Formation of *cis,cis*-1,4-Dicyano-1,3-butadienes by Thermal Decomposition of 1,2-Diazidobenzenes[1]

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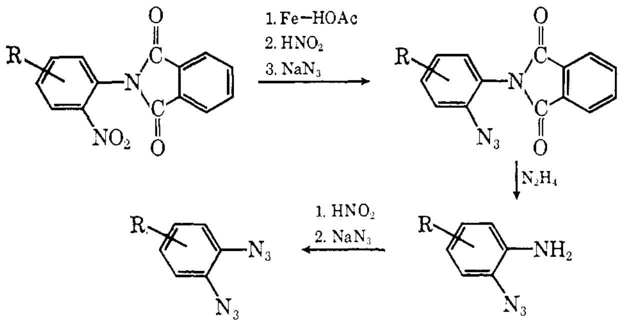
Abstract: 1,2-Diazidobenzene and its 3-methyl, 4-methyl, 4-methoxy, and 4-chloro derivatives have been synthesized; 1,2-diazidonaphthalene has also been prepared. Thermal decomposition of these 1,2-diazidobenzenes has been found to result in cleavage of the aromatic ring to give *cis,cis*-1,4-dicyano-1,3-butadienes. Thermal decomposition of 1,2-diazidonaphthalene gives *o*-cyanocinnamonitrile. The possibility that these reactions involve dinitrenes is discussed. The 60-Mc chemical shifts and the coupling constants of several 1,4-dicyano-1,3-butadienes are reported.

Although 1,3- and 1,4-diazidobenzenes have been known for some time, neither the parent 1,2-diazidobenzene nor any of its derivatives had been reported until recently. Two reports of the synthesis of 1,2-diazidobenzene appeared about the same time.[2,3] The preparation of several substituted 1,2-diazidobenzenes and 1,2-diazidonaphthalene is reported in this paper along with a study of their decomposition products.

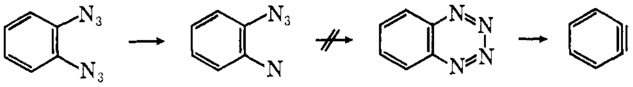
The starting material used for the synthesis of 1,2-diazidobenzenes was the corresponding 2-nitroaniline. The amino group was protected by conversion to the phthalimide. The nitro group was reduced with iron and acetic acid in aqueous acetone. Diazotization of the amino group followed by treatment of the diazonium salt solution with sodium azide gave the 2-phthalimidophenyl azide. The phthalimido group was removed by treatment with hydrazine in methanol at room temperature to give the 2-azidoaniline. Conversion of the 2-azidoanilines to 1,2-diazidobenzenes was effected by diazotization, followed by treatment of the diazonium salt solution with sodium azide. The general procedure is outlined below[4] (see Table I).



The 2-azidoanilines prepared by this route were found to be stable at room temperature, but they decomposed when heated above 80°. In contrast, 1-azido-2-naphthylamine was unstable and decomposed even at room temperature. However, it could be kept at 0° for a few hours.

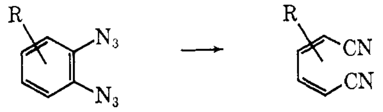
The 1,2-diazidobenzenes and 1,2-diazidonaphthalene were surprisingly stable. All of them were found to be as stable to heat as phenyl azide. However, 1,2-diazidobenzene could be detonated on an anvil by a vigorous stroke of a hammer. The remaining diazides were not appreciably sensitive to shock.

It was felt that thermal decomposition of 1,2-diazidobenzene might result in the formation of benzyne *via* the following route.



In order to check this possibility the initial decomposition of 1,2-diazidobenzene was carried out in hexadecane solution containing anthracene. It was anticipated that if benzyne was formed, it could be trapped by anthracene to give tryptycene. However, no tryptycene was isolated. Instead, two solids, mp 187 and 129°, were obtained.

The solid melting at 129° was identified as *cis,cis*-1,4-dicyano-1,3-butadiene (Ia). It was found that it could be obtained in high yield (79%) by the dropwise addition of a decalin solution of 1,2-diazidobenzene to a larger volume of refluxing decalin.



Ia, R = H	IIa, R = H
b, R = 3-CH_3	b, R = 1-CH_3
c, R = 4-CH_3	c, R = 2-CH_3
d, R = 4-CH_3O	d, R = 2-CH_3O
e, R = 4-Cl	e, R = 2-Cl

The compound melting at 187° was found to be the Diels–Alder adduct of anthracene and Ia. It was prepared in low yield by direct reaction of Ia and anthracene in refluxing *m*-xylene.

The structure of Ia was indicated initially by its molecular formula of $C_6H_4N_2$, a peak in its infrared spectrum at 2200 cm^{-1} characteristic of cyano groups, its lack of reaction with bromine in carbon tetrachloride, its sensitivity to permanganate oxidation, and finally, its hydrolysis to *trans,trans*-muconic acid in boiling concentrated hydrochloric acid. The *cis,cis* configuration of Ia was shown by the presence of an intense peak at

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(1) Acknowledgment is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) J. H. Hall, *J. Am. Chem. Soc.*, 87, 1147 (1965).

(3) W. L. Mosby and M. L. Silva, *J. Chem. Soc.*, 1003 (1965).

(4) The preparation used for the substituted 2-azidoanilines is essentially that reported for 2-azidoaniline. See P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Am. Chem. Soc.*, **84**, 485 (1962). A variation in this procedure in which the amino group was converted to the succinimide has been reported by L. Krbechek and H. Takimoto, *J. Org. Chem.*, **29**, 3630 (1964).

Table I. Intermediates in the Formation of Aromatic 1,2-Diazides

Compd	Recrystn solvent	Mp, °C	Yield, %	Formula	Found, % C	Found, % H	Found, % N	Calcd, % C	Calcd, % H	Calcd, % N
2-Phthalimidonitrobenzenes										
5-Cl	C_6H_6–C_2H_5OH	202	57	$C_{14}H_7N_2O_4Cl$	55.9	2.24	9.54	55.6	2.33	9.24
2-Phthalimidoanilines										
5-Cl	C_2H_5OH	183	68	$C_{14}H_9ClN_2O_2$	62.1	3.28	9.95	61.7	3.33	10.3
3-CH_3	C_2H_5OH	199	92	$C_{15}H_{12}N_2O_2$	71.0	4.80	11.0	71.4	4.79	11.1
2-Phthalimidophenyl Azides										
3-CH_3	C_2H_5OH	139(148–150)[a]	100[b]	$C_{15}H_{10}N_4O_2$	64.6	3.74	20.0	64.7	3.62	20.1
5-CH_3	C_6H_6	170	94[b]	$C_{15}H_{10}N_4O_2$	64.3	3.67	20.2	64.7	3.62	20.1
5-CH_3O	C_6H_6	180	89[b]	$C_{15}H_{10}N_4O_3$	61.0	3.45	19.5	61.2	3.42	19.1
5-Cl	C_6H_6	195 dec	97[b]	$C_{14}H_7ClN_4O_2$	56.1	2.20	19.1	56.3	2.36	18.7
2-Azidoanilines										
6-CH_3	C_2H_5OH	44	75[c]	$C_7H_8N_4$	56.3	5.23	38.2	56.7	5.44	37.8
4-CH_3	Pet. ether	38	76[c]	$C_7H_8N_4$	57.7	5.19	37.4	56.7	5.44	37.8
4-CH_3O	Pet. ether	60	68[c]	$C_7H_8N_4O$	51.5	4.95	34.2	51.2	4.99	34.1
4-Cl	Pet. ether	70	92[c]	$C_6H_5ClN_4$	42.8	3.00	32.7	42.8	2.99	33.2
1,2-Diazidobenzenes										
H		22–23	89	$C_6H_4N_6$	44.9	2.45	52.6	45.0	2.52	52.4
3-CH_3		*d*	38[e]	$C_7H_6N_6$	48.6	3.46	47.5	48.3	3.47	48.2
4-CH_3		*d*	83	$C_7H_6N_6$	48.7	3.71	48.1	48.3	3.47	48.2
4-CH_3O		27–28	55	$C_7H_6N_6O$	44.5	3.04	44.3	44.2	3.18	44.2
4-Cl	Pet. ether	42–43	90	$C_6H_3ClN_6$	36.5	1.71	43.4	37.0	1.56	43.2
1-Azido-2-phthalimidonaphthalene										
	C_2H_5OH	158 dec	88	$C_{18}H_{10}N_4O_2$	68.8	3.54	17.7	68.4	3.82	17.7
1,2-Diazidonaphthalene										
	Pet. ether	108	16[f]	$C_{10}H_6N_6$	57.4	3.02	39.9	57.1	2.88	39.9

[a] Melts initially at 139°, solidifies and remelts at 148–150°. [b] Yield is based on the amount of 2-phthalimidoaniline consumed. See Experimental Section. [c] Yield based on the amount of 2-phthalimidophenyl azide that reacted. See Experimental Section. [d] Liquids which were not distilled due to explosive hazard. [e] Yield of recovered 6-methyl-2-azidoaniline was 41%. [f] Based on 1-azido-2-phthalimidonaphthalene. The intermediate 1-azido-2-naphthylamine was not isolated.

Table II. 1,4-Dicyano-1,3-butadienes

Compd	Recrystn solvent	Yield, %[a]	Infrared, cm^{-1}	Mp, °C[c]	Formula	Found, % C	Found, % H	Found, % N	Found, % Mol wt	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % Mol wt
cis,cis-1,4-Dicyano-1,3-butadienes													
1-CH_3	CCl_4	57		63–65(71)	$C_7H_6N_2$	70.7	4.99	24.3	123	71.2	5.11	23.7	118
2-CH_3	CCl_4	74	778	55(57)	$C_7H_6N_2$	71.3	5.12	24.2	126	71.2	5.11	23.7	118
2-CH_3O	CCl_4	85	781	116(117)	$C_7H_6N_2O$	62.4	4.64	21.1	139	62.7	4.51	20.9	134
2-Cl	CCl_4	83	778	90(90)	$C_6H_3ClN_2$	52.1	2.14	20.2	136	52.0	2.18	20.2	138
Unsubstituted 1,4-Dicyano-1,3-butadienes													
cis,cis	CCl_4	79(2)[b]	752	129(129)	$C_6H_4N_2$	69.3	3.80	26.9	104	69.2	3.89	26.9	110
trans,trans		(29)[b]	982	160[d]									
cis,trans	C_6H_6–CCl_4	(33)[b]	752, 982	69–70[e]									
cis-2-Cyanocinnamylnitrile													
	C_6H_{14}–CCl_4	69	785	68(70)	$C_{10}H_6N_2$	77.7	3.57			77.9	3.92		

[a] From the diazide decomposition except as noted. [b] Numbers in parentheses are yields obtained by dehydrobromination of 2,3-dibromo-1,4-dicyanobutane. [c] Melting points in parentheses are those reported for the products of oxidation of the corresponding *o*-phenylenediamines, ref 11 and 12. [d] Lit.[5] mp 161–162°. [e] Lit.[5] mp 65–66°.

757 cm^{-1} in its infrared spectrum and the absence of appreciable absorption in the vicinity of 990 cm^{-1}. Comparison of the infrared spectrum of Ia with that published by Kurtz and co-workers of a compound, mp 124°, prepared from 1,4-dichloro-2-butyne and hydrogen cyanide in the presence of cupric salts,[5,6] showed the sprectra to be identical. The nmr spectrum of Ia (Table III) in deuteriochloroform showed the protons as an A_2B_2 system centered at 390 cps downfield relative to tetramethylsilane. The coupling constant J_{ab} was calculated to be 11.2 cps, a value consistent with *cis* protons.

All three isomeric 1,4-dicyano-1,3-butadienes were prepared by treatment of 2,3-dibromo-1,4-dicyanobutane[7] with sodium acetate in refluxing ethanol.[8] The yields and melting points are given in Table II along with a comparison of the reported melting points. The *cis,cis* isomer prepared in this manner gave no melting point depression with Ia.

Thermal decomposition of substituted 1,2-diazidobenzenes (Ib–e) in decalin gave essentially the same results as with the parent compound. In each case, a

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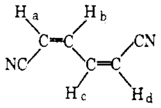
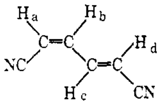
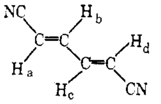
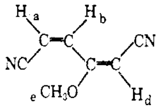
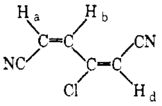
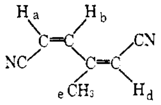
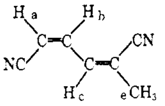
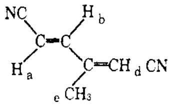
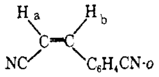
(5) P. Kurtz, H. Schwarz, and H. Disselnkotter, *Ann.*, **624**, 38 (1960).

(6) P. Kurtz, H. Gold, and H. Disselnkotter, *ibid.*, **624**, 1 (1959).

(7) F. S. Fawcett and C. M. Langkammer, U. S. Patent 2,564,102 (Aug 14, 1951).

(8) A modification of a procedure used with the corresponding dichloro compound; see H. F. Piepenbrink, *Ann.*, **572**, 83 (1961).

Table III. Chemical Shifts and Coupling Constants of 1,4-Dicyano-1,3-butadienes[a]

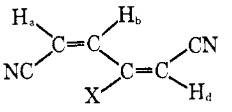
Compound	Chemical shifts, cps[b]					Coupling constants, cps						
	H_a	H_d	H_c	H_b	H_e	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}	J_{de}
	342(8)[c]		438(8)[c]			11.2[d]	−1.2[d]	0.6[h]	12.1	−1.2	11.2	
	339(2)	349(2)	446(4)	415(3)		10.0	<0.5	<0.5[h]	11.0	<0.5	15.3	
	343(8)[c]		422(8)[c]			16.5[d]	−1.0[d]	1.4[h]	10.3	−1.0[d]	16.5[d]	
	341(4)[e]	290(2)		424(2)[e]	231(1)	12.0		1.4		<0.5		
	350(4)[e]	354(2)		433(2)[e]		12.1		1.7		<0.5		
	348(4)[e]	339[f]		439(2)[e]	144(2)	12.0		1.2		<0.5		1.6
	333(6)[g]		425(3)[g]	432(4)[g]	130(1)	11.9		−2.5	8.7			
	343(2)	334(1)		422(2)	131(2)	16.0		<0.5		<0.5		
	350(2)			455(2)		12.5						

[a] All spectra were run in deuteriochloroform. All are 60-Mc spectra. [b] Numbers in parentheses indicate the number of observable peaks in the multiplet. [c] One side of an A_2X_2 system. [d] J_{ab} has been assumed positive and larger than J_{ac}. [e] H_a and H_b appear as an AB system, but the H_a half of the AB system shows a finer splitting due to coupling with H_d. [f] Complex multiplet. [g] Treated as an ABX system. [h] J. A. Elvidge and P. S. Ralph, *J. Chem. Soc.*, 387 (1966), reported the nmr spectra of the three isomeric 1,4-dicyano-1,3-butadienes in acetonitrile. The coupling constants reported here are in general agreement with their work except for J_{ad}, where Elvidge and Ralph reported values of 1.5 cps for the *cis,cis* isomer and 0.9 cps for the *trans,trans* isomer.

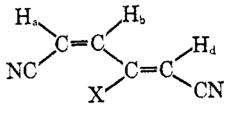
single compound was isolated which was uncontaminated by other isomers, as shown by their nmr spectra. It therefore seemed likely that in these cases the stereochemistry of the starting 1,2-diazidobenzenes was also retained. That this is the case is shown by the nmr spectral data in Table III. If the original configuration of the substituted 1,2-diazidobenzene was retained, the 1,4-dicyano-1,3-butadienes (IIb–e) formed should contain one set of *cis*-hydrogens. That this is the case is shown by the value of the coupling constants J_{ab} in Table III. The values obtained for the substituted 1,4-dicyano-1,3-butadienes are all in the range 11.9–12.1 cps, which is the normal value for coupling of *cis*-hydrogens. The *trans*-hydrogens normally have a coupling constant of about 16 cps. As seen in Table III, the coupling constant for the *trans*-hydrogens in *trans,-trans* 1,4-dicyano-1,3-butadiene is 16.5 cps.

Further evidence for the presence of a set of *cis*-hydrogens in IIb–e was obtained from their infrared spectra. All of these dinitriles absorb infrared radiation in the range 778–781 cm^{-1} (Table II), the region where olefins with *cis*-hydrogens absorb.

The configuration of the second double bond can also be obtained from the nmr data in Table III. For example, in the 2-substituted 1,4-dicyano-1,3-butadienes, there are two possibilities.



and



III IV

In structure III, H_a and H_d are located *trans–trans* with respect to one another whereas in structure IV they are located *cis–trans*. Bothner-By and Harris[9] have shown *trans–trans*-hydrogens to have coupling constants in

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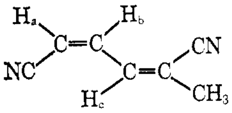
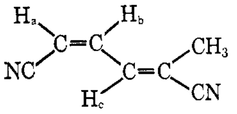
(9) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445, 3451 (1965).

the range of 1.3 to 1.9 whereas *cis–trans*-hydrogens have a coupling constant of about 0.5 to 0.8. As can be seen in Table III all of the J_{ad} coupling constants for the 2-substituted 1,4-dicyano-1,3-butadienes (IIc, d, and e) are in the range 1.2–1.7, indicating that structure III is correct.

In the one example of a 1-substituted 1,4-dicyano-1,3-butadiene (IIb) the possibilities are


V

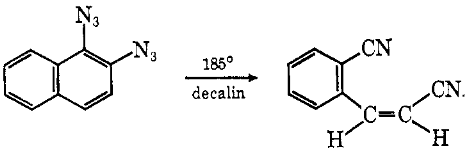
and


VI

It is not possible to distinguish between these possibilities by nmr, but it is assumed that V is the correct structure by analogy to the previous examples.

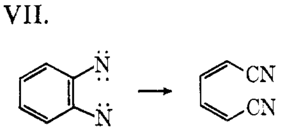
The 1,4-dicyano-1,3-butadienes underwent partial polymerization when stored in the light at room temperature for several months. A sample of IIc that had partially polymerized was recrystallized from carbon tetrachloride in an effort to recover pure IIc. Instead of IIc, however, an isomeric compound, mp 92–93°, was obtained. The nmr spectrum (Table III) of this compound indicated by the value of 16.0 cps for the coupling constant J_{ab} that it contained a set of *trans*-hydrogens. That IIc should rearrange is not surprising since models indicate that there is steric interference between the 2-methyl group and the 4-cyano group. Whether both bonds isomerized or just the one could not be determined from the nmr spectrum.

That cleavage of aromatic rings by decomposition of 1,2-diazides is a general reaction was shown further by its extention to the naphthalene ring system. Decomposition of 1,2-diazidonaphthalene in refluxing decalin gave *cis*-2-cyanocinnamonitrile.

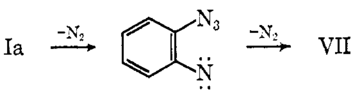


That the *cis* stereochemistry was retained was shown by the coupling constant J_{ab} which was 12.5 cps.

The *cis,cis*-1,4-dicyano-1,3-butadiene produced by decomposition of 1,2-diazidobenzene is a bond isomer of the dinitrene VII.

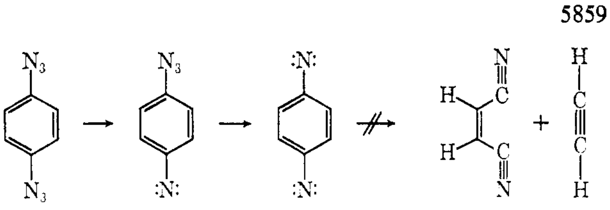

VII IIa

There are several possible routes by which the dinitrene VII could be formed in these reactions. One route could simply involve stepwise loss of nitrogen.

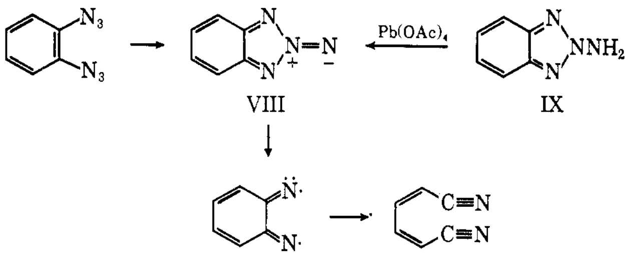


If this mode of decomposition is correct, it was felt that a similar fragmentation reaction might be observed when *p*-diazidobenzene was decomposed.

However, when 1,4-diaziodobenzene was decomposed in decalin, no products containing nitrile groups could be detected by infrared spectroscopy, nor could acetylene be detected by reaction with bromine. Also no *p*-phenylenediamine could be detected among the reaction products. The material formed in this decomposition is a bright red viscous oil believed to be polyazobenzene.



The above results suggest that there is something special about the *ortho* relationship of the two azido groups. It is well known that compounds containing an azido group located *ortho* to groups with α,β unsaturation normally undergo cyclization to give five-membered heterocyclic rings. It seems likely that this type of cyclization should occur with *o*-diazidobenzene to give the intermediate VIII.



VIII IX
X

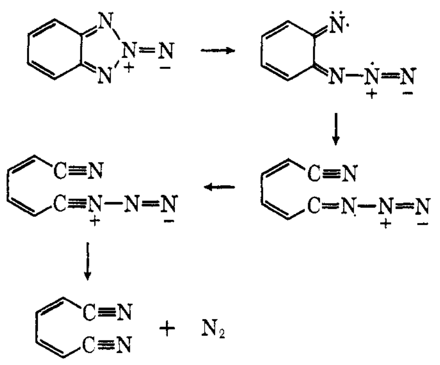
Evidence that VIII is a possible precursor of the *cis,-cis*-1,4-dicyano-1,3-butadiene was provided by Campbell and Rees,[10] who after seeing our original communication[2] postulating the existence of VIII oxidized 2-aminobenzotriazole (IX) with lead tetraacetate. As expected, the product was *cis,cis*-1,4-dicyano-1,3-butadiene.

The question then arises as to what the actual intermediate is that results in ring cleavage. A reasonable pathway to the observed product is *via* the intermediate X, formed by homolytic cleavage of the nitrogen–nitrogen bonds of VIII.[10] The diradical X could give rise to the observed product directly by homolytic cleavage of the carbon–carbon bond. This would result in complete retention of the configuration of the aromatic ring system, as was observed. If the diradical X were produced initially in the triplet state, the nitrogen evolved in the process would also be in triplet state. However, since triplet nitrogen is 140 kcal/mole above the ground state, the driving force for this mode of cleavage would seem to be lost. Decomposition of VIII to produce X initially in the singlet state would seem therefore to be the more energetically favorable process, since the nitrogen would be produced in the singlet ground state.

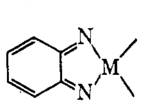
The preceding mechanism assumes that the second mole of nitrogen is lost before the ring is cleaved. However, it is possible to write a reasonable mechanism in which there is carbon–carbon bond cleavage before nitrogen is lost. Such a mechanism is given below.

Another reaction that may be related to this system is the oxidation of *o*-phenylenediamines with lead tetraacetate or nickel peroxide. Nakagawa and Onoue[11,12]

(10) C. D. Campbell and C. W. Rees, *Chem. Commun.*, 192 (1965).
(11) K. Nakagawa and H. Onoue, *Tetrahedron Letters*, 1433 (1965).
(12) K. Nakagawa and H. Onoue, *Chem. Commun.*, 396 (1965).



have found that this system also gives rise to *cis,cis*-1,4-dicyano-1,3-butadienes. A comparison of the melting points of the compounds prepared by nickel peroxide oxidation[11] and by the diazide decomposition is given in Table II. These workers have suggested that VII is an intermediate in these oxidations. However, the possibility that X is an intermediate should be considered. For example, X could arise *via* an intermediate XI which is similar in structure to VIII.



XI

Further work is in progress on the thermal decomposition of homocyclic and heterocyclic 1,2-diazides.

Experimental Section

All melting points were taken on a calibrated Kofler hot bench. Analyses were by Alfred Bernhardt Microanalytical Laboratory, Mulheim (Ruhr), West Germany, and by Spang Microanalytical Laboratory, Ann Arbor, Mich. All 60-Mc nmr spectra were run in deuteriochloroform on an A56-60 Varian spectrometer. The coupling constants from the A_2B_2 spectra of *cis,cis*- and *trans,trans*-1,4-dicyano-1,3-butadiene were obtained by peak assignment and calculations as given by Pople, Schneider, and Bernstein.[13] The values of the coupling constants were confirmed by Dr. Donald Moore, Naval Ordnance Test Station, China Lake, Calif., by computer calculation of the spectra.

2-Phthalimidonitrobenzenes. All of the 2-phthalimidonitrobenzenes used in this work were prepared in 57–92% yield by the same method. The following procedure is representative.

Phthalic anhydride (29.6 g, 0.2 mole) and 2-nitro-4-chloroaniline (34.5 g, 0.2 mole) were melted together in an open beaker and heated to 230–240° for 45 min, at which time the evolution of water had ceased. The reaction mixture was allowed to cool somewhat, but before the melt began to crystallize, 100 ml of glacial acetic acid was added. The solution was heated to dissolve any phthalimide that precipitated. Slow cooling of the acetic acid solution gave 34.6 g (57%) of 5-chloro-2-phthalimidonitrobenzene, mp 202°.

2-Phthalimido-1-nitronaphthalene. In 400 ml of glacial acetic acid were placed 20 g (0.106 mole) of 1-nitro-2-naphthylamine and 32 g (0.216 mole) of phthalic anhydride. The resulting solution was refluxed 48 hr. The solution was cooled and poured on ice and the solid filtered; yield 28.7 g (85%), mp 200–202° (lit.[14] mp 203°).

2-Phthalimidoanilines and 2-Phthalimido-1-naphthylamine. Reduction of the nitro compounds was effected by use of iron and acetic acid in aqueous acetone. The following procedure has been found to give good yields.

In 800 ml of hot acetone was dissolved 29.3 g (0.104 mole) of 3-methyl-2-phthalimidonitrobenzene. To this solution was added 80 ml of glacial acetic acid and 80 ml of water. To this stirred, refluxing solution was added 70 g (1.25 moles)) of finely powdered iron (Fisher I-61) over a period of 1 hr. The reaction mixture was refluxed and stirred rapidly for an additional 6 hr. The excess iron and iron salts were filtered and washed with acetone. The filtrate was neutralized by the addition of a nearly saturated solution of sodium carbonate. The acetone layer was separated and concentrated on the steam bath to half volume. Dilution with 2 l. of water gave 24.2 g (92%) of 3-methyl-2-phthalimidoaniline, mp 198°.

2-Phthalimidophenyl Azides and 2-Phthalimido-1-azidonaphthalene. The 2-phthalimidoanilines were converted to the corresponding azides by diazotization with sodium nitrite in dilute hydrochloric acid, followed by treatment of the diazonium salt solution with sodium azide. The 2-phthalimidoaniline hydrochlorides were quite insoluble in water and the success of the following procedure depends on the salt being in finely divided form.

Finely powdered 5-methoxy-2-phthalimidoaniline (34.6 g, 0.129 mole) was placed in 500 ml of water and stirred rapidly. Concentrated hydrochloric acid (120 ml) was added all at once, followed immediately by the addition of ice. To the slurry of the amine hydrochloride and ice was added 9.3 g (0.129 mole) of sodium nitrite in 50 ml of water. After stirring for 3 hr, the still undissolved solid (2.9 g of starting material) was filtered. To the filtrate, 8.4 g (0.129 mole) of sodium azide in 50 ml of water was slowly added. During this addition, small portions of ether were also added to prevent excessive foaming. After 30 min, the insoluble azide was filtered to give 31.1 g (89%), mp 170°.

2-Azidoanilines. The 2-phthalimidophenyl azides were converted to the corresponding *o*-azidoanilines by reaction with hydrazine. As the hydrazine was added to a slurry of the phthalimide in methanol, the phthalimide dissolved as it reacted. In some cases the amine salt of phthalhydrazide precipitated before all of the phthalimide had dissolved. When this happened some of the starting phthalimide was always recovered. The following procedure is typical.

5-Methyl-2-phalimidophenyl azide (34.2 g, 0.123 mole) was finely powdered and was slurried in 80 ml of methanol. To this slurry was added 7.7 ml (0.135 mole) of 85% hydrazine hydrate all at once. The reaction mixture was stirred rapidly by hand with a spatula. After a few minutes the reaction became very thick. An additional 40 ml of methanol was added and stirring was continued. Any lumps were broken up with the spatula. The reaction was allowed to proceed for about 30 min with occasional stirring. To the paste was then added 500 ml of water and 50 ml of 3 *N* sodium hydroxide. The insoluble solid was filtered and washed thoroughly with water. The crude solid was placed in 95% ethanol and the insoluble solid filtered to give 3.1 g of recovered 5-methyl-2-phthalimidophenyl azide. Dilution of the filtrate with water gave 12.6 g of 4-methyl-2-azidoaniline.

The crude 2-azidoanilines prepared by this method are sufficiently pure for preparation of the 1,2-diazidobenzenes. If desired, they may be recrystallized from petroleum ether (bp 30–60°) by cooling to −10°. The pure 2-azidoanilines decompose when heated at 80–90°. They are also somewhat light sensitive and should be stored in the dark.

1,2-Diazidobenzenes. The following procedure is representative. To 100 ml of water and 200 ml of concentrated hydrochloric acid was added 7.49 g (0.0551 mole) of crude 4-methyl-2-azidoaniline. The solution was cooled to 0° by the addition of ice, and the amine was diazotized with 3.64 g of sodium nitrite in a minimum of water. After stirring for 1 hr at 0°, the solution was filtered to remove 1.48 g of 5-methyl-2-phthalimidophenyl azide, a major impurity in the crude 5-methyl-1,2-azidoaniline. The filtrate was then treated with 3.29 g of sodium azide in 25 ml of water. After standing 2 hr at 0°, the diazide was extracted with petroleum ether (bp 30–60°). The petroleum ether extracts were concentrated and treated with charcoal to remove traces of colored material. The remainder of petroleum ether was removed under vacuum to give 5.85 g of pure 4-methyl-1,2-diazidobenzene as a pale yellow oil.

In the preparation of 4-chloro-1,2-diazidobenzene, the diazide separated as a solid. It was filtered and recrystallized from petroleum ether.

All of the 1,2-diazidobenzenes are high explosives. They are somewhat sensitive to shock. It was found possible to detonate 1,2-diazidobenzene on an anvil with a hammer. However, they are surprisingly stable to thermal decomposition. For example, when a drop of pure *o*-diazidobenzene was placed on a hot bench, it showed little decomposition below 140°, rapid but controlled decomposition at 170°, and detonation at 205°.

1,2-Diazidonaphthalene. To a slurry of 1.38 g (0.0044 mole) of 1-azido-2-phthalimidonaphthalene in 10 ml of methanol was added 1 ml of 85% hydrazine hydrate. After a few minutes, all of the azide had dissolved and the evolution of nitrogen began as the

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(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 138–151.

(14) C. B. Crippa and P. Galimberti, *Gazz. Chim. Ital.*, **59**, 514 (1929).

unstable 1-azido-2-naphthylamine began to decompose. The solution was quickly poured into ice water and made strongly basic with sodium hydroxide. The cold solution was extracted three times with benzene. The benzene solution was extracted several times with dilute hydrochloric acid. These acid extracts were immediately cooled by addition of ice and diazotized by addition of 0.53 g of sodium nitrite in water. The solution was filtered, and the filtrate was treated with an aqueous solution of sodium azide (0.50 g). After standing overnight, filtration gave 0.15 g of crude 1,2-diazidonaphthalene, mp 100–104°. Recrystallization from petroleum ether (bp 60–90°) raised the melting point to 108°.

***cis,cis*-1,4-Dicyano-1,3-butadienes and *cis*-2-Cyanocinnamylnitrile.** In order to minimize the possibility of explosive decomposition, all of the 1,2-diazides were decomposed in dilute solution. The following procedure is typical. 4-Methoxy-1,2-diazidobenzene (2.06 g, 0.0108 mole) was dissolved in 15 ml of decalin. This solution was added dropwise over a period of 1 hr to 25 ml of refluxing decalin. After standing overnight at room temperature, the crude solid was filtered and washed thoroughly with petroleum ether (bp 30–60°). Recrystallization (charcoal) from 50 ml of carbon tetrachloride gave 1.24 g of *cis,cis*-2-methoxy-1,4-dicyano-1,3-butadiene. An additional 0.07 g was obtained by concentration of the filtrate.

Preparation of the Isomeric 1,4-Dicyano-1,3-butadienes by Elimination. To a mixture of 300 ml of 95% ethanol, 20 ml of water, and 26.4 g (0.3 mole) of anhydrous sodium acetate was added 26.6 g (0.1 mole) of 2,3-dibromo-1,4-dicyanobutane. The mixture was refluxed for 23 hr. Ethanol was distilled out of the reaction mixture until the volume was reduced to 100 ml. Chilling of this solution in ice gave a precipitate which was filtered and washed with solid alcohol and then with water; yield 3.06 g (29%) of *trans,trans*-1,4-dicyano-1,3-butadiene, mp 156–157° (lit.[5] mp 161–162°). The infrared spectrum indicated that this compound was free from the other two isomers.

The water–alcohol filtrates after removal of the *trans,trans* isomer were boiled until all of the alcohol had distilled. An oil separated which solidified on cooling. The solid was filtered and washed with water. This solid was dissolved in benzene and placed on an alumina (100 g of Fisher A-540) column. Elution of the column with 50 ml of benzene gave 0.19 g (1.8%) of *cis,cis*-1,4-dicyano-1,3-butadiene, mp 127–128°. Its infrared spectrum was identical with that prepared by decomposition of 1,2-diazidobenzene. Continued elution of the column with an additional 300 ml of benzene gave 3.28 g (33%) of crude *cis,trans*-1,4-dicyano-1,3-butadiene, mp 58–68°. After several recrystallizations from carbon tetrachloride, a pure product, mp 69–70° (lit.[5] 65–66°), was obtained.

Acknowledgment. I am indebted to Dr. Donald Moore, U. S. Naval Ordinance Test Station at China Lake, Calif., for the theoretical calculations of the nmr spectra of the isomeric 1,4-dicyano-1,3-butadienes.

Free-Radical Addition of Trimethyltin Hydride to Dienes[1]

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Abstract: The free radical catalyzed addition of trimethyltin hydride to 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, 1,3-cyclohexadiene, 4-vinylcyclohexene-1, 1,3-cyclooctadiene, and 1,5-cyclooctadiene has been studied. Structures and configurations of all the adducts have been assigned on the basis of infrared and nmr spectroscopy, degradation, or comparison with authentic samples prepared by other methods. Information regarding direction of addition and stereochemistry thus obtained is discussed in terms of a probable mechanism and the roles which electronic and steric factors play in determining the course of the reactions.

The addition of electrophilic free radicals such as halogens and thiyl radicals to dienes has been studied extensively.[4] On the other hand, parallel studies involving radicals which might be nucleophilic have received little attention. While the work reported in this paper was in progress, Neumann and Sommer[5] reported on the addition of organotin hydrides to dienes. This reaction has been shown[6] to proceed by a free-radical mechanism with reactions 1 and 2 as the probable chain-carrying steps.[6,7] The organotin radical might be expected to display nucleophilic character.

$$\mathrm{Sn\cdot + RCH{=}CH_2 \longrightarrow R\underset{\cdot}{C}HCH_2Sn} \qquad (1)$$

$$\mathrm{R\underset{\cdot}{C}HCH_2Sn + Sn{-}H \longrightarrow RCH_2CH_2Sn + Sn\cdot} \qquad (2)$$

We have examined the products of addition of trimethyltin hydride to six conjugated dienes and two un-

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(1) This research was supported by a grant from the National Science Foundation (G10,000). The purchase of the nuclear magnetic resonance spectrometer was also made possible by a grant from the foundation.

(2) Taken in part from the Ph.D. dissertations of R. H. F. (1965) and I. J. T. (1967) submitted to the Graduate School of the University of New Hampshire, Durham, N. H.

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