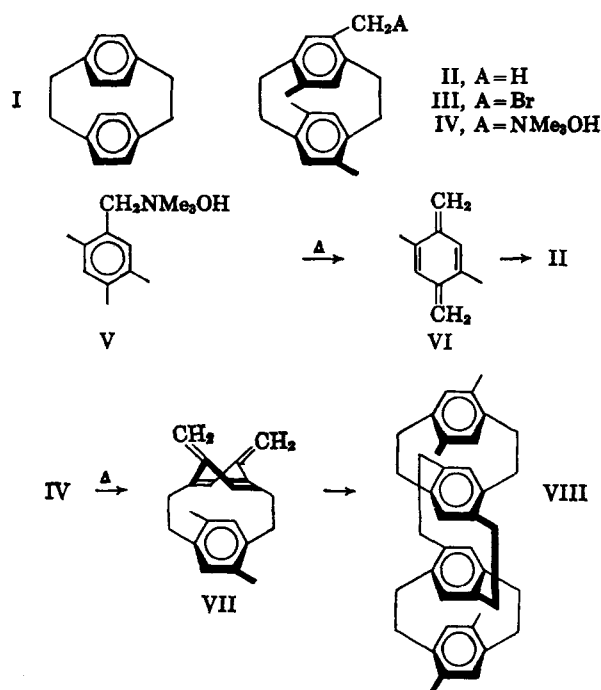


structurally equivalent and bear the necessary *para* relationship for subsequent conversion of II to a higher arylog. Reaction of II with N-bromosuccinimide yields the bromomethyl<sup>6</sup> compound III which is converted to the Hofmann base IV in the usual manner. Pyrolysis of IV in a toluene-water medium<sup>7</sup> results in the smooth evolution of trimethylamine. The resulting reaction filtrate readily yields a microcrystalline hydrocarbon (m.p. ca. 265° dec.<sup>8</sup>) which analyzes correctly for a dimer of the *p*-xylylene-cyclophane VII.

*Anal.* Calcd. for C<sub>40</sub>H<sub>44</sub>: C, 91.55; H, 8.45; mol. wt., 525. Found: C, 91.63, 91.71; H, 8.36, 8.32; osmometric mol. wt., 528 (C<sub>8</sub>H<sub>8</sub>).

The dimer, isolated in 10% yield, is inert to permanganate and bromine solutions. Its infrared spectrum displays only aromatic unsaturation and is virtually identical with that of II. On the basis of chemical genesis and its chemical and physical properties, structure VIII can be assigned to the product. A structure which involves two isolated (noninteracting) paracyclophane moieties can be rejected on spectral grounds.



It would be premature to report the existence of long range (ca. 9 Å.) electronic interactions between the first and fourth rings of VIII; however, the spectral properties give some insight into the electronic nature of the system. The ultraviolet spectrum, devoid of fine structure, is similar to that of II at shorter wave lengths. At longer wave lengths VIII exhibits a marked hyperchromic effect.<sup>9</sup> Compound VIII has  $\lambda_{\text{max}}^{\text{isooctane}}$  228 (log  $\epsilon$  4.30), 258 sh (3.84), 294 (3.45),

and 330 sh (2.65) m $\mu$  while II has  $\lambda_{\text{max}}^{\text{isooctane}}$  226 (4.20), 248 sh (3.53), 287 sh (2.38), and 300 sh (2.31) m $\mu$ .

The n.m.r. spectrum<sup>10</sup> of VIII is noteworthy. Much like II, the bridge-methylene protons appear as an A<sub>2</sub>B<sub>2</sub> multiplet centered at  $\tau$  7.4 and the methyl protons as a singlet at  $\tau$  8.19. While the aromatic protons in II appear as a singlet at characteristically<sup>2</sup> high field ( $\tau$  3.77), in VIII both sets of aromatic protons (inner and outer rings) appear as singlets at very high fields,  $\tau$  4.38 and 4.48. These chemical shifts are concentration insensitive. With II as a model, we had anticipated that the two structurally equivalent pairs of protons on the inner rings of VIII (each shielded by two adjacent aromatic rings) would be found at ca.  $\tau$  4.5 while the protons on the outer rings would appear close to  $\tau$  3.8. Clearly, transannular shielding due to induced ring currents cannot alone account for the nearly identical chemical shifts of the two types of aromatic protons. A qualitative explanation might be offered by simply assuming disruption of ring currents brought about by severe puckering of all aromatic rings; however, this argument does not appear attractive to us. Until a crystallographic structure analysis becomes available we cannot adequately explain the observed chemical shifts.

Compound VIII forms an insoluble, blue-black 1:1 complex with tetracyanoethylene. The complex has  $\lambda_{\text{max}}^{\text{KBr}}$  680 m $\mu$  while the tetracyanoethylene complex of II absorbs at 565 m $\mu$  in the same medium and at 580 m $\mu$  in methylene chloride solution. The relative positions<sup>4</sup> of the absorption maxima reflect a significant enhancement in  $\pi$ -basicity of VIII with respect to II.

The properties of VIII will be discussed in detail in a subsequent publication.

(10) Varian A-60 instrument, ca. 10% solutions in carbon tetrachloride. Integrated peak areas correct for the assigned structures.

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RECEIVED JULY 15, 1964

### Regulation of Structural Isomerism in Simple Diels-Alder Adducts

Sir:

A few years ago, two research groups reported the very pronounced catalytic effect of Lewis acids on the Diels-Alder reaction.<sup>1,2</sup> We now wish to report that Lewis acids not only accelerate the Diels-Alder reaction, but also regulate the structural isomerism of the adducts.

It is well known that two structural isomeric adducts are obtained from the reaction of an unsymmetrical diene with an unsymmetrical dienophile. Nazarov, *et al.*,<sup>3</sup> have shown that when 1- or 2-alkyl-1,3-butadienes are allowed to react with esters of  $\alpha$ -alkylacrylic acids, two structural adducts are formed in which the predominant isomer is the one that has the greatest separation between bulky groups.<sup>4</sup>

(1) P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960).

(2) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).

(3) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **124**, 586 (1959); *Chem. Abstr.*, **53**, 11,268f (1959).

(4) H. B. Hennis, *J. Org. Chem.*, **28**, 2570 (1963), has found in the Diels-Alder reaction of isoprene with methyl acrylate that methyl 4-methyl-3-cyclohexene-1-carboxylate accounts for 70% of the two isomeric adducts formed and that the reaction is temperature independent.

(6) The reduced reactivity of the bridge-methylene hydrogens allows selective bromination of the methyl groups: K. C. Dewhirst and D. J. Cram, *J. Am. Chem. Soc.*, **80**, 3115 (1958).

(7) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).

(8) Analytically pure material fuses instantly when placed on a heated block at or above the recorded temperature; below this temperature the sample is rapidly converted to a high-melting (>300°) polymer.

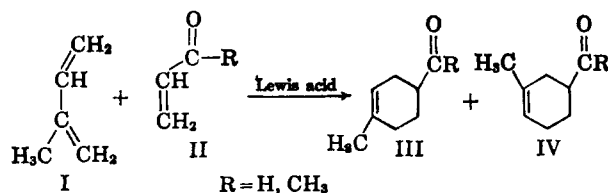
(9) We have noted a similar hyperchromic effect in the spectrum of the overcrowded octamethyl[2.2]paracyclophane and have attributed it to aromatic ring distortions (ref. 1).

TABLE I  
DIELS-ALDER REACTION BETWEEN ISOPRENE AND DIENOPHILE

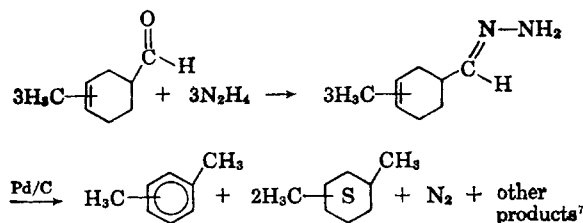
Dienophile	Catalyst	Solvent	Reaction temp., °C.	% of isomeric adducts	
				III	IV
1 Methyl vinyl ketone <sup>a</sup>	None	Toluene	120	71 <sup>b</sup>	29
2 Methyl vinyl ketone <sup>c</sup>	SnCl <sub>4</sub> ·5H <sub>2</sub> O	Benzene	<25	93 <sup>b</sup>	7
3 Acrolein <sup>d</sup>	None	None	150	59 <sup>e,f</sup>	41
4 Acrolein <sup>c</sup>	SnCl <sub>4</sub> ·5H <sub>2</sub> O	Benzene	<25	96 <sup>e,g</sup>	4

<sup>a</sup> Carried out in a sealed tube for 15 hr. in conventional manner according to H. L. Holmes in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 132. <sup>b</sup> Direct analysis by gas chromatography, using an F. and M. Model 609 instrument equipped with 220 ft. of R' (Ucon Lubricant 50-HB-2000), capillary column, and flame ionization detector. The physical properties of the ketones matched those reported by A. A. Petrov and N. P. Sopov, *Zh. Obshch. Khim.*, **22**, 591 (1952); *Chem. Abstr.*, **47**, 2735i (1953). Elemental analyses (Galbraith Laboratories, Knoxville, Tenn.) for both ketones were acceptable. Adduct mixture 2 spiked with mixture 1 showed only two peaks with the expected peak area alteration. <sup>c</sup> Carried out according to the method of Fray and Robinson, ref. 2. <sup>d</sup> Reaction in sealed tube according to the procedure of ref. a, p. 98. <sup>e</sup> Indirect analysis, see discussion and example below. <sup>f</sup> Melting point of 2,4-DNP derivative of adduct mixture 161.3–166.5°. Elemental analysis (Huffman Microanalytical Laboratory, Wheatridge, Colo.) acceptable with theory and with that of 2,4-DNP below. <sup>g</sup> Melting point of 2,4-DNP derivative of adduct mixture, 176.4–177.5°. Elemental analysis (Huffman Microanalytical Laboratory) acceptable.

We have now found that Lewis acid catalysis of the Diels-Alder reaction of simple, unsymmetrical reactants markedly affects the structural isomeric distribution of the resulting adducts.<sup>5</sup> Our studies have been confined to the reaction of isoprene (I) and methyl vinyl ketone or acrolein (II). The results obtained are summarized in Table I.



The relative amounts of the two ketone adducts were determined by gas chromatography (g.c.) and the analysis of the thermal adducts checked closely with the work of Hennis.<sup>4</sup> The aldehyde adducts, which we were unable to separate by g.c., were analyzed indirectly by conversion to their mixed hydrazones followed by reduction<sup>6</sup> and disproportionation in a single step over Pd/C to *p*- and *m*-xylenes.



(5) H. M. Walborsky, L. Barash, and T. C. Davis, *Tetrahedron*, **19**, 2333 (1963), have observed asymmetric synthesis via Lewis acid catalyzed Diels-Alder reactions at low temperatures. The product after LiAlH<sub>4</sub> reduction had the opposite sign and configuration.

(6) This is an unusual Wolff-Kishner reduction, which does not appear to be general: unpublished data of E. F. Lutz.

Although the disproportionation and reduction of the isomeric hydrazones is not clean cut,<sup>7</sup> it is believed that the ratio of the aromatics obtained is, at least qualitatively, representative of the isomeric adducts initially formed. Analyzing the ketone adducts by this method and comparing the results with those obtained by g.c. showed excellent agreement (90 vs. 93%) for adduct III from the Lewis acid catalyzed reaction. The comparison for the thermal reaction was less satisfactory (54 vs. 71%).<sup>8</sup>

It is believed that the adduct distribution here is regulated by coordination of the large Lewis acid with the carbonyl oxygen to increase greatly the steric bulk at the carbonyl group, causing the approaching isoprene molecule to orient in such a fashion that the pendant methyl group does not lie above the complexed carbonyl. This intermediate configuration leads to the formation of the 1,4-disubstituted adduct. This correlates well with the work of Nazarov,<sup>3</sup> summarized above, and with the accepted mechanism of adduct formation by the approach in parallel planes of diene and dienophile so that maximum accumulation of double bonds is achieved.<sup>9</sup>

An example illustrative of the procedure used to synthesize and analyze the aldehyde adducts follows. Using the catalyst and conditions<sup>10</sup> shown for expt. 4 in Table I, the aldehyde adduct of isoprene and acrolein was synthesized in a 53.6% yield by the method of Fray and Robinson.<sup>2</sup> The hydrazone was prepared by adding 3.7 g. (0.03 mole) of the mixed methylcyclohexenecarboxaldehydes to a refluxing solution of 9.6 g. (0.3 mole) of hydrazine in 20 ml. of absolute ethanol. The product was isolated by pouring the reaction solution on ice, extracting rapidly with ether, drying the ether extract, and stripping the solvent under vacuum. The crude hydrazone was distilled at 82–87° (0.08–0.06 mm.), *n*<sub>D</sub><sup>20</sup> 1.5168, and gave an acceptable elemental analysis (Table I, ref. f).<sup>12</sup> To a 5-ml. round-bottomed flask equipped with magnetic stirrer, condenser, and gas buret, was added 0.3607 g. of methylcyclohexenecarboxaldehyde hydrazone, 0.7231 g. of *n*-decane, and 0.0962 g. of 10% Pd/C. This solution was maintained at about 100° until gas evolution ceased. G.c. analysis<sup>13</sup> of the reaction solution showed the relative percentages of the xylenes formed were 96% *p*- and 4% *m*-xylene. The *p*-xylene was further identified by spiking with the authentic compound and by trapping the g.c. peak to obtain its ultraviolet spectrum, which was identical with that in the A.P.I. file. G.c. analysis further indicated that about 30% of the reaction had proceeded with disproportionation and reduction, with the remaining 70% going to nitro-

(7) In addition to the products of disproportionation and reduction that are shown, other products were also obtained which were presumed to be primarily nitrogen-containing compounds (e.g., azines, etc.).

(8) We feel that our data on the aldehyde adducts are somewhat more accurate than this because they represent an average of several determinations.

(9) See R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959), for discussion and leading references.

(10) Hydrated catalysts can be used so long as the temperature of reaction is low enough that the catalyst will not hydrolyze to produce protons. Proton formation leads to trimerization of the aldehyde adducts.<sup>11</sup>

(11) E. F. Lutz, unpublished research.

(12) The hydrazone appeared to decompose in the presence of air and apparently oxidizes to the corresponding azine upon prolonged contact with air.

(13) G. c. analysis was performed on an F. and M. Model 720 gas chromatograph, equipped with 2 m. of 5% Bentone-34–5% diisodecyl phthalate on Chromosorb W, and programmed from 50 to 170° at 7.5°/min.

gen coupled or reduced products (e.g., azines and hydrazines).

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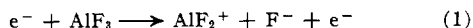
RECEIVED APRIL 18, 1964

### The Heat of Atomization of Aluminum Difluoride

Sir:

Although gaseous  $\text{AlF}$  and  $\text{AlF}_3$  are well-known species, no direct evidence for the existence of  $\text{AlF}_2$  has been heretofore presented. We wish to report here mass spectrometric evidence for the existence of  $\text{AlF}_2(\text{g})$  and a third law value for its heat of atomization.

Earlier mass spectrometric studies of the aluminum-reduced alkaline earth fluorides<sup>1,2</sup> indicated that only in the  $\text{Al-MgF}_2$  system were both  $\text{AlF}_3$  and  $\text{AlF}$  present. Careful re-examination of the species effusing from a heated tantalum Knudsen cell containing magnesium fluoride and aluminum using ordinary mass spectrometric techniques has revealed the presence of  $\text{AlF}_2^+$ , the chief ionic species resulting from  $\text{AlF}_3$ ,<sup>3</sup> below the onset of the pair production process (1), 11.7 e.v., and having an appearance potential of  $9 \pm$



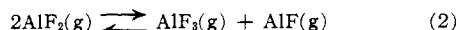
1 e.v. Table I gives the suggested interpretation of the appearance potential data.

TABLE I  
IONIC SPECIES AND THEIR PRECURSORS IN THE  $\text{MgF}_2\text{-Al}$  SYSTEM

Ion	Appearance potential, e.v. <sup>a</sup>	Probable precursor
$\text{Mg}^+$	7.6	$\text{Mg}$
$\text{MgF}^+$	$7.8 \pm 0.3$	$\text{MgF}$
$\text{Al}^+$	$9.2 \pm 0.3$	$\text{AlF}$
$\text{AlF}^+$	$9.7 \pm 0.3$	$\text{AlF}^b$
$\text{AlF}_2^+$	$9 \pm 1$	$\text{AlF}_2$
$\text{AlF}_2^+$	$15.2 \pm 0.3$	$\text{AlF}_3^b$

<sup>a</sup> Calibration measurements yielded appearance potentials for ( $\text{Mg}^+$ ) = 6.8 and ( $\text{Hg}^+$ ) = 9.6 e.v. vs. ionization potentials of 7.6 and 10.4 e.v. for Mg and Hg, respectively, whereby the experimental appearance potential values have been increased by 0.8 e.v.<sup>b</sup> These values agree well with those obtained by R. F. Porter, private communication, 1963.

To obtain  $\Delta H_a[\text{AlF}_2(\text{g})]$ , equilibrium 2 was studied



over the range 1243 to 1301°K. With the JANAF<sup>4</sup> free energy functions and equilibrium constants derived from the ion-current constants, one calculates an average third law heat of  $-49.5 \text{ kcal. mole}^{-1}$  with  $\pm 1.9 \text{ kcal. mole}^{-1}$  as the standard deviation. Uncertainties in the experimental quantities and accessory data (for example, whether  $\text{AlF}_2$  is linear or bent) bring the uncertainty to about  $\pm 4 \text{ kcal. mole}^{-1}$ . From the known heats of formation of  $\text{AlF}_3(\text{g})$ ,<sup>4,5</sup>  $\text{AlF}(\text{g})$ ,<sup>4,5</sup>  $\text{Al}(\text{g})$ ,<sup>4</sup> and  $\text{F}(\text{g})$ ,<sup>4</sup> one calculates  $\Delta H_a^\circ_{298}$

(1) G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, *Nature*, **199**, 804 (1963).

(2) T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, *J. Chem. Phys.*, October, 1964.

(3) R. F. Porter, *ibid.*, **33**, 951 (1960).

(4) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Company, Midland, Mich., revised through Sept. 30, 1963.

(5) D. Hildenbrand, Ford Motor Co., Aeronutronic Division, Report No. U-2055, March 15, 1963.

$[\text{AlF}_2(\text{g})] = 264.9 \pm 4$  and  $\Delta H_f^\circ_{298}[\text{AlF}_2(\text{g})] = -149.2 \pm 4 \text{ kcal. mole}^{-1}$ .

With these results, the stepwise dissociation energies for  $\text{AlF}_3(\text{g})$  are  $D(\text{AlF}_2 - \text{F}) = 156 (6.8)$ ,  $D(\text{AlF} - \text{F}) = 106 (4.6)$ , and  $D(\text{Al} - \text{F}) = 159 \text{ kcal. mole}^{-1} (6.9 \text{ e.v.})$ , which shows the decreased bond strength in  $\text{AlF}_2$ , apparently because of the lack of spin correlation in this "odd-electron" molecule.

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### The Microwave Spectrum, Dipole Moment, and Polarizability of Acetylene- $d_1$ <sup>1</sup>

Sir:

It is well established that substitution of deuterium for ordinary hydrogen causes a change in the electronic distribution in molecules. For example, optical activity has been detected<sup>2</sup> in molecules  $\text{RR}'\text{CHD}$ , proton n.m.r. chemical shifts are found to change upon adjacent deuterium substitution,<sup>3</sup> and the average length for CH bonds has been shown to be longer than for the corresponding CD bonds.<sup>4</sup> It is to be expected, therefore, that molecular dipole moments will show a change when deuterium is substituted for ordinary hydrogen. Studies in this laboratory have shown that a change does occur.<sup>6</sup> A logical extension is to look for a permanent dipole moment in an unsymmetrically deuterated, but otherwise symmetrical, molecule. A permanent dipole moment created by such substitution could be detected by studying the pure rotational spectrum of the molecule.

We have observed the  $J = 0 \rightarrow 1$  transition of  $\text{HC}\equiv\text{CD}$  at 59,450.6 Mc. In the detection of this transition, we have employed Stark modulation. In order to achieve sufficient modulation, a d.c.-based square wave was employed, providing fields from 82 to 110 kv./cm. In the presence of such large fields, the observed Stark shift is produced by an induced moment, as well as by the permanent dipole moment. However, it should be pointed out that the observation of a  $\Delta J = 1$  transition is unequivocal evidence of a permanent dipole moment. In this case of a  $J = 0 \rightarrow 1$  transition, only one Stark component is observed, and separation of the two contributions to the Stark shift cannot be obtained since both are proportional to the square of the field. However, it has been found<sup>5</sup> that the dipole moment of  $\text{CH}_3\text{C}\equiv\text{CD}$  is 0.012 D. lower than that of  $\text{CH}_3\text{C}\equiv\text{CH}$ , and we may assume that the permanent moment of  $\text{HC}\equiv\text{CD}$  is approximately equal to the

(1) This research was supported by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society.

(2) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaefer, *Tetrahedron*, **6**, 338 (1959).

(3) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959).

(4) V. W. Laurie and D. R. Herschbach, *ibid.*, **37**, 1687, (1962).

(5) Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963; and Abstracts, Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, 1964.