Syn-Anti Selectivity in Cycloadditions. 6. Cycloadditions of Benzonitrile Oxide, 2-Diazopropane, and Diphenylnitrilimine to Polychloronorbornadienes[1]

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Benzonitrile oxide, 2-diazopropane, and diphenylnitrilimine react smoothly at the unsubstituted double bond of 2,3-dichloro-, 1,2,3,4-tetrachloro-, 1,2,3,4,7-pentachloro-, and 1,2,3,4,7,7-hexachloronorbornadiene to give mixtures of syn and anti adducts. The sole syn adduct is formed in the reaction of 2-diazopropane with norbornadiene. Structures were attributed on the basis of spectroscopic (^{1}H NMR) and chemical evidence. Competition experiments allowed us to evaluate the relative reactivities of the anti face of the polychloronorbornadienes in the reaction with 2-diazopropane. The results are discussed on the basis of steric and electronic effects of the chlorine atoms of the dipolarophiles.

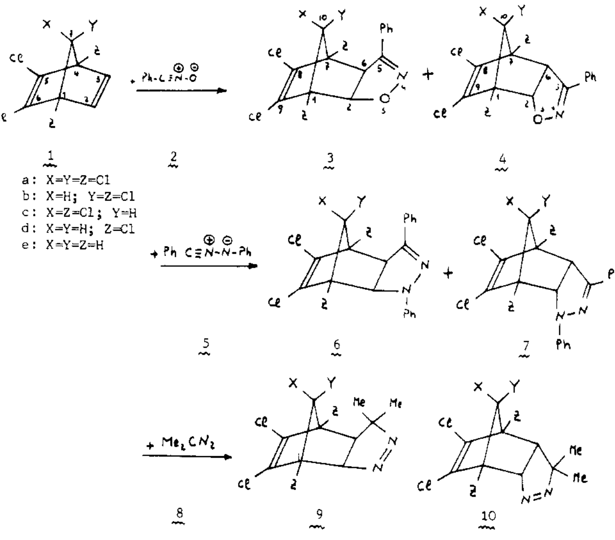
The study of syn-anti isomerism in 1,3-dipolar[3] and Diels-Alder[4] cycloadditions has recently raised considerable interest for its theoretical and synthetic aspects. It has been shown that norbornene exhibits 100% syn selectivity in the reaction with dienes[5] and 1,3-dipoles.[6] A 100% syn selectivity was also observed for some reactions of norbornadiene with both dienes[5b,7] and 1,3-dipoles;[6c,8] in several instances, however, mixtures of syn (dominant)/anti adducts were detected[6,9] (see Figure 1). The prevalent formation of anti-syn adduct was observed in the reaction of 7-*tert*-butoxynorbornadiene with phenyl azide[10] and hexachlorocyclopentadiene.[9,11] MO calculations[12] (MINDO/2) on 7-methoxynorbornadiene have shown that the HOMO of this diene is largely $\pi_{2,3}$. This data accounts for the observation from kinetic experiments, where 7-*tert*-butoxynorbornadiene and norbornadiene were reacted with hexachlorocyclopentadiene, that the substituted dienophile, although 10 times less reactive than norbornadiene, underwent anti addition to $\pi_{2,3}$ at a rate ca. 65-90 times faster than the unsubstituted dienophile.[11] This means that cycloadditions governed by the interaction LUMO (1,3-dipole or diene)-HOMO (norbornadiene) such as those reported go through an anti attack on the C_2-C_3 double bond of 7-substituted norbornadienes. (Indeed the *syn*-methylene attack on $\pi_{2,3}$ is prevented by steric shielding of the 7-*tert*-butoxy group.)

Table I. Syn-Anti Isomer Ratios in the Cycloadditions of BNO (2), DPNI (5), and DP (8) to Compounds 1[a]

dipolarophile	isomer ratios		
	syn-3:*anti*-4	*syn*-6:*anti*-7	*syn*-9:*anti*-10
1a	*b*	*c*	*d*
1b	*b*	*c*	*d*
1c	40.5:59.5	16:84	61.5:38.5
1d	83:17	76:24	98.8:1.2
1e	82.5:17.5	93.5:6.5	*e*

[a] The results are the average of three runs. [b] 100% *anti*-4. [c] 100% *anti*-7. [d] 100% *anti*-10. [e] 100% *syn*-9.

Scheme I



Cycloadditions which are HOMO (1,3-dipole)-LUMO (norbornadiene) controlled are less documented. Diazomethane and diazoethane add to 7-halonorbornadienes, yielding the sole anti-anti adduct in moderate yield;[13] reaction of diphenyldiazomethane with 7-chloronorbornadiene gives a mixture of three adducts [syn-anti (26%), anti-anti (58%), and anti-syn (16%)] with a slight prevalence of the anti-anti isomer.[15,16] Because no kinetic

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[1] Part 4: D. Cristina, C. De Micheli, and R. Gandolfi, *J. Chem. Soc., Perkin Trans. 1*, 2891 (1979); part 5: C. De Micheli, R. Gandolfi, M. Ratti, and L. Toma, *Heterocycles*, 12, 897 (1979).

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[4] N. T. Anh, *Tetrahedron*, **29**, 3227 (1973).

[5] (a) J. M. Coxon and M. A. Battiste, *Tetrahedron*, **32**, 2053 (1976); (b) D. N. Butler, H. Barrette, and R. A. Snow, *Synth. Commun.*, **5**, 101 (1975).

[6] (a) Reference 3, pp 438-9, 451-3, 458-9; (b) H. Taniguchi, T. Ikeda, Y. Yoshida, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **50**, 2694 (1977); (c) T. Saito and S. Motoki, *J. Org. Chem.*, **44**, 2493 (1979).

[7] D. W. Jones and C. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 1647 (1976).

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[9] L. T. Byrne, A. R. Rye, and D. Wege, *Aust. J. Chem.*, **27**, 1961 (1974).

[10] (a) G. W. Klumpp, A. H. Weefkind, W. L. de Graaf, and F. Bickelhaupt, *Justus Liebigs Ann. Chem.*, **706**, 47 (1967); (b) B. Halton and A. D. Woolhouse, *Aust. J. Chem.*, **26**, 619 (1973).

[11] M. A. Battiste, J. F. Timberlake, and H. Malkus, *Tetrahedron Lett.*, 2529 (1976).

[12] K. B. Astin and K. Mackenzie, *J. Chem. Soc., Perkin Trans. 2*, 1004 (1975). Similar results were found by ab initio MO calculations on 7-chloronorbornadiene[13] and other 7-substituted (F, Cl, OH, HCOO) norbornadienes.[14]

[13] M. Franck-Neumann and M. Sedrati, *Angew. Chem., Int. Ed. Engl.*, **13**, 606 (1974).

[14] P. V. Alston and R. M. Ottenbrite, *J. Heterocycl. Chem.*, **14**, 1443 (1977).

[15] J. W. Wilt and W. N. Roberts, *J. Org. Chem.*, **43**, 170 (1978).

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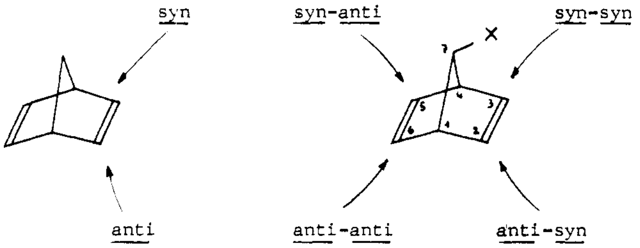


Figure 1.

Table II. ^{1}H NMR [$\delta(CDCl_3)$] Data and (in Parentheses) $\Delta\delta$ Values [$\delta(CDCl_3) - \delta(C_6D_6)$] of Compounds 3 and 4

	H-2	H-6	H-10_Y	H-10_X	$J_{2,6}$[c]	$J_{2,10X}$[c]
3c	5.18 (0.68)	4.46 (1.01)	4.60 (0.10)		9.0	
4c	5.33 (0.67)	4.58 (1.00)	4.48 (1.22)		9.0	
3d	5.06 (0.53)	4.33 (0.83)	2.76 (0.35)	2.41 (0.66)	10.0	2.0
4d	5.48 (0.67)	4.58 (0.81)	2.61 (1.01)	2.41 (0.81)	10.0	
3e[a]	5.10 (0.40)	4.01 (0.63)	1.91 (0.58)	1.66 (0.33)	8.0	1.5
4e[b]	5.46 (0.68)	4.20 (0.92)	2.01 (0.80)	1.51 (1.00)	9.0	
4a	5.50 (0.49)	4.80 (0.72)			8.5	
4b	5.55 (0.47)	4.78 (0.68)		4.18 (1.12)	8.5	

[a] δ 3.28 (0.42) (H-1, $J_{1,2}$ = 1.5 Hz), 3.11 (0.50) (H-7).
[b] δ 3.43 (0.60) (H-1, $J_{1,2}$ = 4.0 Hz), 3.43 (0.75) (H-7).
[c] J in Hz.

data are available for these reactions, the electronic effect of the substituent at the 7-position on the activation of the anti face of $\pi_{5,6}$ or on deactivation of the unhindered sites of attack (e.g., *syn*-methylene attack on $\pi_{5,6}$ and anti attack on $\pi_{2,3}$) cannot be evaluated. The present study reports data on the cycloadditions of various 1,3-dipoles to polychloronorbornadienes. The influence of a chlorine atom at the 7-position of a norbornadiene system on syn–anti isomerism and the reactivity of the dipolarophile has been evaluated.

Results

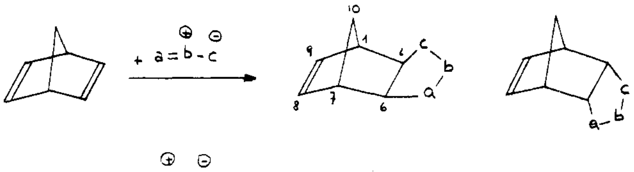
Benzonitrile oxide (BNO, **2**), diphenylnitrilimine (DPNI, **5**), and 2-diazopropane (DP, **8**) reacted smoothly with polychloronorbornadienes **1**, at room temperature, to give adducts **3**, **4**, **6**, **7**, **9**, and **10**, respectively, in quantitative yield. Isomer ratios were evaluated by column chromatography and, in some cases, were confirmed by VPC analysis (Table I and Scheme I).

The structures were assigned on the basis of ^{1}H NMR spectra whose characteristic patterns are illustrated by the data of adducts **3** and **4** reported in Table II.

The aromatic solvent-induced shift on H-10_Y allowed one to choose between adducts **3c**, **6c**, and **9c** and adducts **4c**, **7c**, and **10c**. As a matter of fact, the signal corresponding to H-10_Y was practically unaffected in the spectra of the former compounds while it was shifted to higher field (~1.0 ppm) in the spectra of the latter compounds on changing $CDCl_3$ for C_6D_6. The syn-disposed heterocycle in **3c**, **6c**, and **9c** prevents solvation of such a proton.

A long-range coupling constant (~1.5–2.0 Hz, "W" coupling path) between H-10_X and H-2 (or H-6) was present in the NMR spectra of **3d**, **6d**, and **9d** and absent in the spectra of **4d** and **7d**, as expected for the assigned structure. The long-range "W" coupling constant was also absent in the NMR spectra of all cycloadducts derived from **1b**; structures **4b**, **7b**, and **10b** were consequently confirmed. Finally, the anti structure attributed to compounds derived from **1a** was also based on the following chemical evidence: (i) Zn/AcOH reduction of compound **4a** gave a mixture of **4b** and **4c**; (ii) a similar reduction of adduct **10a** and subsequent oxidation of the crude reaction mixture (most seemingly acetylpyrazolidines) with a methanolic solution of Ag_2O yielded a mixture of compounds **10c** and **10d**. 2-Diazopropane reacted readily with norbornadiene to give, in high yield, the sole syn adduct **11**: NMR ($CDCl_3$) δ 4.87 (dt, 1 H, H-1, $J_{2,6}$ = 6.3 Hz and $J_{1,2} = J_{2,10\text{-anti}}$ = 1.4 Hz) (Scheme II, in the same scheme are also reported the known results of cycloadditions of BNO[17] and DPNI[6b] to norborandiene).

Scheme II



$\overset{\oplus}{a}=b-\overset{\ominus}{c}$	11	12
	Relative Yield (%)	
$Me_2C=\overset{\oplus}{N}=\overset{\ominus}{N}$	100	-
$Ph-C\equiv\overset{\oplus}{N}-\overset{\ominus}{N}-Ph$	87	13
$Ph-C\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$	80	20

Table III. Partial Rate Factors for Addition of 2-Diazopropane to the C_2–C_3 Double Bond of Norbornadienes 1 and to Norbornadiene[a]

	cycloaddition side	
dipolarophile	*syn*-methylene	*anti*-methylene
norbornadiene	1	<0.01
1a	<0.01	11.6
1b	<0.01	1.9
1c	4.2	2.6
1d	8.4	0.1

[a] At 20 °C in diethyl ether solutions. The values are the average of three runs.

For the evaluation of the relative reaction rates of norbornadiene and dipolarophiles **1a–d** with 2-diazopropane, binary mixtures of **1a** with **1b**, **1c**, **1d**, and norbornadiene, respectively, were treated with a deficiency of 1,3-dipole. We were able to evaluate the relative rates of cycloaddition with the following equation (where Dip = dipolarophile):

$$R_{\text{rel}} = \frac{R_{\text{Dip}_1}}{R_{\text{Dip}_2}} = \frac{\ln \dfrac{[\text{Dip}_1]_{\text{initial}}}{[\text{Dip}_1]_{\text{final}}}}{\ln \dfrac{[\text{Dip}_2]_{\text{initial}}}{[\text{Dip}_2]_{\text{final}}}}$$

The values in Table I and the kinetic data permitted one to evaluate the partial rate factors (Table III) for syn and anti cycloaddition of 2-diazopropane to compounds **1a–d**; the syn addition rate per double bond of norbornadiene was chosen as a standard value.

In order to discuss the relative syn reactivity of **1c** and **1d**, we need to know their geometrical structure. MIN-

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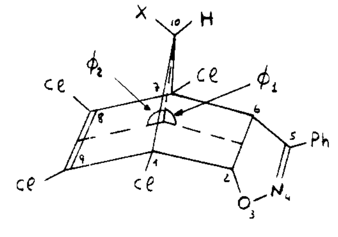
[16] In the reaction of diphenyldiazomethane with 7-*tert*-butoxynorbornadiene the anti–anti isomer is a minor component (26%): J. W. Wilt and D. R. Sullivan, *J. Org. Chem.*, **40**, 1036 (1975).

[17] R. Lazar, F. G. Cocu, and N. Barbulescu, *Rev. Chim.* (*Bucharest*), **20**, 3 (1969); *Chem. Abstr.*, **70**, 11341 (1969).



4c: X = Cl
4d: X = H

Figure 2.

Table IV

Dihedral Angles (deg) between Least-Squares Planes

structure	ϕ_1	ϕ_2
$4c_1$[a]	117.8	130.6
$4c_2$	117.7	127.2
4d	120.3	126.4

Average Deviation (Å) from Least-Squares Planes[b]

structure	plane 1	plane 2	plane 3
$4c_1$	0.008	0.003	0.001
$4c_2$	0.009	0.005	0.009
4d	0.008	0.013	0.005

[a] Subscripts refer to the two independent molecules in the asymmetric units. [b] Plane 1: C_1-C_{10}-C_7; plane 2: C_1-C_2-C_6-C_7; plane 3: C_1-C_9-C_8-C_7.

DO/2 calculations show that the methylene bridge in 7-methoxynorbornadiene is deflected ca. 1.5° away from vertical plane through C_1–C_4 toward $\pi_{2,3}$ due to the repulsion between the substituent and $\pi_{5,6}$.[12] In order to ascertain a possible similar change in the geometry of **1c** in comparison to **1d**, we performed X-ray analysis of compounds **4c** and **4d** (Figure 2) which, in our opinion, are suitable models for **1c** and **1d**. The relevant data are reported in Table IV.

The data of Table IV confirm that the 10-*anti*-chlorine atom in **4c** increases the geometrical distortion of the methylene bridge away from plane 3 toward plane 2, already present in **4d**. Therefore, it is likely that a similar structural change on passing from **1d** to **1c** results in a higher steric shielding of the syn face of $\pi_{2,3}$ for the latter compound in comparison to the former.

Discussion

The reactivity trend of the anti face of compounds **1a–d**, as evidenced by the data reported in Table III, agrees with the expectation that cycloadditions of the electron-rich 1,3-dipole DP **8** to compounds **1** are governed by the HOMO (DP)–LUMO (dipolarophile) interaction. Therefore, the increase in reactivity of the anti face on going from **1d** to **1a** may be considered a consequence of the parallel decrease in the LUMO energy of dipolarophiles. In fact, perturbation theory states that the energy of interaction increases with a decrease in the energy separation between the interacting orbitals.[18] Interestingly, pentachloronorbornadiene **1c**, with a chlorine atom located in the 7-anti position, is more efficient than the isomer **1b** in promoting an anti attack to $\pi_{2,3}$. This result seems to indicate that the effect of the 7-anti substituent not only is inductive in origin but also bears a stereoelectronic component. A plausible explanation of this fact lies in the π–σ^* interaction, first proposed by Franck-Neumann[13] (Figure 3), which permits the accommodation of the partial negative charge arising on the dipolarophile moiety in the oriented complex, with the 1,3-dipole attacking from the *anti*-methylene side of **1c**. This effect may not be at work in the 7-syn-substituted derivative **1b**.[19] However, it should be noted that the difference in the rates for anti addition on **1c** and **1b** is small if compared to the specificity reported for the reaction of 7-chloronorbornadiene with diazomethane and diazoethane[13] but in agreement with the result of cycloaddition of diphenyldiazomethane.[15,22]

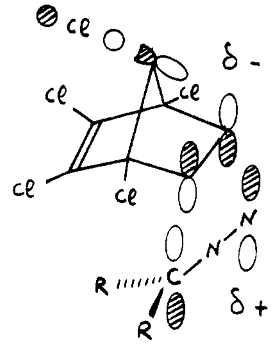


Figure 3.

Table V. $\Delta\Delta G^{\ddagger}$ ($\Delta G^{\ddagger}_{anti} - \Delta G^{\ddagger}_{syn}$)[a] of the Reactions of 1,3-Dipoles 2, 5, and 8 with 1c and 1d at 20 °C

1,3-dipole	IP_v, eV	$\Delta\Delta G^{\ddagger}_{1c}$	$\Delta\Delta G^{\ddagger}_{1d}$	$\Delta\Delta G^{\ddagger}_{1d} - \Delta\Delta G^{\ddagger}_{1c}$
2	8.9 and 10.5[b]	−0.23	0.94	1.17
5	9.3[c]	−0.98	0.68	1.66
8	7.9[d]	0.28	2.61	2.33

[a] In kcal mol^{-1}. [b] Experimental.[26a] [c] Estimated from MINDO/2 for formonitrilimine.[26b] [d] Experimental.[25]

Concerning the syn–anti selectivity, Table I and Scheme II show that isomer ratios found for compounds **1d** and **1e** are very similar to those of norbornadiene. Substituents in positions 1, 2, 3, and 4 of **1** therefore do not affect

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[18] Reference 3, p 395; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969, pp 191–247.

[19] Another effect which may lower the reaction rate of DP (**8**) with **1b** is the increase in nonbonded interactions between the 7-*syn*-chlorine with H-2 and H-3 in the transition state.[11] This unfavorable steric factor is difficult to estimate due to a lack of precise knowledge of the transition-state structure (reactant-like or product-like) for 1,3-dipolar cycloadditions. However, an early transition state (reactant-like) was recently proposed on the basis of both experimental[20] and LCAO–SCF–MO calculations[21] for these cycloadditions, and, consequently, the above-cited steric effect should not appreciably influence the anti reactivity of **1b** in comparison to **1c**.

[20] (a) R. Huisgen, *Angew, Chem., Int. Ed. Engl.*, **2**, 633 (1963); (b) J. Geittner, R. Huisgen, and H. U. Reissig, *Heterocycles*, 11, 109 (1978).

[21] G. Leroy and M. Sana, *Tetrahedron*, **32**, 709 (1976).

[22] Wilt and Roberts suggest that, while the diazomethane–7-chloronorbornadiene reaction is controlled by a HOMO (1,3-dipole)–LUMO (dipolarophile) interaction, both frontier molecular orbital interactions need to be considered for the reaction of diphenyldiazomethane with the same dipolarophile. We do not agree with this suggestion as kinetic data [R. Huisgen and G. Geittner, *Heterocycles*, **11**, 105 (1978)] clearly show that the diphenyldiazomethane–norbornene reaction is controlled by the sole HOMO (1,3-dipole)–LUMO (dipolarophile) interaction. It is therefore quite reasonable to think that the reaction of diphenyldiazomethane with 7-chloronorbornadiene is governed by the same type of interaction.

[23] The decreasing nucleophilic character of 1,3-dipoles (diazoalkanes > DPNI > BNO) is also supported by a large amount of experimental data [see the following: ref 3 and 20b; J. Geittner and R. Huisgen, *Tetrahedron Lett.*, 881 (1977); E. Stephan, *Bull. Soc. Chim. Fr.*, 364 (1978)]. Estimated values for the HOMO energies of BNO (10.0 eV) and DPNI (7.5 eV)[24] confirm that the latter 1,3-dipole is more nucleophilic than the former.

[24] K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973).

significantly the syn–anti selectivity whereas with a 7-*syn*-chlorine (Y = Cl) a 100% anti selectivity is found. This anti selectivity obtained both with **1a** and **1b** may be attributed mainly to the steric shielding on the *syn*-methylene side by the 7-syn substituent.

Noteworthy is the observed decrease in syn reactivity on going from **1d** to **1c** (Table III). In our opinion, this behavior may be attributed, at least in part, to the higher deflection of the methylene bridge toward the $\pi_{2,3}$ bond in **1c** with an increase in steric shielding of its syn face in comparison to **1d**. The correlations of syn–anti ratios and activation free energies for reactions of 1,3-dipoles **2**, **5**, and **8** with **1c** and **1d** were evaluated and summarized in Table V. The correlation between the difference $\Delta\Delta G^{\ddagger}_{1d} - \Delta\Delta G^{\ddagger}_{1c}$ and the donor character of the 1,3-dipoles expressed by the ionization potential (IP_v) is apparent. 2-Diazopropane (**8**), for example, the 1,3-dipole that is the best electron donor (IP_v = 7.9 eV),[25] gives the maximum value (2.33 kcal/mol) whereas the minimum value (1.17 kcal/mol) was found for benzonitrile oxide (**2**) which possesses the highest IP_v values (8.9 and 10.5 eV).[26] The IP_v values indicate a stronger HOMO (1,3-dipole)–LUMO (dipolarophile) interaction for the DP–**1d** reaction than for the BNO–**1d** reaction. Consequently the change in this FMO interaction (due to a lowering of the LUMO dipolarophile) is higher on passing from the DP–**1d** to the DP–**1c** reaction than from the BNO–**1d** to the BNO–**1c** reaction, and this is in agreement with the higher difference, $\Delta\Delta G^{\ddagger}_{1d} - \Delta\Delta G^{\ddagger}_{1c}$, found for DP than for BNO. It appears, therefore, with regard to electronic effects, that both reactivity and syn–anti selectivity are controlled, for all reactions studied, by the HOMO (1,3-dipole)–LUMO (dipolarophile) interaction. Nevertheless, it is strange in this framework that DP reacted with **1c** to give a lower anti/syn ratio than did BNO and DPNI. In view of the high steric requirements of DP, it is tempting to propose as an explanation for this anomaly a higher steric shielding of the anti face than the syn face of $\pi_{2,3}$ in **1c**. Consequently, the same steric effect, which favors *syn*-methylene attack, should also be at work in the reactions of 1,3-dipoles with **1d** and norbornadiene.

Experimental Section

Compound **1a** was purchased from Aldrich; all 1,3-dipoles and dipolarophiles **1b**,[27] **1c**,[27] **1d**,[27] and **1e**[28] were prepared by standard methods. NMR spectra were recorded on a Varian A-60 spectrometer (Me_4Si as internal standard); microanalysis were performed on a Carlo Erba analyzer, Model 1106. All compounds gave satisfactory elemental analysis (±0.3%). Reaction mixtures were analyzed by TLC on silica gel GF_{254}, and the spots were detected under a UV lamp or by spraying with a 3% solution of chromic anhydride in sulfuric acid (50%) followed by charring at 120 °C.

Reactions of 1a–e with Diphenylnitrilimine and Benzonitrile Oxide. To a solution of **1a**, **-b**, **-c**, **-d**, or **-e** (10.0 mmol) and (α-chlorobenzylidene)phenylhydrazine or benzhydroximic acid chloride (3.0 mmol) in ether (50 mL) was added a stoichiometric amount of triethylamine in ether (20 mL) over a period of 2 h with stirring. The mixture was left at room temperature for 24 h and then poured into water. The organic layer was separated, dried, and evaporated to give a residue which was column chromatographed with ethyl acetate–cyclohexane (1:4) as eluent. In all cases the syn isomer was eluted as the first component. Physical data of the compounds are reported in Table VI.

Table VI. Physical Data for Compounds 3–11

compd	cryst solvent	mp, °C
3c	EtOH[a]	195–197
3d	petroleum ether[b]	155–157
3e	EtOH[b]	139–141
4a	EtOH[b]	157–159
4b	petroleum ether[b]	145–147
4c	petroleum ether[b]	125–127
4d	petroleum ether[b]	94–96
4e	EtOH[a]	156–158
6c	ethyl acetate[a,c]	150–152
6d	EtOH[a,c]	137–138
6e	ethyl acetate[b,c]	111–113
7a	EtOH[b,c]	152
7b	ethyl acetate[b]	144–146
7c	ethyl acetate[a,c]	142–144
7d	EtOH[b,c]	143–145
7e	EtOH[a,c]	139–141
9c	EtOH[a]	161–162
9d	EtOH[a]	121–123
9e	petroleum ether[a]	87–88
10a	EtOH[a]	125–128
10b	EtOH[a]	113–114
10c	EtOH[a]	133–135
10d	EtOH[a]	125–126
11	yellow oil	114 (20 mmHg)[d]

[a] Compound recrystallized as needles. [b] Compound recrystallized as prisms. [c] Compound was yellow-green. [d] Boiling point.

Reactions of 1a–e and Norbornadiene with 2-Diazopropane. A solution of 2-diazopropane and excess of **1a**, **-b**, **-c**, **-d**, **-e**, or norbornadiene in ether was allowed to stand at room temperature until the orange color of the diazoalkane disappeared. The solvent was evaporated, and column chromatography of the residue (ethyl acetate–cyclohexane, 1:4) afforded compounds **9**, **10**, and **11** (Table VI, Schemes I and II) in almost quantitative yield. The syn isomer was always eluted as the first component.

Reduction of Adduct 4a. A mixture of **4a** (500 mg), acetic acid (80 mL), and zinc dust (6 g) was refluxed with stirring for 24 h and then poured into water, neutralized with sodium carbonate, and extracted with ether. The ether extracts were dried and evaporated in vacuo to give a residue from which **4b** (10%) and **4c** (5%) were isolated by column chromatography.

Reduction of Adduct 10a. **10a** (500 mg) was reduced with zinc dust as described above. To a solution of the residue, from evaporation of the ether extracts, in methanol was added Ag_2O (2.5 g), and the mixture was refluxed under stirring for 24 h. After the usual workup, column chromatography afforded **10d** (20%) and **10c** (15%).

Competition Reactions. To a solution of **1a** (3.0 mmol), **1b** (3.0 mmol), and pentachlorobenzene (1.5 mmol) in anhydrous ether (30 mL) was added a deficiency of **8** (in ether, 2 M) at 20 ± 1 °C. The reaction mixture was allowed to stand at 20 ± 1 °C until the orange color of the diazoalkane disappeared. The ether was then evaporated under reduced pressure, and the amount of unreacted **1a** and **1b** was determined by ^1H NMR with pentachlorobenzene as internal standard. Similarly, other competition experiments were performed by using binary mixtures of **1a**/**1c** and **1a**/**1d**.

In the competition reaction of norbornadiene and **1a** (10:1) the amounts of unreacted **1a** and of cycloadduct **11** were determined by VPC (3% OV-17 column, 80 °C) with pentachlorobenzene as internal standard. The results were evaluated according to Huisgen et al.[29] taking as unreacted norbornadiene the value [initial norbornadiene] – [**11**].

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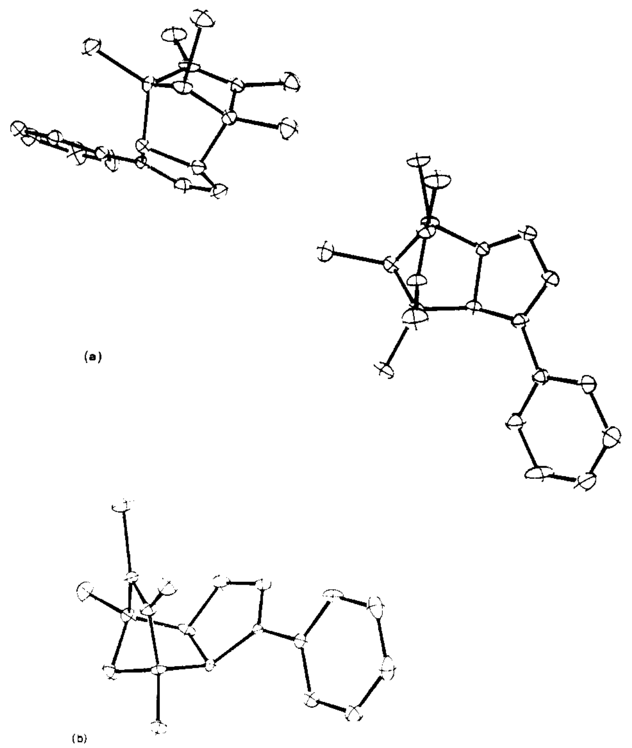

Figure 4. ORTEP perspective view[30] of compounds **4c** (a) and **4d** (b). Thermal elliposids are drawn at 20% probability.

X-ray Analysis and Structure Determination of Compounds 4c and 4d. ORTEP perspective views of compounds **4c** and **4d** are given in Figure 4. The following data were obtained. **4c**: $C_{14}H_8NOCl_5$, triclinic, a = 11.426 (1) Å, b = 13.136 (1) Å, c = 11.208 (1) Å, α = 105.0 (1)°, β = 94.7 (1)°, γ = 102.5 (1)°, space group $P\bar{1}$, Z = 4 [Mo Kα radiation (λ = 0.7107 Å)]. **4d**: $C_{14}H_9NOCl_4$, monoclinic, a = 16.368 (1) Å, b = 10.858 (1) Å, c = 8.302 (1) Å, β = 94.2 (1)°, space group $P2_1/n$, Z = 4 [Mo Kα radiation (λ = 0.7107 Å)].

X-ray structure investigation was performed for both compounds by using a Philips PW 1100 four-circle computer-controlled diffractometer. Intensity measurements were made with $\omega/2\theta$ (**4c**) and ω (**4d**) scan techniques in a θ range of 2–20°, yielding 2918 (**4c**) and 1356 (**4d**) independent reflections. Both sets of intensities were corrected for Lorentz and polarization factors but not for absorption.

The structures were solved by direct methods using the MULTAN 78 computer system.[31] After three cycles of isotropic full-matrix least-squares refinement, R fell to 12.3% (**4c**) and to 4.3% (**4d**) (only reflections with $I > 3\sigma(I)$ were regarded as observed).

Positional parameters for H atoms were calculated on the basis of geometrical considerations and checked on difference Fourier maps; they were inserted but not allowed to vary in two cycles of anisotropic refinement. The H atom positional parameters were then recalculated and used in one further cycle of anisotropic refinement, which yielded R = 5.8% (**4c**) and 4.3% (**4d**) for the observed reflections.

Scattering factors were taken from the literature.[32] Positional and thermal parameters for nonhydrogen atoms as well as bond distances and angles, torsion angles, and lists of structure factors are available as supplementary material.

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Registry No. 1a, 3389-71-7; **1b**, 18451-28-0; **1c**, 18367-86-7; **1d**, 5450-91-9; **1e**, 18990-07-3; **2**, 873-67-6; **3c**, 72727-17-4; **3d**, 72727-18-5; **3e**, 72727-19-6; **4a**, 72727-20-9; **4b**, 72777-21-0; **4c**, 72777-22-1; **4d**, 72777-23-2; **4e**, 72777-24-3; **5**, 15409-32-2; **6c**, 72727-21-0; **6d**, 72727-22-1; **6e**, 72727-23-2; **7a**, 72727-24-3; **7b**, 72777-25-4; **7c**, 72777-26-5; **7d**, 72777-27-6; **7e**, 72777-28-7; **8**, 2684-60-8; **9c**, 72727-25-4; **9d**, 72727-26-5; **9e**, 72727-27-6; **10a**, 72727-28-7; **10b**, 72843-03-9; **10c**, 72843-04-0; **10d**, 72778-02-0; **11** ($a{=}b^+{-}c^-$ = $Me_2C{=}N^+{=}N^-$), 72727-29-8; **11** ($a{=}b^+{-}c^-$ = $Ph{-}C{\equiv}N^+{-}N^-{-}Ph$), 61880-00-0; **11** ($a{=}b^+{-}c^-$ = $Ph{-}C{\equiv}N^+{-}O^-$), 21469-66-9; **12** ($a{=}b^+{-}c^-$ = $Ph{-}C{\equiv}N^+{-}N^-{-}Ph$), 61915-10-4; **12** ($a{=}b^+{-}c^-$ = $Ph{-}C{\equiv}N^+{-}O^-$), 22155-18-6; (α-chlorobenzylidene)phenylhydrazine, 15424-14-3; benzhydroximic acid chloride, 698-16-8; norbornadiene, 121-46-0.

Supplementary Material Available: Table A, elemental analyses of compounds **3**, **4**, **6**, **7**, and **9–11**; Table B, ^1H NMR data for compounds **6–11**; Table C, atomic coordinates and thermal parameters for the nonhydrogen atoms of **4c**; Table D, interatomic distances for the nonhydrogen atoms of $\mathbf{4c_1}$ and $\mathbf{4c_2}$; Table E, bond angles for nonhydrogen atoms of $\mathbf{4c_1}$ and $\mathbf{4c_2}$; Table F, torsion angles for $\mathbf{4c_1}$ and $\mathbf{4c_2}$; Table G, atomic coordinates and thermal parameters for nonhydrogen atoms of **4d**; Table H, interatomic distances for nonhydrogen atoms of **4d**; Table I, bond angles for nonhydrogen atoms of **4d**; Table J, torsion angles for **4d**; structure of **4c**; listings of observed and calculated structure factors for **4d** and **4c** (43 pages). Ordering information is given on any current masthead page.

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