Phase-Transfer Synthesis of Arenediazocyanides and Synthesis of Arenediazosulfones from Arenediazonium Cations and the Formation of Reduced Pyridazines by 2 + 4 Cycloaddition Reactions[1]

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Abstract: The remarkably versatile arenediazonium cations are also convenient to use and nondangerous when utilized as the BF_4 or PF_6 salts. Arenediazonium compounds have recently been shown to undergo the 2 + 4 Diels–Alder cycloaddition, but the reaction is solvent dependent and far from general. To augment this reactivity and to prevent potential side reactions, we converted the arenediazonium compounds into the corresponding diazosulfonyl (Ar—N=N—SO_2Ph) or diazocyanide (Ar—N=N—CN) derivatives. The former could be prepared under noncatalytic conditions, but crown ether catalyzed phase transfer methods were required for preparation of the latter. Quaternary ion catalysis was unsuccessful. Both ArN=NSO_2Ph and ArN=NCN react readily with dienes. The diazosulfones react with sundry alkenes as well as 1,3-dienes but do not yield identifiable single products in either case. Arenediazocyanides react readily with many conjugated dienes to give 2 + 4 cycloadducts, generally in good to excellent yield. The reactivity of ArN=NCN with 2,3-dimethylbutadiene is found by detailed kinetic analysis to be similar to NCCH=CHCN or PhCOCH=CHCOPh.

Arenediazonium cations have been known, characterized, and studied for over a century,[2] but interest in these versatile and reactive species remains high. Recently, attention has been devoted to the reactions of these substances in nonpolar media where they are either insoluble or only marginally so. Our understanding of the factors which influence their solubilization and the specific complexing agents which do likewise is increasing, but the reactions of these compounds remain complex.[3]

One aspect of the behavior of arenediazonium ions which was especially interesting to us is the observation that certain such salts undergo what appear to be 2 + 4 cycloaddition reactions with 1,3-dienes to form pyridazines or pyridazinium salts rather than the previously reported linear adducts. The report[4] of this observation was relatively limited in scope, and to our knowledge, no full paper on this subject has ever appeared. Nevertheless, it appeared that this cycloaddition reaction might enjoy some generality. It occurred to us that, if the cycloaddition reaction was successful in polar solutions, yields might be even better in nonpolar solution where weaker solvation forces would result in a more electron-deficient dienophile ($-N^+\equiv N$). To our surprise, the cycloaddition reactions invariably failed except when conducted in polar solvents as previously described. In an effort to find a blocking or protecting group which could be added easily and still be conducive to cycloaddition reactions, we investigated the diazocyanides and diazosulfones corresponding to our arenediazonium salts.

Results and Discussion

A number of covalent derivatives of arenediazonium salts are known, and many of these, particularly those containing O–N bonds, are believed to be intermediates in diazonium ion reactions.[3] The examples of stable diazo compounds having C–N or C–S bonds are less common but certainly well-known. As is often the case in diazonium ion chemistry, isolated examples of both diazocyanides and diazosulfones exist, but little general information or unifying data have been presented concerning them. This situation is less pronounced with the arenediazocyanides which figured prominently in the controversy concerning cis–trans isomerism in diazo compounds which raged between 1930 and 1950.[5] Nevertheless, general high yield syntheses for these species had not been described in the literature before our preliminary report of this work.[6]

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Table I. Preparation of (*E*)-Arenediazosulfonylbenzenes

compd no.	subst[a]	stirring time,[b] h	yield,[c] %	obsd mp, °C	lit. mp, °C
1	2-Cl	23	85 (63[d])	100–101	103–104[e]
2	3-Cl	24	89 (70[d])	64–65	*f*
3	4-Cl	2	70 (65[d])	103–105	105–106[g]
3	4-Cl	24	95 (67[d])	101–103	105–106[g]
4	2-Br	23	92 (50[d])	89–90	*f*
5	4-Br	4	75 (60[d])	105–107	115[h]
5	4-Br	19	84 (61[i])	107–108	115[h]
6	4-MeO	4	64 (9[j])	73	*f*
6	4-MeO	24	77 (8[j])	71–72	*f*
7	4-NO_2	21	84 (21[i])	130	132–133[h]

[a] Substituent refers to the aromatic ring attached to nitrogen and corresponds to the substituent in the starting diazonium salt. [b] Reaction conducted at ambient temperature. [c] Yields are for essentially pure material having the anticipated spectral properties. Yields in parentheses refer to analytically pure material obtained by sometimes difficult recrystallizations. [d] Recrystallized from 2-PrOH. [e] See ref 19. [f] Melting point not reported in the literature. [g] See ref 20. [h] See ref 18. The published melting point could not be obtained. The material having the melting point indicated was pure by IR, H^1 NMR, and combustion analyses (see Experimental Section). [i] Recrystallized from 95% ethanol. [j] Recrystallized from hexane; the product oiled and was very difficult to crystallize.

Synthesis of Arenediazosulfones. The (arenediazosulfonyl)-benzenes are remarkably easy to prepare from arenediazonium tetrafluoroborates simply by stirring a suspension of the solid salt in dichloromethane with solid sodium benzenesulfinate as shown

(1) Crown Cation Complex Effects. 15. Paper 14: Schultz, R. A.; Dishong, D. M.; Gokel, G. W. *Tetrahedron Lett.* **1981**, 2623.
(2) Griess, P. *Justus Liebigs Ann. Chem.* **1858**, *106*, 123.
(3) Bartsch, R. A. In "Progress in Macrocyclic Polyether Chemistry"; Izatt, R. M., Christensen, J. J., Eds.; Wiley: New York, 1981; Vol. 2, p 1.
(4) Carlson, B. A.; Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1975**, *97*, 5291.
(5) (a) Le Fevre, R. J.; Vine, H. *J. Chem. Soc.* **1938**, 431. (b) Hodgson, H. H.; Massden, E. *Ibid.* **1944**, *395*, 1097. (c) Anderson, D.; Le Fevre, R. J.; Savage, J. *Ibid.* **1947**, 445. (d) Hodgson, H. H. *Ibid.* **1948**, 1097. (e) Le Fevre, R. J.; Northcott, J. *Ibid.* **1949**, 333, 944.
(6) Ahern, M. F.; Gokel, G. W.; *J. Chem. Soc., Chem. Commun.* **1979**, 1019.

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in eq 1. The crude products were yellow solids having melting

$$Ar—N_2^+BF_4^- + Ph—SO_2^-Na^+ \xrightarrow[CH_2Cl_2]{} Ar—N=N—SO_2—Ph + Na^+BF_4^- \quad (1)$$

points between about 60 and 120 °C and were obtained in yields ranging from 64 to 95%. Although the crude materials were often quite pure, recrystallization proved difficult with some of them and yields for purified material were often artificially low. The addition of 18-crown-6 polyether to the reaction mixture was found to have virtually no effect on the reactivity and, by virtue of its presence in the product mixture, decreased the purity. The results are summarized in Table I.

Synthesis of Arenediazocyanides. The syntheses of the arenediazocyanides posed a greater challenge than did the preparation of the azosulfones. The reason for this is simple: the cyano group is susceptible to further nucleophilic addition, whereas the azosulfones are far less so. When the reaction shown in eq 2 was

$$Ar—N_2^+BF_4^- + KCN \xrightarrow[\text{crown}]{CH_2Cl_2} Ar—N=N—CN + K^+BF_4^- \quad (2)$$

attempted without crown ether, only 30% of 4-chlorobenzenediazocyanide (**11**) was obtained after 120 h. The yield could be dramatically improved, and the reaction time diminished to the order of 5 h by the addition of 5 mol % of 18-crown-6. The syntheses of several arenediazocyanides are shown in Table II. Note that here, as above, the crude materials were essentially pure and considerable yield was lost in our effort to remove trace impurities.

The arenediazocyanides are orange to red crystalline solids with melting points in the range 29–132 °C. Many of these materials were thermally stable enough to permit sublimation and were, as expected, freely soluble in nonpolar organic solvents.

Various attempts were made to synthesize arenediazocyanides by treating homogeneous CH_2Cl_2 or $CHCl_3$ solutions[3] of arenediazonium cations with quaternary ammonium salts (quats) as the phase-transfer agent in place of 18-crown-6 and KCN (either as a solid or in aqueous solution). These efforts were unsuccessful, affording reduced yields or oligomeric material, respectively. The apparent inability of quats to effectively phase transfer CN^- in the presence of BF_4^- is consistent with their known catalytic behavior.[7] If CN^- were transferred, however, diazocyanides once formed are known to undergo addition reactions by a variety of nucleophiles, including CN^-[8] as shown in eq 3.

$$Ar—N_2^+BF_4^- + K^+CN^- \xrightarrow{Q^+X^-} Ar—N=N—CN \xrightarrow{Q^+CN^-} Ar—N=N—C(=N^-)CN \longrightarrow \text{etc.} \quad (3)$$

In the crown-catalyzed reaction using solid KCN and diazonium salt, the further addition of CN^- (shown in eq 3) appears not to be significant. Since KBF_4 is a byproduct in this reaction, crown-complexed K^+ ion may preferentially pair with BF_4^-, a softer anion than CN^-. Thus, as the reaction proceeds, the byproduct gradually siphons off the crown by complexation, thereby retarding further addition of CN^- ion to the arenediazocyanide; i.e., the crown's catalytic activity is gradually reduced. The phenomenon of catalyst poisoning, of which this is an example, is well established in the phase-transfer literature.[7] The success of our particular reaction system may depend, at least in part, on the fortuitous moderating effect of byproduct (KBF_4) on crown catalyst. Although this notion cannot be tested directly, 18-crown-6 mediated, KCN-induced decomposition of pure **11** (in CH_2Cl_2) was dramatically slowed by addition of KBF_4 to the reaction mixture.

(7) Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer Verlag: New York, 1977; p 7.
(8) Putter, R. *Methoden Org. Chem. (Houben-Weyl), 4th Ed.* **1965**, *X13*, 603.

Table II. Preparation of (*E*)-Arenediazocyanides (X–Ar–N=N–CN)[a]

compd no.	subst (X)	crude yield,[b] %	purified yield,[c] %	purif method[d]	obsd mp, °C	lit. mp,[e] °C
8	H[f]	95	15	dist	29	*g, h*
9	4-F	92	71	subl	60–61	*g, i*
10	2-Cl	44	*j*	*j*	*k*	78[l]
11	4-Cl	75–91	53–77	subl	101–104	105[m]
12	2,4-Cl$_2$	15	*j*	*j*	*n*	*o*
13	4-Br	78–84	55–71	subl	124–128	132[m]
14	4-MeO	87–91	87–91	none	117–122	121–122[m]
15	4-NO$_2$	80–91	48–55	extr	82–85	86[l]

[a] All reactions conducted on a 3–6-mmol scale at ambient temperature, for 5 h in the presence of 5 mol % 18-crown-6. [b] Yield is for product having spectral properties consistent with the assigned structures and no evidence of impurity except slightly depressed melting point and darker color. Compound 14 was suitable for use directly in cycloaddition reactions. [c] Yield is for material having the anticipated spectral properties and the melting point indicated. [d] Dist = distillation; extr = extraction; none = no further purification required; subl = sublimation. [e] Literature melting points could be achieved but only at the expense of considerable sample. [f] Yield is for a single reaction conducted on a 40-mmol scale, using 2 equiv of KCN, 10 mol % 18-crown-6, and 18 h reaction time. [g] No melting point reported. [h] LeFevre, R. J.; Northcott, J. *J. Chem. Soc.* 1949, 333. [i] Kazitsnya, L. A.; Vstynyuk, A.; Gurman, V. S.; Pergushov, V. I.; Gruzdneva, V. N. *Dokl. Akad. Nauk SSSR* 1977, *233*, 866. [j] Product not purified further. [k] The dark brown semisolid was not purified sufficiently to obtain a melting point. [l] LeFevre, R. J.; Worth, C. V. *J. Chem. Soc.* 1951, 1814. [m] Ignasiak, T.; Suszko, J.; Ignasiak, B. *J. Chem. Soc., Perkin Trans. 1* 1975, 2122. [n] Product obtained as a brown solid; no melting point determined. [o] Compound not reported in the literature.

Classical methods for the synthesis of arenediazocyanides afford the *Z* isomer as the initial product. Solutions of this isomer in nonpolar solvents transform into the *E* isomer on standing. The rates for such isomerization processes have been measured in several solvents.[9] The products we ultimately isolated were the pure trans (*E*) compounds, and it is these isomers which are reported in Table II and used in the cycloaddition reactions.

Cycloaddition Reactions of Arenediazosulfones and Arenediazocyanides. Many (2 + 4) cycloaddition and ene reactions are known for azodicarbonyl compounds, but there are relatively few examples in the literature of any such reactions with azobenzenes and none, to our knowledge, preceded our preliminary report of such reactions with arenediazosulfones or arenediazocyanides.[6] One example of a (2 + 2) cycloaddition of **11** to diphenylketene has been reported[10] and 4,4′-dinitroazobenzene reportedly reacts with 2,3-dimethyl-1,3-butadiene, although in unspecified yield.[11] Furthermore, there is a single report of arenediazonium ions themselves undergoing cycloadditions,[3] although this reactivity may be more general than communicated.

We have found that arenediazocyanides react quite readily with 1,3-dienes to yield 1-cyano-2-aryl-1,2,3,6-tetrahydropyridazines in generally good yield. Some of the reactions were successful at ambient temperature and all of the examples reported in Table III required less than 3 h at 100 °C. In general, 4-methoxybenzenediazocyanide appeared to be the least reactive of the compounds examined, and the corresponding 4-nitro derivative (**15**) was the most reactive, as expected. In fact, **15** reacted so readily with both isoprene and 1,3-cyclohexadiene that the method of reaction had to be altered somewhat to reduce the formation of dark, tarry by products (see Experimental Section). The re-

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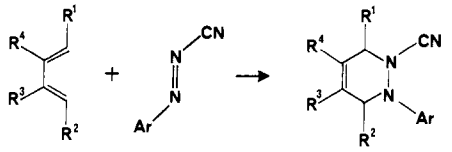
(10) (a) Bird, C. W. *J. Chem. Soc.* **1964**, 5284. (b) Bird, C. W. Twibell, J. D. *Tetrahedron* **1972**, *28*, 2813. (c) Bird, C. W.; Kaczmar, M. W.; Wong, C. K. *Ibid.* **1974**, *30*, 2549.
(11) Baranger, P.; Levisalles, J.; Vuidart, M. *C. R. Hebd. Seances Acad. Sci.* **1953**, *236*, 1365.

Table III, Cycloaddition Reactions between Arenediazocyanides and 1,3-Dienes

product no.	diene	diazocyanide 4-subst (no.)	yield,[a] %	structure of product[b] R¹	R²	R³	R⁴
16	butadiene	Cl (11)	85	H	H	H	H
	butadiene	MeO (14)	0	H	H	H	H
17	butadiene	NO_2 (15)	84	H	H	H	H
18	chloroprene	Cl (11)	100[c]	H	H	Cl	H
19	(*E*)-piperylene	Cl (11)	100[d]	CH_3	H	H	H
20	(*E*)-piperylene	MeO (14)	47[e]	CH_3	H	H	H
21	(*E*)-piperylene	NO_2 (15)	96[f]	CH_3	H	H	H
22	isoprene	Cl (11)	67	H	H	CH_3	H
23	isoprene	MeO (14)	46	H	H	CH_3	H
24	isoprene	NO_2 (15)	55	H	H	CH_3	H
25	2,3-dimethyl-1,3-butadiene	Cl (11)	90	H	H	CH_3	CH_3
26	2,3-dimethyl-1,3-butadiene	MeO (14)	70	H	H	CH_3	CH_3
27	2,3-dimethyl-1,3-butadiene	NO_2 (15)	94	H	H	CH_3	CH_3
28	cyclopentadiene	Cl (11)	58	CH_2		H	H
	cyclopentadiene	MeO (14)	0	CH_2		H	H
29	cyclopentadiene	NO_2 (15)	100	CH_2		H	H
30	cyclohexadiene	Cl (11)	43	CH_2CH_2		H	H
	cyclohexadiene	MeO (14)	0	CH_2CH_2		H	H
31	cyclohexadiene	NO_2 (15)	26	CH_2CH_2		H	H
	norbornadiene	Cl (11)	0				

[a] Yield is for pure product including isomer mixtures where applicable. [b] According to eq 4. [c] Isomer ratio is approximately 10:1. [d] Isomer ratio is approximately 4:1. [e] Isomer ratio is approximately 8:1. [f] Isomer ratio is approximately 2:1.

action is summarized in eq 4, and the data are presented in Table III.



(4)

1,3-Cyclopentadiene and 1,3-cyclohexadiene afford (2 + 4) cycloaddition products rather than products of the ene reaction as might have been expected. The ene reaction pathway often predominates with azodicarboxylate esters and related species.[12] These substances are of a reactivity similar to the arenediazocyanides, at least as judged by the reaction parameters for the reactions described here (see below).

Our attempts to identify products from the reactions of arenediazosulfones were frustrating. Considerable evidence was accumulated, indicating that the arenediazosulfones are reactive toward both alkenes and 1,3-dienes, but none of our experiments yielded definitive information on the nature of the products. The reactions of either (4-chlorobenzenediazosulfonyl)benzene (**3**) or (4-methoxybenzenediazosulfonyl)benzene (**6**) with 2,3-dimethylbutadiene yielded product mixtures containing at least three species (by TLC analysis) whether the reaction was conducted at room temperature or at 100 °C, either by itself or in chloroform solution. Similar results were obtained for **3** and isoprene in CH_2Cl_2 at 100 °C.

During the course of these studies, it became apparent that when both components were present in equimolar amounts, only half of the diene was consumed and then the composition of the reaction mixture remained constant for a time before continuing to react. We felt that this might indicate an initial ene reaction followed by a secondary process. We were unable, however, to isolate a single product even when 2 equiv of arenediazosulfone and 1 equiv of diene were allowed to react.

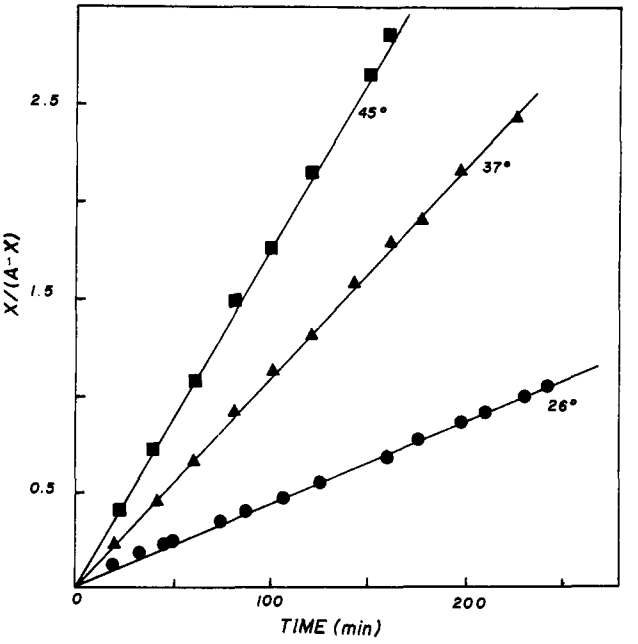


Figure 1. Kinetics for the reaction between **11** and 2,3-dimethylbutadiene (X = [product]; A = [starting material]).

An initial ene reaction suggested that the diazosulfones might react with simple olefins. Cyclohexene and **3** failed to react in $CDCl_3$ solution (ca. 45 °C) even after 144 h, but styrene reacted quite rapidly with **11** at room temperature. Again, however, at least three products were formed, causing us to abandon these studies with the unsatisfying conclusion that the (arenediazosulfonyl)benzenes are reactive partners for alkenes and dienes but lead to complex product mixtures.

Kinetics of the Arenediazocyanide Cycloaddition Reaction. In order to better understand the cycloaddition reactions of arenediazo compounds, we undertook the detailed kinetic analysis of the reaction between 4-chlorobenzenediazocyanide (**11**) and 2,3-dimethyl-1,3-butadiene (DMBD). Three kinetic runs were conducted in $CDCl_3$ solution at 26, 37, and 46 °C and monitored by ^1H NMR spectroscopy. NMR analysis was based on the fact that the vinyl protons of DMBD become allylic protons in the symmetrical cycloadduct and change absorption positions from 4.95 to 3.77 ppm, respectively. Integration of the broad, two-line signal in the starting material was unencumbered by the broad single line due to product, nor did it overlap with any other resonance in the system. The reaction mixtures were approximately 0.6 M in each reactant and a minimum of 32 points determined each line. Clean, second-order kinetics were obtained which were linear for a minimum of 2 half-lives (see Figure 1).

The reaction rates determined as described above were 1.08, 2.92, and 5.04 × 10^{-4} M^{-1} s^{-1} at 26, 37, and 45 °C, respectively. A plot of log (rate constant) vs. $1/T$ yielded a straight line (correlation coefficient −0.998). From this, the activation energy was determined to be 15.5 kcal mol^{-1}, log A^* = 7.36, and ΔS^* = −26.9 eu. For comparison, note that both (*E*)-Ph—CO—CH=CH—CO—Ph[13] and (*E*)-NC—CH=CH—CN[13] are known to react with 2,3-dimethylbutadiene. The activation energies are 15.9 and 17.9 kcal/mol, respectively. The conclusion is that **11** is more reactive than (*E*)-maleonitrile and about as reactive as dibenzoylethylene in the (2 + 4) cycloaddition reaction.

^{13}C NMR Spectra of Arenediazocyanides and the Corresponding Cycloadducts. To our knowledge, only one report of the ^{13}C NMR spectrum of any benzenediazocyanide compound has previously appeared.[19] The aromatic rings of all the diazocyanide derivatives

(12) (a) Cinnamon, J. M.; Weiss, K. *J. Org. Chem.* **1961**, *26*, 2644. (b) Cohen, S. G.; Zand, R. *J. Am. Chem. Soc.* **1962**, *84*, 586. (c) Gillis, B. T.; Beck, P. E. *J. Org. Chem.* **1962**, *27*, 1947. (d) Franzus, B.; Surridge, J. M. *Ibid.* **1962**, *27*, 1951. (e) Franzus, B. *Ibid.* **1963**, *28*, 2954. (f) Flitsch, W.; Heinrich, J. *Tetrahedron Lett.* **1980**, 3673.

(13) Sauer, J.; Lang, D.; Wiest, H. *Chem. Ber.* **1964**, *97*, 3208, *Z. Naturforsch, B, Anor. Chem., Org. Chem., Biochem., Biophys. Biol.* **1962**, *17B*, 206.

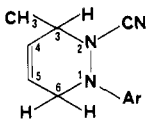
Table IV. ^{13}C NMR Spectra for Reduced Pyridazines As Shown in Eq 4[a]

product no.	CN	C3	C4	C5	C6	ipso	ortho	meta	para
16	114.0	50.9	123.8 or	122.8	45.2	127.3	116.5	129.2	144.7
17	no	51.3	123.4 or	122.8	44.6	141.7	113.4	125.8	150.9
18 (major)	113.3	50.0	119.7	127.9	50.0	128.1	116.9	129.4	143.7
18 (minor)	no	54.5	128.0	120.6	45.9	no	116.8	no	no
19 (major)	112.65	56.4	128.4	122.8	44.6	126.8	116.1	129.0	145.0
19 (minor)	115.76	47.0	120.9	129.4	52.1	no	116.9	129.2	144.5
20 (major)	no	56.3	128.5	123.4	45.2	140.1	117.4	114.4	155.3
20 (minor)	no	46.6	121.1	130.1	52.2	*b*	*b*	*b*	*b*
21 (major)	no	56.8	128.5	122.3	44.0	141.4	113.0	125.6	151.2
21 (minor)	no	49.0	121.1	129.0	52.3	141.4	112.1	126.0	151.2
22	114.1	50.5	116.7	131.4	48.9	127.1	116.5	129.2	144.7
23	no	50.2	116.7	131.8	49.5	139.8	117.7	114.5	155.4
24	113.7	50.8	116.8	131.0	48.1	141.4	113.2	125.7	150.8
25	114.2	54.1	127.9 or	122.3	49.1	126.9	116.3	129.1	144.6
26	114.6	53.9	123.3 or	122.2	49.7	139.7	117.5	114.4	155.3
27	113.7	54.4	122.5	122.5	48.2	141.3	113.1	125.6	150.8
28	no	69.9	137.6 or	134.3	69.3	127.9	119.2	128.9	147.9 bridge 47.1
29	115.8	70.5	137.7 or	134.4	68.4	142.5	117.0	125.1	154.6 bridge 47.8
30	116.0	54.7	133.1 or	130.7	53.6	127.5	119.1	128.7	142.2 bridge 20.2 and 21.7
31	115.3	54.4	133.3 or	131.7	53.8	142.4	116.6	125.2	154.8 bridge 20.6 and 21.7

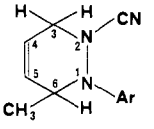
[a] no = not observed. [b] Separate signals were not observed.

examined exhibit predictable shifts. The carbon attached to sp^2 nitrogen appears at 148–155 ppm for the eight cases we have examined. The nitrile carbon is observed at 115.5 ± 0.9 ppm.

The reduced pyridizines reported here were previously unknown and the ^{13}C NMR spectra for these systems were recorded not only for structure proof but also as an aid in determining the regiochemistry of the cycloadducts arising from unsymmetrical dienes. Structural assignments for the cycloadduct (**19**) formed from 4-chlorobenzenediazocyanide (**11**) and (*E*)-piperylene proved crucial. The two possible products are shown below as **19**(major) and **19**(minor). The fully coupled (i.e., non-proton-decoupled)



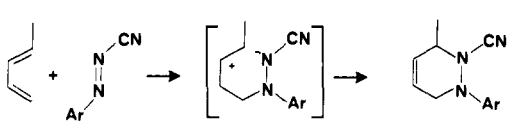
19 (major)



19 (minor)

^{13}C NMR spectrum of each isomer was recorded and the multiplicity of the cyano carbon determined. In the major isomer, there is a single proton at C-3 and the cyano carbon resonance should, therefore, be observed as a doublet. In the minor isomer, the methyl group is attached to C-6 and both protons at C-3 should couple to the cyano carbon. Indeed, the latter resonance is a triplet. Once exact assignments are known for these two isomers, comparison with the related structures leads to the assignments shown in Table IV.

The regiochemistry of arenediazocyanide cycloadditions with unsymmetrical dienes is consistent with a simple dipolar reaction model. Such a model has been previously invoked to rationalize the often high degree of regioselectivity observed for similar cycloadditions involving heteroatom dieneophiles.[14] If one assumes that the arenediazocyanides react as simple dipoles, the nitrogen atom bonded to cyanide should be best able to accommodate a negative charge and the aniline nitrogen should be positive. The model is illustrated for the reaction with piperylene in eq 5.



(5)

This orientation of the diazocyanide dipole should be most stabilized with a para-methoxy group present on the aromatic ring and correspondingly be least favored for a para-nitro substituent. Accordingly, the regioselectivity for cycloadduct **20** should be the highest and that for **21** the lowest in the group **19–21**.

Summary

(Arenediazosulfonyl)benzenes may be prepared readily from arenediazonium tetrafluoroborates as may be the arenediazocyanides although the latter preparation requires phase-transfer catalytic conditions for success. Crown catalysis is much more effective for the synthesis of Ar—N=N—CN than quaternary ammonium salts because of an apparently fortuitous catalyst poisoning effect. Both diazoarene species react with dienes, but only the arenediazocyanides afford products of (2 + 4) cycloaddition. Although the diazosulfones react readily with both dienes and alkenes, complex product mixtures result which remain uncharacterized. The reactivity of the arenediazocyanides in the (2 + 4) cycloaddition is quite similar to that of maleonitrile.

Experimental Section

Melting points (mp) were recorded on either a Thomas-Hoover capillary melting point apparatus or a Mel-temp device using Kimax soft glass tubes and are corrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 267 diffraction grating spectrophotometer and were calibrated against both the 2851- and 1601-cm^{-1} bands of polystyrene. Spectral bands are reported in reciprocal centimeters (cm^{-1}). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Associates Model A-60A, T-60 or XL-100 NMR spectrometer as ca. 10% solutions in $CDCl_3$ unless otherwise noted. Variable-temperature kinetic experiments were carried out on the A-60A instrument equipped with a Varian Model 6040 variable-temperature controller. Chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si. Coupling constants (J) are reported in hertz (Hz). Data are reported in the following order: chemical shift, spin multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; Ψ = pseudo), integration, coupling constant, and interpretation. ^{13}C NMR spectra were recorded on a JEOL JNM-PS-100 or Varian XL-100 NMR spectrometer equipped with a Nicolet Instrument Corp. computer. $CDCl_3$ was used as solvent and provided an internal deuterium lock. ^{13}C NMR data were obtained in the ^{1}H fully decoupled mode unless otherwise indicated. Carbon chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si. In cases where off-resonance-decoupled (ord) ^{13}C spectra were obtained, spin multiplicity is reported as in ^{1}H NMR spectra. Combustion analyses were performed by Dr. Franz Kasler of University of Maryland. Mass spectral data were obtained by using a Finnegan Model 3200 GC-MS equipped with a Finnegan Model 6000 data center using a 5 ft × 0.079 in. 3% OV-1 on 60–80 mesh NAW Chromosorb Q column.

Solvents were of analytical reagent grade and were used without further purification, except for tetrahydrofuran which was distilled from sodium–benzophenone ketyl immediately prior to use. KCN was dried in vacuo (0.2–1.0 torr) at ca. 95 °C for 48 h and powdered prior to use. Arenediazonium salts were prepared essentially by the method of Roe,[15]

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(15) Roe, A. *Org. React.* **1949**, *5*, 193.

reprecipitated from acetone–ether, and air-dried for ca. 2 h immediately prior to use.

Synthesis of Arenediazosulfones from Arenediazonium Tetrafluoroborates, General Procedure. To a 500-mL Erlenmeyer flask, fitted with a magnetic stirrer, was added the arenediazonium BF_4 salt (0.02 mol), sodium benzenesulfinate (0.02 mol %) and CH_2Cl_2 (200 mL); a yellow color developed immediately. The mixture was stirred at ambient temperature for 2–24 h, during which time the mixture gradually darkened from yellow to orange. After stirring was complete, the mixture was filtered to remove salts and the CH_2Cl_2 evaporated. The (arenediazosulfonyl)benzene was generally obtained as a yellow to orange solid which was purified by recrystallization and then dried at high vacuum.

(2-Chlorobenzenediazosulfonyl)benzene (1). Compound **1** was prepared according to the general procedure (23 h of stirring) in 85% yield. After crystallization (2-PrOH) **1** was obtained (63%) as a yellow solid, mp 100–101 °C (lit.[16] mp 97–98.5 °C).

Preparation of (3-Chlorobenzenediazosulfonyl)benzene (2). Compound **2** was prepared according to the general procedure (24 h of stirring) in 89% yield. After crystallization from (2-PrOH) **2** was obtained (70%) as a yellow solid, mp 64–65 °C. Anal. Calcd for $C_{12}H_7ClN_2O_2S$: C, 51.34; H, 3.23, N, 9.98. Found: C, 51.06, H, 3.13, N, 10.26.

(4-Chlorobenzenediazosulfonyl)benzene (3). Compound **3** was prepared according to the general procedure (2 h of stirring) in 70% yield. After crystallization (2-PrOH), **3** was obtained (65%) as a yellow solid, mp 103–105 °C (lit.[17] mp 105–106 °C). When the stirring time was extended to 24 h, the crude yield increased to 95% but only 67% of pure material was obtained after crystallization. The melting point of the latter compound was also slightly depressed (mp 101–103 °C).

(4-Bromobenzenediazosulfonyl)benzene (5). Compound **5** was prepared according to the general procedure (4 h of stirring) in 75% yield. After crystallization (2-PrOH), **5** was obtained (60%) as a yellow solid, mp 105–107 °C (lit.[8] mp 115 °C). Extending the stirring time to 10 h afforded the crude product in 85% yield, but pure material was obtained in 61% yield after crystallization from 95% EtOH. This change in the crystallization solvent did not appreciably improve the melting point (107–108 °C). The material was pure by ^1H NMR and IR analysis. Anal. Calcd for $C_{12}H_9BrN_2O_2S$: C, 44.32; H, 2.79; N, 8.61. Found: C, 44.60; H, 2.77; N, 8.90.

(4-Methoxybenzenediazosulfonyl)benzene (6). Compound **6** was prepared according to the general procedure (4 or 24 h of stirring) in 64% and 77% yields, respectively. Crystallization proved difficult due to oiling of the product. A 9% yield of material having a melting point of ca. 73 °C was obtained from hexane in either case. Anal. Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.37; N, 10.13. Found: N, 10.27.

(4-Nitrobenzenediazosulfonyl)benzene (7). Compound **7** was prepared according to the general procedure (21 h of stirring) in 84% yield. After crystallization (95% EtOH), **7** was obtained (21%) as an orange solid, mp 130 °C (lit.[17] mp 132–133 °C).

Synthesis of Arenediazocyanides, General Procedure. A 100-mL, 3-necked flask fitted for N_2 purge and magnetic stirring was charged with arenediazonium BF_4 salt (3 mmol) and dichloromethane (30 mL). Stirring was commenced, and 18-crown-6 (0.04 g, 5 mol %) was added; the resulting mixture was allowed to stir ca. 5 min. Solid KCN (0.20 g, 1 equiv) was then added in one portion; the solution turned yellow. The heterogeneous mixture was stirred vigorously at ambient temperature for 5 h, during which time the reaction mixture gradually darkened from yellow to red-orange or red-brown. After being stirred, the mixture was suction filtered and the filtrate washed with 10% (w/w) aqueous KOAc (3 × 20 mL). The organic layer was then dried over Na_2SO_4 in the dark ca. 24 h, filtered, and evaporated in vacuo to yield the crude arenediazocyanide as an orange to red-brown solid. The crude products were purified by sublimation, extraction, or distillation as appropriate.

Benzenediazocyanide (8). Benzenediazonium BF_4 (7.68 g, 40.0 mmol) was stirred in CH_2Cl_2 (400 mL) with KCN (5.2 g, 2 equiv) in the presence of 18-crown-6 (1.06 g, 10 mol%) for 18 h as described in the general procedure. Crude **8** was obtained as a dark brown oil (5.0 g, 95%). Vacuum distillation (60–65 °C (0.1 torr)) afforded 0.8 g (16% recovery) of red oil which solidified into prisms, mp 29 °C (lit.[19] oil).

4-Fluorobenzenediazocyanide (9). 4-Fluorobenzenediazonium BF_4 (0.63 g, 3.0 mmol) was stirred in CH_2Cl_2 (30 mL) with KCN (0.20 g, 1 equiv) in the presence of 18-crown-6 (0.04 g, 5 mol %) for 5 h as described in the general procedure. Crude **9** was obtained as an orange solid (0.41 g, 92%), mp 58–64 °C. The crude solid was sublimed (45–45 °C (0.1 torr)) to yield **9** as orange needles (0.32 g, 71%), mp 60–61 °C;[9] ^1H NMR δ 8.11, 8.02, 7.95, 7.87 ($J_{F-Hmeta}$ = 5 Hz), 7.37, 7.25, 7.22, 7.10 ($J_{F-Hortho}$ = 8 Hz).

2-Chlorobenzenediazocyanide (10). 2-Chlorobenzenediazonium BF_4 (1.36 g, 6.0 mmol) was stirred in CH_2Cl_2 (60 mL) with KCN (0.40 g, 1 equiv) in the presence of 18-crown-6 (0.08 g, 5 mol %) as described in the general procedure. Crude **10** was obtained as a dark brown semisolid (0.44 g, 44%). No further purification was carried out: IR (CH_2Cl_2) 2190, 1585, 1465, 1405, 1215, 1165, 1130, 1070 cm^{-1}; ^1H NMR δ 7.90–7.15 (m).

4-Chlorobenzenediazocyanide (11). 4-Chlorobenzenediazonium BF_4 (0.68 g, 3.0 mmol) was stirred in CH_2Cl_2 (30 mL) with KCN (0.20 g, 1 equiv) in the presence of 18-crown-6 (0.04 g, 5 mol %) for 5 h as described in the general procedure. Crude **11** was obtained as an orange solid (0.45 g, 91%), mp 96–101 °C. The crude solid was sublimed (60–65 °C 3 h) (1.0 torr) to yield pure **11** as red-orange needles (0.38 g, 77%), mp 100–104 °C, (lit.[20] mp 105 °C).

2,4-Dichlorobenzenediazocyanide (12). 2,4-Dichlorobenzenediazonium BF_4 (0.78 g, 3.0 mmol) was stirred in CH_2Cl_2 (30 mL) with KCN (0.20 g, 1 equiv) in the presence of 18-crown-6 (0.04 g, 5 mol %) for 5 h as described in the general procedure. Crude **12** was obtained as a brown semisolid (0.09 g, 15%). No further purification was carried out: IR (CH_2Cl_2) 2195, 1570, 1458, 1423, 1375, 1248, 1210, 1135, 1108, 823 cm^{-1}.

4-Bromobenzenediazocyanide (13). 4-Bromobenzenediazonium BF_4 (0.81 g, 3.0 mmol) was stirred in CH_2Cl_2 (30 mL) with KCN (0.20 g, 1 equiv) in the presence of 18-crown-6 (0.04 g, 5 mol %) for 5 h as described in the general procedure. Crude **13** was obtained as a red-orange solid (0.53 g, 84%), mp 107–115 °C. The crude solid was sublimed (95–100 °C 1 h) (0.15 torr), to yield (*E*)-4-bromobenzeneazocyanide as red-orange needles (0.36 g, 57%), mp 124–128 °C (lit.[20] mp 132 °C).

4-Methoxybenzenediazocyanide (14). 4-Methoxybenzenediazonium BF_4 (0.67 g, 3.0 mmol) was stirred in CH_2Cl_2 (30 mL) with KCN (0.20 g, 1 equiv) in the presence of 18-crown-6 (0.04 g, 5 mol %) for 5 h as described in the general procedure. Essentially pure **14** was obtained as a red solid (0.42 g, 87%), mp 117–122 °C (lit.[20] mp 121–122 °C).

4-Nitrobenzenediazocyanide (15). 4-Nitrobenzenediazonium BF_4 (0.71 g, 3.0 mmol) was stirred in CH_2Cl_2 (30 mL) with KCN (0.20 g, 1 equiv) in the presence of 18-crown-6 (0.04 g, 5 mol %) for 5 h as described in the general procedure. Crude **15** was obtained as a red-brown semisolid (0.42 g, 80%), mp 70–77 °C. The crude product was purified by extraction with boiling hexane–THF (4:1, v/v). Pure **15** was obtained after evaporation as bright orange platelets (0.25 g, 48%), mp 83–85 °C (lit.[20] mp 86 °C).

Reaction of 4-Chlorobenzenediazonium BF_4 with KCN in the Absence of Crown. 4-Chlorobenzenediazonium BF_4 (1.36 g, 6.0 mmol) was stirred in CH_2Cl_2 (60 mL) with KCN (0.4 g, 1 equiv) in the absence of 18-crown-6 for 5 h according to the general procedure. During the course of reaction, the mixture turned yellow. The mixture was suction filtered, dried over Na_2SO_4, and evaporated in vacuo to yield (*E*)-4-chlorobenzenediazocyanide (0.05 g, 5%). When the experiment was repeated by using 5 equiv KCN, 0.84 g (34%) of **11** was isolated after the mixture was stirred for 5 days.

Determination of Initial Isomer Formed during Phase-Transfer Synthesis of 11 at Ambient Temperature. 4-Chlorobenzenediazonium BF_4 (1.36 g, 6.0 mmol) was stirred in CH_2Cl_2 with KCN (1 equiv) and 18-crown-6 (5 mol %) at ambient temperature according to the general procedure. The pale orange mixture was suction-filtered after being stirred only 2 h. The filtrate was evaporated in vacuo on a cold water bath; no attempt was made to remove residual crown. The orange, semisolid residue was quickly redissolved in CH_2Cl_2 and its infrared spectrum examined as a function of time. The following spectral results were obtained: time = 0 h, ν_{CN} 2190 (weak), ν_{ring} 1395 (medium); time = 18 h, ν_{CN} 2190 (medium), ν_{ring} 1395 (strong); time = 27 h, ν_{CN} 2190 (strong), ν_{ring} 1395 (strong).

Attempted Cycloaddition Reactions between (Arenediazosulfonyl)benzenes and Dienes. A. 2,3-Dimethylbutadiene and 3. 2,3-Dimethylbutadiene (2 mmol) and **3** (2 mmol) were dissolved in $CDCl_3$ (2 mL) and filtered (glass wool) into a 5-mm NMR tube which was then sealed with a rubber septum cover. The 60-MHz ^1H NMR spectrum was recorded at several intervals. At t = 0, the spectrum showed only starting materials: δ 7.4–8.0 (m, aromatic), 5.0 (d, vinyl), 1.9 (s, methyl). Ratio of integral values: aromatic/vinyl, δ 1.86. After 1.0 h, the signal positions were unchanged but the aromatic/vinyl ratio was 2.60 after 21 h; the signal positions were observed as follows: δ 7.0–8.0 (m, aromatic), 5.0 (d, vinyl), 3.8–4.6 (q), 1.9 (s), 1.4 (s). The new aromatic/vinyl ratio: 4.6.

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At the end of 72 h, all the diene had reacted. The NMR signals observed were as follows: δ 6.8–7.9 (m, aromatic), 1.4 (s), 1.5–1.9 (b s), 3.8–4.6 (q). Thin-layer chromatographic analysis (Al_2O_3, 1:3 v/v CH_2Cl_2/hexane) revealed the presence of at least 3 products. Preparative TLC proved unsuccessful because even more products appeared to be present in the reaction mixture.

B, **Isoprene and 3**. Isoprene (0.68 g, 0.01 mol) and **3** (2.80 g, 0.01 mol) were dissolved in $CDCl_3$ (7.0 mL). The reaction mixture was warmed to 50 °C for a total of 5 h. TLC analysis, as above, indicated at least two products in addition to unreacted **3**. Preparative thin layer (Al_2O_3, 1:1 v/v CH_2Cl_2/hexane) afforded separation. The low and medium r_f bands were isolated and found by TLC to be mixtures of at least four components each.

Cycloaddition of Arenediazocyanides and Dienes, General Procedures. Arenediazocyanide (3.0 mmol) and the diene (2.4 equiv) were placed in a Carius pressure tube fitted with a Teflon screw cap and a magnetic stirring bar. The tube was capped; the mixture was heated (100 °C, oil bath) and stirred for 3 h. After being cooled to ambient temperature, the mixture was washed from the tube with CH_2Cl_2 and then absorbed onto silica gel. Chromatography using ether/hexane solvent mixtures afforded the cycloaddition product as a white or off-white solid.

Synthesis of 6. To a pressure tube containing **11** (0.50 g, 3.0 mmol) was added 1,3-butadiene (2.24 g, 14 equiv) by condensation at −45 °C. The tube was capped and stirring was continued for 5 days at ambient temperature. The tube was then opened and the excess butadiene allowed to boil off; a yellow solid remained in the tube. This solid was dissolved in MeOH and warmed with a small portion of activated charcoal. This procedure was repeated by using ether/hexane (50:50 v/v). Evaporation of the resulting filtrate in vacuo yielded 1-(4-chlorophenyl)-2-cyano-1,2,3,6-tetrahydropyridazine **16**. (0.56 g, 85%) as a straw-colored solid: mp 68–70 °C; ^{1}H NMR δ 7.42, 7.27, 7.08, 6.94 (AB quartet, 4 H, J = 9 Hz, 6.00 (pseudo-s, 2 H, vinyl), 3.98 (pseudo-s, 3 H). Anal. Calcd for $C_{11}H_{10}ClN_3$: C, 60.14; H, 4.59; N, 18.91. Found: C, 59.87; H, 4.54; N, 18.91.

Attempted Reaction of Butadiene with 14. The reaction was conducted as described above, and **14** was recovered in 95% yield.

Synthesis of 17. 1,3-Butadiene (2.43 g, 15 equiv) and **15** (0.53 g, 3.0 mmol) were allowed to react as described above, except that a pale yellow solid formed after only 3 h; and the reaction was immediately worked up. Evaporation of the butadiene afforded a brown oil which was chromatographed on silica gel (1:1 v/v ether/hexane) to yield 1-(4-nitrophenyl)-2-cyano-1,2,3,6-tetrahydropyridazene (**17**) (0.65 g, 84%) as a pale yellow solid, mp 78–83 °C. Crystallization from ether/hexane afforded pure **17**: mp 83–85 °C; ^{1}H NMR δ 8.33, 8.15, 7.16, 6.98 (AB quartet, 4 H, J = 11 Hz), 6.02 (pseudo-s, 2 H), 4.08 (pseudo-s, 4 H). Calcd for $C_{11}H_{10}N_4O$: C, 57.39; H, 4.38; N, 24.33. Found: C, 56.79; H, 4.27; N, 24.35.

Synthesis of 18. Chloroprene (1.06 g, 4 equiv) and **11** (0.50 g, 3.0 mmol) were heated for 3 h at 100–105 °C as described in the general procedure. Chromatography (SiO_2, 1:3, v/v ether/hexane) afforded **18** (0.78 g, 100%) as an off-white solid, mp 94–96 °C, which proved to be a regioisomer mixture. ^{13}C NMR analysis (see Table IV) indicated that the major isomer was the expected 1-(4-chlorophenyl)-2-cyano-5-chloro-1,2,3,6-tetrahydropyridazine. The minor product is the 4-chloro isomer. Anal. Calcd for $C_{11}H_9Cl_2N_3$: N, 16.54. Found, N, 16.20.

Synthesis of 19. (*E*)-Piperylene (0.41 g, 2 equiv) and **11** (0.50 g, 3.0 mmol) were heated (3 h, 95–108 °C) according to the general procedures. Chromatography (SiO_2, (1:1 v/v ether/hexane) afforded **19** (0.72 g, 100%) as a yellow oil. The isomer ratio (4:1) was determined by ^{1}H NMR and should be considered approximate. ^{13}C NMR analysis (see Table IV) showed that 1-(4-chlorophenyl)-2-cyano-3-methyl-1,2,3,6-tetrahydropyridazine was the major isomer of **19** and the 6-methyl isomer was the minor component: ^{1}H NMR δ 7.30, 7.15, 6.97, 6.82 (AB quartet, 4 H, J = 9 Hz), 5.82 (pseudo-s, 2 H), 3.84 (pseudo-s, 3 H), 1.50, 1.40 (d, J = 6 Hz, CH_3), 1.44, 1.33 (d, J = 6 Hz, CH_3). Anal. Calcd for $C_{12}H_{12}N_3Cl$: N, 17.98. Found: N, 17.85.

Synthesis of 20. (*E*)-Piperylene (0.41 g, 2 equiv) and **14** (0.48 g, 3.0 mmol) were heated (3 h, 94–105 °C) as described in the general procedure. Chromatography (SiO_2, 1:1 v/v ether/hexane) afforded **20** (0.32 g, 47%) as a yellow oil. The isomer ratio (8:1) was determined by ^{1}H NMR and should be considered approximate. ^{13}C NMR analysis (see Table IV) showed that 1-(4-methoxyphenyl)-2-cyano-3-methyl-1,2,3,6-tetrahydropyridazine was the major isomer of **20** and the 6-methyl isomer was the minor component: ^{1}H NMR δ 6.90, 6.85 (4 H), 5.81 (2 H), 3.74 (6 H, one and allyl), 1.45, 1.33 (d, J = 7 Hz, CH_3), 1.42, 1.30 (d, J = 7 Hz, CH_3). Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 67.91; H, 6.62; N, 18.19.

Synthesis of 21. A 5-mL, round-bottomed flask fitted with a magnetic stirring bar was charged with **15** (0.53 g, 3.0 mmol). (*E*)-Piperylene was poured in and stirring commenced. An exothermic reaction ensued affording a dark red mixture. The exotherm lasted ca. 2–3 min; a dark orange oil remained suspended in the excess diene. The mixture was stirred an additional 10 min and the excess diene allowed to evaporate, leaving a tan solid. The reaction mixture was washed out of the flask with dichloromethane; evaporation of this solution in vacuo left a brown oil, which resolidified upon trituration with ether/hexane. This solid was filtered off, washed with cold hexane, and air-dried to afford a pale yellow solid (0.70 g, 96%), mp 63–75 °C. The major isomer of **21** was identified by ^{13}C NMR as 1-(4-nitrophenyl)-2-cyano-3-methyl-1,2,3,6-tetrahydropyridazine, and the 6-methyl regioisomer was the minor component. The isomer ratio was estimated by ^{1}H NMR to be 2:1 and should be considered approximate. An analytical sample was obtained after recrystallization from ether/hexane as a pale yellow solid: mp 64–70 °C; ^{1}H NMR δ 8.36, 8.21, 7.23, 7.09 (AB quartet, 4 H, J = 9 Hz), 6.03 (2 H), 4.16 (3 H), 1.66, 1.54 (d, J = 7 Hz, CH_3), 1.50, 1.40 (d, J = 7 Hz, CH_3). Anal. Calcd for $C_{12}H_{12}N_4O_2$: N, 22.94. Found: N, 22.53.

Synthesis of 22. 2-Methyl-1,3-butadiene (isoprene, 0.41 g, 2 equiv) and **11** (0.50 g, 3.0 mmol) was heated and stirred (3 h, 95–105 °C) according to the general procedure. Chromatography (SiO_2, 1:3 v/v ether/hexane) afforded **22** (0.47 g, 67%) as an off-white solid, mp 80–82 °C. ^{13}C NMR analysis (see Table IV) showed that 1-(4-chlorophenyl)-2-cyano-5-methyl-1,2,3,6-tetrahydropyridazine was the major product, and only a trace of the 4-methyl regioisomer was present. Crystallization from THF/petroleum ether and then ether/petroleum ether afforded analytically pure **22**, as a straw-colored solid: mp 88–91 °C; ^{1}H NMR δ 7.41, 7.26, 7.07, 6.92 (AB quartet, 4 H, J = 9 Hz), 5.63 (m, 1 H), 3.85 (pseudo-s, 4 H), 1.85 (3 H, CH_3). Anal. Calcd for $C_{12}H_{12}ClN_3$: C, 61.67; H, 5.18; N, 17.98. Found: C, 61.77; H, 5.09, N, 18.07.

Synthesis of 23. Isoprene (1.19 g, 5 equiv) and **14** (0.56 g, 3.5 mmol) were heated (3 h, 100–115 °C) according to the general procedure. Chromatography (SiO_2, 1:19 → 1:3 v/v ether/hexane) afforded a red-orange oil. Trituration with petroleum ether afforded 1-(4-methoxyphenyl)-2-cyano-5-methyl-1,2,3,6-tetrahydropyridazine (**23**) (0.37 g, 46%, mp 64–66 °C). Two crystallizations (petroleum ether/hexane) afforded analytically pure **23** as long, off-white needles: mp 70–71.5 °C; ^{1}H NMR δ 7.03, 6.98 (4 H), 5.64 (m, 1 H), 3.82 (m, pseudo-s, 7 H, OMe and allyl), 1.86 (3 H). Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.55; N, 18.33. Found: C, 67.73; H, 6.60; N, 18.26.

Synthesis of 24. A solution of **15** (0.53 g, 3.0 mmol) in C_6H_6 (2 mL) was added dropwise over a period of 25 min to a stirred solution of isoprene (0.82 g, 4 equiv in 3 mL of C_6H_6) at ambient temperature. During the addition, the mixture darkened slowly; some dark brown solid material deposited. After an additional 4 h of stirring the mixture was diluted with CH_2Cl_2, filtered, and absorbed onto silica gel. Chromatography using ether/hexane (1:1 v/v) afforded a yellow oil. After trituration with ether/hexane (1:3 v/v), 1-4-nitrophenyl)-2-cyano-4-methyl-1,2,3,6-tetrahydropyridazine (**24**), was obtained as a yellow solid (0.40 g, 55%) which slowly softened and melted from 90 to 105 °C. Recrystallization from hexane/THF afforded an analytical sample: yellow platelets; mp 104–108 °C; ^{1}H NMR δ 8.39, 8.23, 7.25, 7.08 (AB quartet, 4 H, J = 10 Hz), 5.77 (1 H), 4.02 (4 H), 1.88 (3 H). Anal. Calcd for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.65; H, 5.00; N, 23.24.

Synthesis of 25. 2,3-Dimethyl-1,3-butadiene (0.49 g, 2 equiv) and **11** (0.50 g, 3.0 mmol) were heated (3 h, 95–105 °C) as described in the general procedure. Chromatography (SiO_2, 1:3 v/v ether/hexane) afforded 1-(4-chlorophenyl)-2-cyano-4,5-dimethyl-1,2,3,6-tetrahydropyridazine (**25**) (0.67 g, 90%) as an off-white solid, mp 97–99 °C. Crystallization from THF/petroleum ether afforded an analytical sample of **25** as small, white plates; mp 102.5–104.5 °C; ^{1}H NMR δ 7.30, 7.16, 6.97, 6.82 (AB quartet, 4 H, J = 9 Hz), 3.71 (4 H), 1.71, 1.63 (pseudo-d, 6 H, CH_3). Anal. Calcd for $C_{13}H_{14}ClN_3$: C, 63.03; H, 5.70; N, 16.96. Found: C, 62.98; H, 5.74; N, 16.94.

Synthesis of 26. 2,3-Dimethyl-1,3-butadiene (0.49 g, 2 equiv) and **14** (0.48 g, 3.0 mmol) were heated (3 h, 95–105 °C) as described in the general procedure. Chromatography (SiO_2, 1:3 v/v ether/hexane) afforded 1-(4-methoxyphenyl)-2-cyano-4,5-dimethyl-1,2,3,6-tetrahydropyridazine (**26**) (0.51 g, 70%) as a yellow oil which crystallized on standing (mp 62–65 °C). Two crystallizations from THF/petroleum ether afforded an analytical sample of **26** as long, pale yellow needles: mp 69–70 °C; ^{1}H NMR δ 7.02, 6.96 (4 H), 3.78 (pseudo-s, 7 H, OMe and allyl), 1.76, 1.68 (pseudo-d, 6 H). Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.23; H, 7.19; N, 17.36.

Synthesis of 27. A solution of **15** (0.53 g, 3.0 mmol) in C_6H_6 (3 mL) was added dropwise over 25 min to a 5-mL, round-bottomed flask containing a stirred solution of 2,3-dimethyl-1,3-butadiene in C_6H_6 (1 mL) at ambient temperature. A solid formed during addition; stirring was continued for 3 h after addition. The mixture was diluted with CH_2Cl_2, absorbed onto silica gel, and chromatographed (1:3 v/v ether/hexane)

to afford 1-(4-nitrophenyl)-2-cyano-4,5-dimethyl-1,2,3,6-tetrahydropyridazine (**27**) as a pale yellow solid (0.73 g, 94%), mp 143–147 °C. Crystallization from THF/hexane afforded pure **27** as short, yellow needles: mp 147–149 °C. ^{1}H NMR δ 8.36, 8.19, 7.23, 7.06 (AB quartet, 4 H, J = 10 Hz), 3.96 (pseudo-d, 4 H), 1.79 (pseudo-s, 6 H). Anal. Calcd for $C_{13}N_{14}O_2$: C, 60.46; H, 5.46; N, 21.69. Found: C, 60.48, H, 5.53; N, 21.68.

Synthesis of 28. Freshly distilled cyclopentadiene (0.40 g, 2 equiv) and **11** (0.50 g, 3 mmol) were heated (1 h, 50–56 °C) according to the general procedure. Chromatography (SiO_2, 1:3 v/v ether/hexane) afforded 1-(4-chlorophenyl)-2-cyano-1,2-diazabicyclo[2.2.21]hept-4-ene, **28** (0.40 g, 58%) as an off-white solid, mp 92–95 °C. Preparative TLC (SiO_2, 3:1 v/v ether/hexane) followed by slow evaporation of the solvent afforded analytically pure **28**, as small plates: mp 95–96 °C; ^{1}H-NMR: 7.38, 7.22, 7.10, 6.94 (AB quartet, 4 H, J = 9 Hz), 6.47 (m, 2 H), 4.85 (m, 2 H), 2.25, 2.10, 1.94, 1.79 (AB quartet, 2 H, J = 9 Hz, methylene bridge). Anal. Calcd for $C_{12}H_{10}N_3Cl$: C, 62.21; H, 4.35; N, 18.14. Found: C, 62.52; H, 4.43; N, 18.18.

Attempted Reaction of 14 with Cyclopentadiene. Freshly distilled cyclopentadiene (0.40 g, 2 equiv) and **14** (0.48 g, 3.0 mmol) were heated (4 h, 50–52 °C) as described in the general procedure. During the course of heating, **14** neither dissolved nor reacted. The latter was confirmed by TLC analysis (SiO_2, 1:1, v/v ether/hexane).

Synthesis of 29. A 10-mL, round-bottomed flask was charged with **15** (0.53 g, 3.0 mmol). Freshly distilled cyclopentadiene (2.5 g, 13 equiv) was poured in, and the mixture was stirred with a spatula. The solution became red-orange and homogeneous immediately but faded during 5 min with deposition of **29**. Evaporation of excess cyclopentadiene afforded 1-(4-nitrophenyl)-2-cyano-1,2-diazabicyclo[2.2.1]hept-4-ene (**29**) as a yellow solid (0.73 g, 100%), mp 100–108 °C. Crystallization from ether/hexane afforded analytically pure **29** as yellow needles: mp 110–112 °C; ^{1}H NMR δ 8.26, 8.12, 7.23, 7.10 (AB quartet, 4 H, J = 8 Hz), 6.57 (2 H), 5.27 (1 H), 5.00 (1 H), 2.37, 2.20, 2.10, 1.95 (AB quartet, 2 H, J = 10 Hz, methylene bridge). Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.31; H, 4.10; N, 23.27.

Synthesis of 30. 1,3-Cyclohexadiene (0.48 g, 2 equiv) and **11** (0.50 g, 3.0 mmol) were heated (3 h, 95–105 °C) as described in the general procedure. Chromatography (SiO_2, 1:9 v/v ether/hexane) afforded 1-(4-chlorophenyl)-2-cyano-1,2-diazabicyclo[2.2.2]oct-4-ene (**30**) (0.32 g, 43%) as a yellow oil which slowly crystallized under vacuum; mp 93–99 °C. Two crystallizations from hexane afforded pure **30** as off-white needles: mp 99–99.5 °C; ^{1}H NMR δ 7.38, 7.23, 7.12, 6.96 (AB quartet, 4 H, J = 9 Hz), 6.51 (m, 2 H), 4.41 (m, 2 H), 2.42, 2.28 (pseudo-d, 2 H), 1.58, 1.39 (pseudo-d, 2 H, bridge hydrogens). Anal. Calcd for $C_{13}H_{12}ClN_3$: C, 63.55; H, 4.92; N, 17.10. Found: C, 63.58; H, 4.90; N, 17.23.

Attempted Reaction between 1,3-Cyclohexadiene and 14. 1,3-Cyclohexadiene (1.2 g, 5 equiv) and **14** (0.48 g, 3.0 mmol) were heated (17 h, 95–97 °C) as described in the general procedure. Thin-layer chromatographic analysis and column chromatography (SiO_2) both proved unsuccessful. Only red semisolid and tarry materials were obtained.

Synthesis of 31. A 10-mL, round-bottomed flask was charged with a solution of 1,3-cyclohexadiene (0.96 g, 4 equiv) in ca. 1 mL of C_6H_6. A solution of **15** (0.53 g, 3.0 mmol) in ca. 3 mL of C_6H_6 was added dropwise with stirring over 1 h; an orange-brown solid formed during addition. After addition was complete, CH_2Cl_2 (3 mL) was added to the mixture, which was then stirred an additional 2 h and then filtered, and absorbed onto silica gel. Chromatography (1:1 v/v ether/hexane) afforded 1-(4-nitrophenyl)-2-cyano-1,2-diazabicyclo[2.2.2]oct-4-ene (**31**) (0.20 g, 26%) as a yellow solid: mp 138–140 °C. ^{1}H NMR δ 8.33, 8.16, 7.30, 7.15 (AB quartet, 4 H, J = 10 Hz); 6.66 (m, 2 H), 4.81, 4.48 (pseudo-d, 2 H), 2.44, 2.27 (pseudo-d, 2 H), 1.64, 1.47 (pseudo-d, 2 H, bridge hydrogens). Anal. Calcd for $C_{13}H_{12}N_4O_2$: N, 21.86. Found: N, 21.82.

Kinetics of the Cycloaddition between 2,3-Dimethyl-1,3-butadiene and 11. Equimolar solutions of **11** and diene were prepared by weighing (±0.1 mg) ca. 1.2 mmol of each into separate, 1.00-mL volumetric flasks and diluting with $CDCl_3$. The reaction solution was prepared by injecting 250-μL of each reagent solution into a 5-mm sample tube which had been sealed with a rubber septum cap. The tube was kept in an ice-water bath until its insertion into the NMR probe. In no case did the time between reagent mixing and tube insertion exceed 20 min.

The probe temperature was determined directly by using the ethylene glycol temperature shift method.[21] Temperature measurements before and after each run agreed within ±1 °C. The spectrometer was tuned by using a sample of diene in $CDCl_3$.

Each data point was determined from five integral scans over the region 5.5–3.5 ppm; these scans were performed in succession as quickly as possible. The integral values thus obtained compared diene and product concentrations almost simultaneously; these five values were then averaged. The time at which the five scans were started and completed was noted; the data point time was taken to be the midpoint of this scanning time period. In this manner, data points were obtained ca. every 5 min during the first half-life and ca. every 10–20 min thereafter until at least 2 half-lives had elapsed.

The reaction rate was determined at 26, 37, and 45 °C by using no fewer than 32 data points to define each rate. The poorest correlation coefficient obtained from linear regression analysis was 0.999. Activation parameters were determined in the usual fashion. ΔS^* was calculated for an average temperature of 36 °C (309 K).

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Registry No. **1**, 79827-98-8; **2**, 79827-99-9; **3**, 79828-00-5; **4**, 79828-01-6; **5**, 79828-02-7; **6**, 52897-41-3; **7**, 52897-40-2; **8**, 64661-86-5; **9**, 79896-01-8; **10**, 58468-77-2; **11**, 20750-84-9; **12**, 79828-03-8; **13**, 33652-51-6; **14**, 52512-40-0; **15**, 32295-71-9; **16**, 73261-66-2; **17**, 79828-04-9; **18** 5-chloro derivative, 79828-05-0; **18** 4-chloro derivative, 79828-06-1; **19** 3-methyl derivative, 73227-40-4; **19** 6-methyl derivative, 79828-07-2; **20** 3-methyl derivative, 73235-89-9; **20** 6-methyl derivative, 79828-08-3; **21** 3-methyl derivative, 73227-41-5; **21** 6-methyl derivative, 79828-09-4; **22**, 73227-42-6; **23**, 79828-10-7; **24**, 79828-11-8; **25**, 73227-44-8; **26**, 73227-43-7; **27**, 73227-45-9; **28**, 73227-37-9; **29**, 73227-38-0; **30**, 73227-39-1; **31**, 79828-12-9; butadiene, 106-99-0; chloroprene, 126-99-8; (*E*)-piperylene, 2004-70-8; isoprene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; cyclopentadiene, 542-92-7; cyclohexadiene, 592-57-4; benzenediazonium BF_4^-, 369-57-3; 4-fluorobenzenediazonium BF_4^-, 459-45-0; 2-chlorobenzenediazonium BF_4^-, 1956-97-4; 4-chlorobenzenediazonium BF_4^-, 673-41-6; 2,4-dichlorobenzenediazonium BF_4^-, 21872-70-8; 4-bromobenzenediazonium BF_4^-, 673-40-5; 4-methoxybenzenediazonium BF_4^-, 459-64-3; 4-nitrobenzenediazonium BF_4^-, 456-27-9.

(21) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 218.