtures, and a formation constant was evaluated for the hydrogen bonded complex of phenylacetylene and pyridine. Esti-