tert-butyl alcohol by weight). All aqueous solutions were made up using glass distilled water.

Analytical grade pyridine was dried over molecular sieve and distilled through a Nester-Faust spinning band column. Purity was checked by an analysis on a Perkin-Elmer gas chromatograph using a 20-ft Carbowax column (<1% impurity).

1,3,5-Trimethylpyridine (commercial sample 99.9% purity claimed) was distilled after treatment with boron trifluoride etherate.

Methyl 4-nitrovalerate was prepared by a triethylamine-catalyzed Michael reaction of nitroethane and methyl acrylate according to published procedure.[14] The procedure used for preparation and analysis of the D ester was essentially that of Allen,[11] except that sodium carbonate was used as the base. Protio ester was combined with a large excess of D_2O (99.8%) and a small quantity of sodium carbonate to effect exchange. The mixture was heated at 45° for 24 hr, being stirred continuously. The organic layer was separated and fractionally distilled after each exchange. Four such exchanges were usually necessary. Yields were poor because of a competing reaction leading to the formation of levulinic acid. The extent of deuteration was readily estimated by nmr, approximately by disappearance of the 1 H sextet at τ 5.1–5.7, more accurately by the change of the 3 H doublet at τ 8.4–8.6 into a symmetric triplet.

Optically active ester was prepared by Fischer esterification of the optically active acid, which was prepared by published procedures.[7] Resolution of the deuterated acid (obtained by acid hydrolysis of the D ester) was found to be possible with only a small amount of exchange by the same method. Fischer esterification gave the optically active D ester.

All the materials had nmr spectra consistent with their assigned structures.

Rate Measurements.—All iodinations were carried out exactly according to the earlier procedure.[7]

Racemization data were obtained using a Bendix automatic polarimeter; a jacketed cell was thermostated at 30°.

Solutions for observation were made by mixing thermostated solutions of reagents, of known concentration, in a definite ratio. Prior to this the polarimeter had been zeroed with solvent in the cell. The cell was rinsed four or five times with the reaction mixture before being filled for measurement. The change of rotation with time was recorded automatically. Reactions were normally followed (where possible) over 3 half-lives.

With slower reactions ($t_{1/2}$ >1 week) an offset zero method was used to follow the change more accurately. The scale was chosen so that a change in rotation of 10 millidegrees would give readings across the full scale, *i.e.*, a full-scale deflection = 10 millidegrees, and the zero was set at the end of the chart instead of the middle. This increased sensitivity enabled measurements to be made a little more accurately, but prevented scale changes.

Product Studies.—Attempted iodination of methyl 4-nitrovalerate under the same conditions as those used in the kinetic studies were not fruitful because of equilibration. It was believed that bromination would overcome the problem of reversibility and that the position of bromination would be analogous to that of iodination, and rough rate measurements confirmed this.

Bromine was added, dropwise, to an alkaline solution of the ester until no additional bromine was consumed. The mixture was twice extracted with ether. After drying, the ether was removed and a gc analysis of the residue was made. This indicated the formation of a new higher boiling product which was purified by preparative gc on a 2.5 ft × 0.5 in. column (25% SE-30 on 60/80 mesh Chromosorb P) at 200°. It was identified as methyl 4-bromo-4-nitrovalerate by spectral methods: nmr, 3 H singlet τ 7.8, 3 H singlet 6.4, 4 H irregular multiplet 7.2–7.7; ir 1370, 1560 cm^{-1}, characteristic of the NO_2 group; mass spectrum showed the characteristic bromine doublets and the heaviest ion corresponded to loss of NO_2 only. The ester was independently synthesized by esterification of the corresponding acid[13] and was found to have the same spectral characteristics.

Registry No.—Methyl 4-nitrovalerate, 10312-37-5.

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(14) J. Colonge and S. Pouchol, *Bull. Soc. Chim. Fr.*, 832 (1962).

Structural Directivity in the Diels–Alder Reaction. Dependence on Dienophile Cis–Trans Geometry

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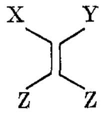
Citracononitrile and mesacononitrile were treated with six unsymmetrical dienes, and the structural isomer ratios were determined. Substantial differences between the ratios obtained from citracononitrile and mesacononitrile were observed in the reactions with 1,3-pentadiene and 3-phenyl-1,3-pentadiene. Determination of structural isomer ratios involved a one-step degradation of the dinitrile adducts to mixtures of substituted benzonitriles by treatment with potassium *tert*-butoxide and anthraquinone. This is a new reaction apparently involving the quinone dehydrogenation of carbanions.

The wealth of information available concerning structural directivity in the Diels–Alder reaction deals almost exclusively with orienting effects of diene and dienophile substituent groups as they vary in electronic character and size.[2] In general, any substituents X and Y located on the same olefinic carbon atom of the dienophile **1**, regardless of their electronic character, reinforce each other's structural directing influence in Diels–Alder reactions with unsymmetrical dienes. On the other hand, dienophiles **2** and **3**, with substituents X and Y located on opposite ends of the olefinic bond, whether they be cis or trans to each other in any particular compound, compete for structural directivity.



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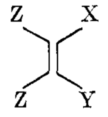

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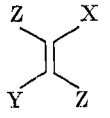

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The possibility that dienophile geometry may play a significant role in determining structural directivity is suggested by an example reported by Bachmann, who found that diene **4** reacted with citraconic anhydride (**5**) to give predominantly structural isomer **6**, while mesaconic acid (**7**) gave predominantly isomer **8**.[3] The opposing structural directing substituents are a methyl group and a hydrogen atom in both of these dienophiles. If one considers only the nature of these opposing groups, without regard to geometry or nature of the

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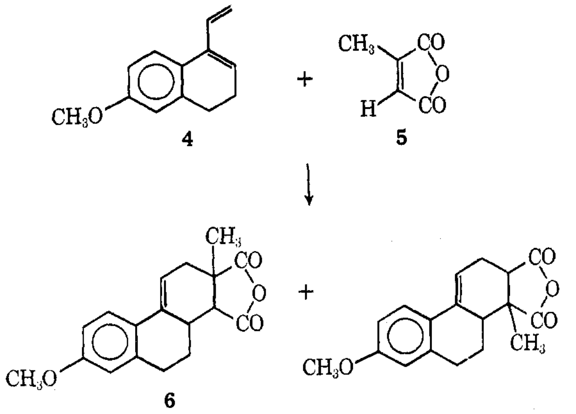
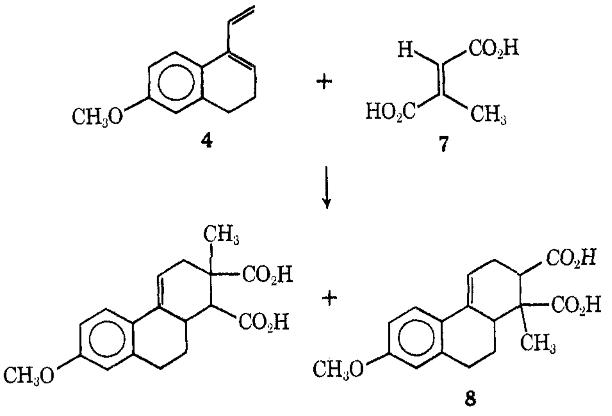
[1] (a) To whom correspondence should be addressed: The University of Connecticut. (b) NASA Fellow, The University of Connecticut, 1966–1969.

[2] (a) Y. A. Titov, *Usp. Khim.*, **31**, 529 (1962); *Russ. Chem. Rev.*, **31**, 267 (1962). (b) A. S. Onishchenko, "Diene Synthesis," Daniel Davey, New York, N. Y., 1964.

[3] (a) W. E. Bachmann and J. M. Chemerda, *J. Amer. Chem. Soc.*, **70**, 1468 (1948); (b) W. E. Bachmann and J. Controulis, *ibid.*, **73**, 2636 (1951).



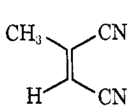
4 **5** **6**



4 **7** **8**

symmetrically disposed dienophile substituents, one would expect that the same structural isomer would predominate in each case. It should be noted, however, that these two dienophiles differ in both geometry and in identity of the symmetrically located activating groups, both factors which must be considered in light of the experimental facts.

The purpose of this work was to investigate the possibility that the cis–trans geometry of dienophiles such as **2** and **3** has a significant influence on structural directing ability. A cis–trans isomeric pair of dienophiles, citracononitrile (**9**) and mesaconoitrile (**10**),



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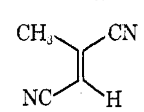
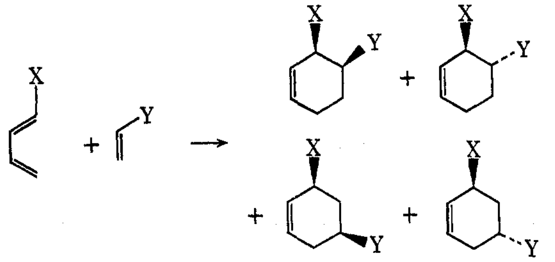


10

which exhibits this behavior, was, in fact, found. That is, with certain dienes, the cis dienophile **9** gives structural isomer ratios significantly different from the ratios obtained by reaction of the trans dienophile **10** with the same dienes.

It was predicted that citracononitrile (**9**) and mesaconoitrile (**10**) could be studied conveniently under identical reaction conditions, since the closely related dienophiles maleonitrile and fumaronitrile show nearly identical Diels–Alder reactivities.[4] It was found that citracononitrile actually reacts slightly faster than mesaconoitrile in reactions using excess dienophile, and both dienophiles were shown to be thermally stable toward isomerization under the reaction conditions used. The chance that solvent polarity might influence the structural directivity was minimized by running the Diels–Alder reactions in a fourfold excess of diene, the diene thus serving as a solvent. Kinetic control of adduct isomer ratios at the reaction temperature of 100° is assumed, primarily on the basis of the absence of examples to the contrary for acyclic dienes. For example, some monocyclic adducts which have been thoroughly investigated in this regard do not undergo reverse Diels–Alder reaction, even at 350°.[5,6]

The major concern in carrying out this preliminary work was the development of a suitable method of analysis. Although direct glc analysis of Diels–Alder reaction mixtures containing four isomeric adducts (eq 1) has been accomplished in some cases,[6,7] several

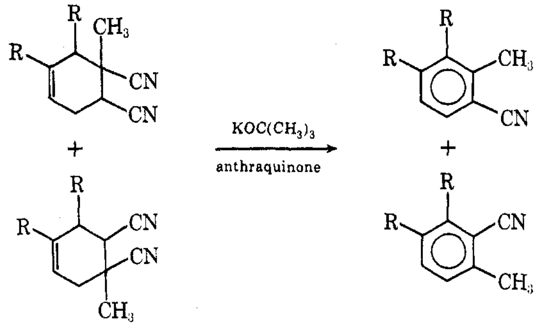


(1)

attempts to so separate the adducts obtained from **9** and **10** were unsuccessful.

In the past, researchers have generally resorted to degradative methods of analysis to obtain information on structural directivity. However, as Sauer has pointed out, most data obtained in this way is at best approximate and is useful only as an indication of the general direction of structural directivity.[8] However, in the present case it is not the absolute value of the isomer ratios that is important, but rather the comparison of ratios obtained *via* a single degradative procedure.

A one-step degradation was developed in which adduct mixtures were treated with potassium *tert*-butoxide and anthraquinone in benzene at room temperature, giving mixtures of the two possible isomeric benzonitriles (eq 2). The ratios of the benzonitriles were conveniently determined by integration of the methyl proton singlets in the nmr spectra[9] of the crude degradation product mixtures.



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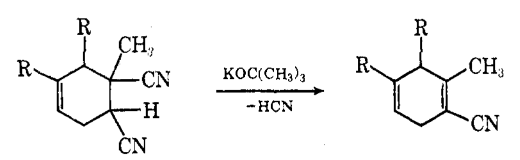

(3)

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[4] (a) J. Sauer, D. Lang, and H. Wiest, *Chem. Ber.*, **97**, 3208 (1964); (b) J. Sauer, D. Lang, and H. Wiest, *Z. Naturforsch. B*, **17**, 206 (1962).

[5] H. E. Hennis, *J. Org. Chem.*, **28**, 2570 (1963).

[6] T. Inukai and T. Kojima, *ibid.*, **32**, 869 (1967).

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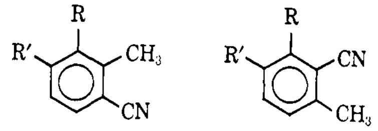
[8] J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

[9] (a) E. D. Becker, "High Resolution NMR, Theory and Chemical Applications," Academic Press, New York, N. Y., 1969, pp 236–240; (b) A. Mathias and D. Taylor, *Anal. Chim. Acta*, **35**, 376 (1966).

TABLE I

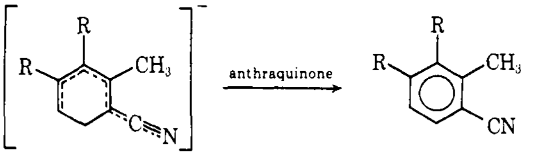
ISOMER RATIOS



				Citracononitrile		Mesacononitrile	
Registry no.	Diene	R	R'	Ratio	Yield,[a] %	Ratio	Yield,[a] %
504-60-9	1,3-Pentadiene	CH_3	H	17:10	69	12:10	59
78-79-5	2-Methyl-1,3-butadiene	H	CH_3	1:1	75	1:1	69
1515-78-2	1-Phenyl-1,3-butadiene	C_6H_5	H	55:10	40	61:10	28
	2-Phenyl-1,3-butadiene	H	C_6H_5				
37580-41-9	3-Phenyl-1,3-pentadiene	CH_3	C_6H_5	21:10	74	10:10	74
37580-42-0	2-Methyl-1-phenyl-1,3-butadiene	C_6H_5	CH_3	36:10	77	33:10	68

[a] Overall yield of aromatized products based on dienophile as limiting reagent. Determined by use of methyl benzoate as a quantitative internal nmr standard.

The degradation is presumed to involve the initial loss of hydrogen cyanide from the adduct in a reverse Michael type elimination (eq 3). Potassium *tert*-butoxide alone in benzene, ether, or dimethyl sulfoxide causes elimination of hydrogen cyanide from the adducts, with formation of a mixture of products containing low yields of the substituted benzonitriles, autoxidation of the cyclohexadienide ion (11) ac-



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counting for the limited aromatization which occurs in these cases.[10] Running the reaction in a pure oxygen atmosphere did not improve the yield of benzonitriles, however.

When anthraquinone is present in the strongly basic reaction mixture, pure benzonitriles can be isolated in about 90% yield. It has been previously suggested that phenanthrenequinone might find use in the dehydrogenation of preformed anions.[11] However, although a logical extension of quinone dehydrogenations, this is the first reported instance of the dehydrogenation of a carbanion (11) by a quinone. While most of the anthraquinone does not dissolve in the reaction mixture, 3 equiv of anthraquinone was required to obtain complete aromatization of the adducts. During the reaction a dark green solid was produced, which rapidly turned yellow on exposure to air. This material has not been characterized, but its properties resemble those of the known sodium salt of phenanthrene quinhydrone.[12]

The four isomeric adducts comprising each adduct mixture (eq 1) probably differ somewhat in the ease with which they lose HCN. The fact that no unreacted adducts are visible in the nmr spectrum of the reaction mixture after the degradation, coupled with the high yields obtained, led us to accept the use of this degradation in the analytical procedure.

The dienes shown in Table I were selected to provide examples with different degrees of structural directing ability. The structural isomer ratios obtained from the analysis are presented in Table I, and represent averages from duplicate determinations. Ratios from duplicate analyses differed by less than 2% of the larger number of the ratio in most cases, and by less than 5% in all cases. The yields determined by the use of methyl benzoate as an internal standard represent minimums, since controls run on known mixtures gave results 0–6% lower than actual. Control experiments using glc and nmr analysis showed that citracononitrile and mesacononitrile do not interconvert under the Diels–Alder reaction conditions used and, in the cases of 1-substituted dienes, only the trans isomers reacted with the dienophiles.

The reactions which show the largest dependence upon dienophile geometry are those of 1,3-pentadiene and 3-phenyl-1,3-pentadiene. Although the number of examples tested so far is not great enough to justify any generalizations, the characteristics that set these two dienes apart from the others should be noted. Both have terminal methyl substituents, which places the methyl group in proximity to the reactive site. The ratios obtained show that both are very weakly directing dienes, and 3-phenyl-1,3-pentadiene especially resembles the diene used by Bachmann.

Differences in structural directivity observed with the four remaining dienes were small or nonexistent. 2-Phenyl-1,3-butadiene polymerizes so rapidly that the yield of adducts produced was insufficient for analysis; and 1-phenyl-1,3-butadiene also polymerizes rapidly, reducing the yield of adducts and thus lowering the significance of the results. A decreased nmr signal to noise ratio and a relatively large difference in yield between the reactions of mesacononitrile and citracononitrile are factors which tend to decrease the reliability of the nmr detection method in general.

2-Methyl-1-phenyl-1,3-butadiene showed a small structural directivity dependence on dienophile geometry. This diene contains a terminal phenyl substituent and, according to the ratios listed in Table I, is more discriminating in its own structural directivity than the 1,3-pentadienes, which showed a greater sensitivity to dienophile geometry.

The degradation mixtures from the reactions of 2-methyl-1,3-butadiene could not be integrated effectively, since the maximum separation of methyl singlets was only 2 Hz. However, the methyl singlet peak heights for the two isomers were identical in the reaction mixtures from both dienophiles, indicating the ab-

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[10] G. A. Russell, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, *Advan. Chem. Ser.*, No. 75, 174 (1968).

[11] L. M. Jackson in "Advances in Organic Chemistry, Methods and Results," Vol. 2, Interscience, New York, N. Y., 1960, pp 331–345.

[12] S. Goldschmidt and F. Christmann, *Chem. Ber.*, **57**, 713 (1924).

sence of any detectable structural directivity dependence on dienophile geometry.

The results obtained from these few examples indicate a structural directivity dependence on dienophile geometry that may, in some cases, be of value in synthesis. It is clear, however, that a theoretical explanation of this phenomenon must be deferred until, as well as the structural isomer ratios, the stereoisomer ratios (eq 1) are determined. A mechanistic interpretation may require consideration of π-orbital overlap and steric interactions similar to those used in explaining the Alder endo rule.[13] However, any predictions based on the endo rule at this time would be premature, since very little data is available relative to acyclic dienes, and cyano activating groups show only weak endo-directing ability in reactions with cyclic dienes[14] and unusual directing effects with acyclic dienes.[15]

Experimental Section

All melting points and boiling points are uncorrected. Microanalyses are by Spang Microanalytical Laboratories, Ann Arbor, Mich. All infrared (ir) spectra were run neat or in potassium bromide pellets on a Perkin-Elmer Model 237B grating spectrometer. Analytical gas chromatography (glc) was done with a Varian Aerograph 90P3 gas chromatograph, using 5 ft × $^{3}/_{16}$ in. i.d. columns. Preparative gas chromatography (glc) was done with a Varian Aerograph Autoprep Model 705 gas chromatograph, using a 20 ft × $^{5}/_{16}$ in. i.d. column of 30% SE-30 on 60/80 mesh Chromosorb W. The nuclear magnetic resonance (nmr) spectra were run on a 60-MHz Varian A-60 spectrometer, with tetramethylsilane as the internal reference. The ultraviolet (uv) spectra were obtained with a Cary Model 14 recording spectrophotometer. Mass spectra were obtained with an AEI MS12 mass spectrometer. Preparative thin layer chromatography (tlc), unless otherwise indicated, was done with Brinkmann silica gel PF_{254} with 5% calcium sulfate.

Diels–Alder Reactions. General Procedure.—A mixture of 2.50–3.50 mmol of diene, 0.430–0.870 mmol of dienophile (citraconomitrile[16] or mesacononitrile[17]), and 1–2 mg of hydroquinone was sealed in a glass tube and heated at 100° for 10 days. A reaction time in excess of 3 days at 100° was necessary to obtain complete reaction in all of the cases studied. Three tubes containing the diene and citracononitrile (**9**), three tubes containing the diene and mesacononitrile (**10**), and one tube containing the diene alone were immersed in the same oil heating-bath and heated at the same time. Examination of the heated diene sample by tlc and glc revealed extensive polymerization in each case.

Purification of Diels–Alder Reaction Mixtures.—The sealed reaction tube was opened and the contents were removed by adding dichloromethane to dissolve the mixture and pipetting the solution. A benzene–dichloromethane solution of the reaction mixture was applied to a 1 × 4 in. area near the bottom ("bottom" refers to one of the 5-in. sides) of a 5 × 8 in. ChromAR 1000 sheet (Mallinkrodt Chemical Co.). The sheet was developed 2–4 times with petroleum ether (bp 30–60°) until the excess diene and diene dimers had moved above a line 5.25 in. from the bottom of the sheet (observed under ultraviolet light). The sheet was then cut at 5.25 in. from the bottom, and the bottom portion was eluted with 50 ml of methanol by descending elution chromatography in an apparatus similar to that usually employed for descending paper chromatography. The methanol was removed from the adduct mixture with a rotary evaporator, the mixture was transferred in dichloromethane solution to a 30 × 100 mm vial, and the solvent was removed with a rotary evaporator.

Only polymeric material remained on the sheet, as evidenced by examination (tlc and ir spectrum) of additional material eluted from the sheet by subsequent elution with acetone and dichloromethane.

The ir spectrum of the material eluted with dichloromethane from the detached upper portion of the sheet showed no absorption in the C≡N stretching region of 2215–2260 cm^{-1}.

It may be concluded from the above results that the isolation of the adduct mixture was quantitative. Although the adduct mixture after this purification contained traces of colored impurities and a small amount of polymeric material, it was suitable for analysis by the procedure used in this work.

Degradation of Adduct Mixtures.—Three equivalents of powdered anthraquinone was added to the adduct mixture (0.430–0.870 mmol, theoretical yield from Diels–Alder reaction) in a 30 × 100 mm glass vial. The vial was then placed in a nitrogen-filled glove bag, where the degradation reaction was run. The adduct mixture was dissolved by stirring (magnetic stirrer) with 15 ml of dry benzene which had been saturated with anthraquinone. Then 0.50–0.60 g (4.4–5.3 mmol) of powdered potassium *tert*-butoxide was added to the rapidly stirred solution. The reaction mixture began to turn dark green immediately, and stirring was continued for 5 min. Then 3 ml of anhydrous ether was added, and stirring was continued for an additional 5 min. The reaction vial was then removed from the glove bag and pipetted directly into a spherical separatory funnel containing a rapidly stirred (magnetic stirrer) mixture of 40 ml of dichloromethane and 20 ml of 5% aqueous ammonium chloride solution. The green color of the reaction mixture disappeared within a few minutes after addition to the separatory funnel. The yellow dichloromethane layer was drawn off, and the clear aqueous solution was extracted with two additional 25-ml portions of dichloromethane. The solvent was removed from the combined dichloromethane extracts on a rotary evaporator. The residue was stirred well with 15 ml of ether, which was then filtered to remove the insoluble anthraquinone. The anthraquinone crystals and flask were thoroughly washed with three additional 15-ml portions of ether. The ether was removed on a rotary evaporator, and the residue was transferred in dichloromethane solution to a 15 × 120 mm test tube. The solvent was removed on a rotary evaporator. One drop of methyl benzoate (quantitative nmr standard) was added to the residue in the test tube and weighed. The reaction residue–methyl benzoate mixture was then mixed well with about 1 ml of chloroform-*d*, and the solution was filtered into an nmr tube.

Nmr Determination of Isomer Ratios.—Nmr spectra of samples prepared according to the procedure described under "Degradation of Adduct Mixtures" were obtained first at 500-Hz sweep width (downfield from internal tetramethylsilane) to determine relative positions of the methyl proton signals. The methyl protons of the substituted benzenecarbonitriles and methyl benzoate were integrated at 50-Hz sweep width and sweep time of 50 sec. The rf field was set low enough to eliminate saturation. Each sweep was started at a sweep offset of 190 Hz downfield from internal tetramethylsilane to integrate the methyl proton singlet of methyl benzoate (δ 3.92 ppm). Then, while the sweep continued, the offset was changed to 130–115 Hz downfield from internal tetramethylsilane for integration of the methyl proton singlets of the substituted benzenecarbonitriles (δ 2.63–2.04 ppm). Each sample was integrated five times and average values were determined. The results of these analyses are presented in Table I.

2,6-Dimethylbiphenyl-3-carbonitrile.—A mixture of 2.9 g (0.020 mol) of 2-methyl-1-phenyl-1,3-butadiene[18] and 3.7 g (0.040 mol) of citracononitrile was heated at 95° in a sealed glass tube for 8 days. The reaction mixture was chromatographed in benzene on 330 g of Florisil (column diameter 35 mm). The 24 100-ml fractions containing crystalline solid after removal of the benzene were combined and recrystallized three times from absolute ethanol to give 0.90 g (0.0038 mol, 19% yield) of colorless needles: mp 170–171°; ir (potassium bromide) 2250 and 2240 cm^{-1} (C≡N); nmr (chloroform-*d*) δ 7.48 (s, 5, C_6H_5), 5.85 (m, 1, C=CH), 3.35 (m, 1), 2.93 (m, 3), 1.63 (s, 3, CH_3), and 1.54 ppm (s, 3, CH_3).

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[13] (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965); (b) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[14] (a) K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958); (b) J. S. Meek and J. W. Ragsdale, *J. Amer. Chem. Soc.*, **70**, 2502 (1948); (c) M. Schwarz and M. Maienthal, *J. Org. Chem.*, **25**, 449 (1960).

[15] J. S. Meek, B. T. Poon, R. T. Merrow, and S. J. Cristol, *J. Amer. Chem. Soc.*, **74**, 2669 (1952).

[16] P. M. Brown, D. B. Spiers, and M. Walley, *J. Chem. Soc.*, 2882 (1957).

[17] L. van de Straete, *Bull. Sci. Acad. Roy. Belg.*, **21**, 226 (1935); *Chem. Abstr.*, **29**, 3985 (1935).

[18] K. Alder, J. Haydn, K. Heimbach, and K. Neufang, *Justus Liebigs Ann. Chem.*, **586**, 110 (1954).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83. Found: C, 81.32; H, 6.82.

A 102-mg (0.432 mmol) sample of the above adduct was treated as described previously under "Degradation of Adduct Mixtures." The product was isolated by preparative tlc followed by sublimation at room temperature (0.3 mm), giving 68 mg (0.329 mmol, 76% yield) of colorless crystals: mp 63–64°; ir (potassium bromide) 2220 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.65–7.05 (m, 7), 2.26 (s, 3, CH_3), and 2.11 ppm (s, 3, CH_3).

Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.93; H, 6.31.

Acidic hydrolysis of this material followed by decarboxylation with copper chromite in quinoline gave 2,6-dimethylbiphenyl.

3,6-Dimethylbiphenyl-2-carbonitrile.—A mixture of 2-methyl-1-phenyl-1,3-butadiene, 3.4 g (0.051 mol) of *trans*-2-butenenitrile, and 5 mg of hydroquinone was heated at 200° in a sealed tube for 3 days. The reaction mixture was dissolved in 200 ml of benzene, 20 g of 28–200 mesh silica gel was added, and the benzene was removed on a rotary evaporator. The silica gel was then thoroughly washed with methanol, which extracted the adduct mixture, leaving most of the polymeric material on the silica gel. The adduct mixture was separated from excess diene and diene dimers by preparative tlc, developed with petroleum ether.

The adduct mixture was aromatized by refluxing under nitrogen for 3 hr with 0.5 g of 5% palladium on charcoal. The mixture was taken up in acetone, filtered, and concentrated. The aromatic nitrile mixture was isolated as 1.2 g (0.0058 mol, 24% yield) of yellow oil by preparative tlc, developed with carbon tetrachloride.

A 60-mg sample of the above nitrile mixture was stirred with a mixture of 20 ml of 30% hydrogen peroxide, 20 ml of acetone, and 1 g of sodium carbonate for 2 days.[19] This effectively removed the undesired 2,6-dimethylbiphenyl-3-carbonitrile by converting it to the amide. The reaction mixture was extracted with two 40-ml portions of dichloromethane, the extract was concentrated, and the residue was purified by preparative tlc, developed with benzene. Further purification by sublimation at room temperature (0.3 mm) gave 47 mg (78% recovery) of colorless crystals: mp 45–46°; ir (neat) 2220 cm^{-1} ($C\equiv N$); nmr (carbon tetrachloride) δ 7.18 (m, 7), 2.45 (s, 3, CH_3), and 2.02 ppm (s, 3, CH_3).

Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.93; H, 6.55.

A sample of the above material gave 1,4-dimethylfluorenone when heated with polyphosphoric acid at 160°.

2,3-Dimethylbiphenyl-4-carbonitrile.—A mixture of 2.9 g (0.020 mol) of 3-phenyl-1,3-pentadiene[18] and 3.7 g (0.040 mol) of mesacononitrile was heated at 95° for 5 days. The reaction mixture was chromatographed on 150 g of Florisil (column diameter 34 mm). The excess diene and diene dimers were removed with petroleum ether eluent. The adduct mixture was then removed with benzene eluent. The adduct mixture was separated into its various isomers by preparative glc (column temperature 237°, nitrogen flow rate 180 ml/min). The third adduct to emerge from the gas chromatograph had mp 97–99°; ir (potassium bromide) 2240 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.30 (m, 5, C_6H_5), 5.72 (m, 1, C=CH), 3.25 (m, 1), 3.06 (m, 1), 2.68 (m, 2), 1.55 (s, 3, CH_3), and 1.10 ppm (d, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83. Found: C, 81.24; H, 6.83.

A 143-mg (0.61 mmol) sample of the adduct was subjected to the reaction conditions described under "Degradation of Adduct Mixtures." The crude product was chromatographed by preparative tlc and further purified by sublimation at room temperature (0.3 mm), giving 86 mg (0.42 mmol, 69% yield) of white solid: mp 57.5–58.0°; ir (potassium bromide) 2220 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.60–7.11 (m, 7), 2.57 (s, 3, CH_3), and 2.21 ppm (s, 3, CH_3).

Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 87.02; H, 6.32.

Acidic hydrolysis of this material followed by decarboxylation with copper chromite in quinoline gave 2,3-dimethylbiphenyl.

2,4-Dimethylbiphenyl-3-carbonitrile.—A mixture of 3.4 g (0.024 mol) of 3-phenyl-1,3-pentadiene and 3.4 g (0.051 mol) of *trans*-2-butenenitrile was treated as described previously under "3,6-Dimethylbiphenyl-2-carbonitrile." The aromatized mixture was taken up in acetone and filtered, and the filtrate was concentrated. Preparative tlc of the residue, developed with carbon tetrachloride, gave a light yellow solid, which was recrystallized three times from absolute ethanol to give 0.90 g (0.0043 mol, 18% yield) of colorless crystals: mp 124.5–125.0°; ir (potassium bromide) 2220 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.38 (m, 7), 2.61 (s, 3, CH_3), and 2.48 ppm (s, 3, CH_3).

Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.85; H, 6.29.

A sample of this material gave 2,4-dimethylbiphenyl when heated with polyphosphoric acid at 160°.[20]

3-Methylbiphenyl-2-carbonitrile.—A mixture of 0.908 g (6.98 mmol) of 1-phenyl-1,3-butadiene[21] and 0.980 g (14.6 mmol) of *trans*-butenenitrile was treated as described previously under "3,6-Dimethylbiphenyl-2-carbonitrile," giving 60 mg of a colorless oil: ir (neat) 2220 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.70–7.23 (m, 8) and 2.63 ppm (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 193 (100, M^+), 192 (60), 165 (28), 117 (38), 91 (35), and 28 (37).

A 25-mg (0.13 mmol) sample of the above material gave 1-methylfluorenone when heated with polyphosphoric acid at 160°.

2-Methylbiphenyl-3-carbonitrile.—A mixture of 0.70 g (7.6 mmol) of mesacononitrile, 1.38 g (10.6 mmol) of 1-phenyl-1,3-butadiene, and 2 mg of hydroquinone was heated at 100° for 10 days in a sealed glass tube, then purified as described previously under "Purification of Adduct Mixtures." The adduct mixture obtained was fractionally crystallized three times from 95% ethanol, giving 0.193 g (0.87 mmol, 11% yield) of colorless needles: mp 156–157°; ir (potassium bromide) 2240 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.40 (m, 5, C_6H_5), 5.87 (m, 2, C=CH), 3.96 (m, 1), 3.42 (m, 1), 2.75–2.45 (m, 2), and 1.21 ppm (s, 3, CH_3).

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.05. Found: C, 81.02; H, 6.36.

A 173-mg (0.780 mmol) sample of this adduct was treated as described previously under "Degradation of Adduct Mixtures." The crude product was chromatographed by preparative tlc, and developed with a mixture consisting of 60% petroleum ether and 40% benzene by volume. The yellow oil obtained was further purified by sublimation at room temperature (0.3 mm) to give 134 mg (0.695 mmol, 89% yield) of white crystals: mp 61.0–61.5°; ir (potassium bromide) 2240 cm^{-1} ($C\equiv N$); nmr (chloroform-*d*) δ 7.77–7.22 (m, 8) and 2.47 ppm (s, 3, CH_3).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74. Found: C, 87.07; H, 5.71.

Acidic hydrolysis of this compound and subsequent decarboxylation with copper chromite and quinoline gave 2-methylbiphenyl.

Registry No.—**9,** 37580-43-1; **10,** 37580-44-2; $C_{16}H_{16}N_2$, mp 170–171°, 37580-45-3; $C_{16}H_{16}N_2$, mp 97–99°, 37580-46-4; $C_{15}H_{14}N_2$, mp 156–157°, 37580-47-5; 2,6-dimethylbiphenyl-3-carbonitrile, 37580-48-6; 3,6-dimethylbiphenyl-2-carbonitrile, 37580-49-7; *trans*-2-butenenitrile, 627-26-9; hydroquinone, 123-31-9; 2,3-dimethylbiphenyl-4-carbonitrile, 37580-50-0; 2,4-dimethylbiphenyl-3-carbonitrile, 37580-51-1; 3-methylbiphenyl-2-carbonitrile, 37580-52-2; 2-methylbiphenyl-3-carbonitrile, 37580-53-3.

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[20] H. R. Snyder and C. T. Elson, *ibid.*, **76**, 3039 (1954).

[21] O. Grummitt and E. I. Becker in "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 771.