Mechanism of Geometrical Isomerization about the Carbon-Nitrogen Double Bond

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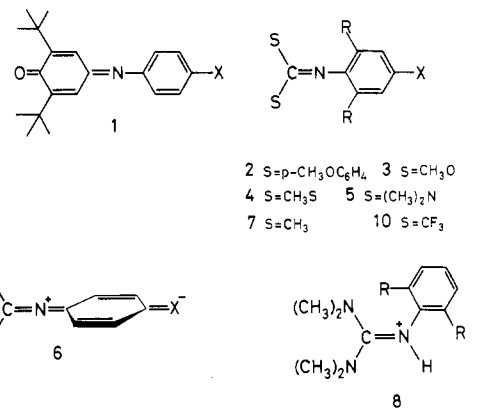
For pyrazolone azomethines and *N*-benzylideneanilines, we report kinetic effects of pressure, solvent, and substituent on geometrical isomerization about the carbon-nitrogen double bond. Our results demonstrate the versatility of the inversion mechanism in these two groups of compounds. Invalidated is the rotation mechanism that had been previously predicted for pyrazolone azomethines with electron-donating substituents in the para position of the aromatic ring attached to the imino nitrogen. Contrary to azobenzene, mere push-pull substitution in *N*-benzylideneanilines is not enough to realize the rotation mechanism even in a relatively polar solvent such as methanol.

Geometrical isomerization about the carbon-nitrogen double bond has been studied in a variety of compounds from a standpoint of reaction mechanism. The compounds studied so far include *N*-benzylideneanilines,[1,2] pyrazolone and benzoylacetanilide azomethines,[3,4] quinone imines,[5,6] ketimines,[7-14] iminomalonates,[15,16] iminocarbonates,[11,17-19] iminodithiocarbonates,[11,19] and guanidines.[6,20-23]

More or less similar results were obtained for syn-anti type isomerizations in unsymmetrical imines and degenerate isomerization in symmetrical ones. Two reaction mechanisms are invoked to explain the observed results. One is the inversion or lateral shift mechanism where the nitrogen atom is rehybridized to sp during the activation step and the lone pair electrons are accommodated in a 2p orbital. The other mechanism is the rotation or torsion mechanism where rotation about the carbon-nitrogen double bond takes place with heterolytic cleavage of the π-bond.[24]

It has been generally agreed that the inversion mechanism is more common than the rotation mechanism, and a number of arguments are adduced in support of this point of view. First of all, there seems to be a fundamental difference between isomerization about the carbon-carbon and carbon-nitrogen double bonds, because the isomerization barrier for the latter, where rotation is the only viable mechanism, is much higher. The retardation of isomerization by complex formation of imines with trimethylaluminum[9] and by protonation[2,21] or hydrogen-bond formation[19,21] on the imino nitrogen atom has also been considered to support inversion. The reaction is facilitated by the electron-withdrawing substituent X in quinone imines **1**,[5,6] ketimines **2**,[7] iminocarbonates **3**,[18,19] iminodithiocarbonates **4**,[19] and guanidines **5**.[6,23] These results have been rationalized by stabilization of the inversion activated complex by the increased contribution of **6**. The fact that pyramidal nitrogen inversion in aziridines is also facilitated by electron-withdrawing substituents[25] has been used to argue that the mechanisms of the stereomutations must be similar.[23] Steric acceleration by the ortho-substituents in guanidines **5**[20,23] and ketimines **7**[8] and retardation of the isomerization in guanidinium ion **8**[20] also provide strong support for the inversion mechanism. Furthermore, Kessler and Leibfritz[22] found that magnetic nonequivalence of the ortho isopropyl groups in **9** is not dissolved by syn-anti isomerization, and this observation was interpreted as providing evidence for inversion.

There are, however, some cases where the evidence favors rotation. For example, CNDO/2 calculations support



rotation for guanidine[26] although inversion for *N*-benzylideneaniline.[27] Marullo and Wagener[11,17] have proposed rotation to explain the isomerization reactivity order of ketimine < iminocarbonate < iminodithio-

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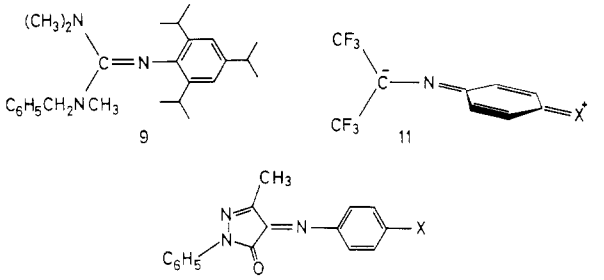
carbonate < guanidine. Frequently the basis for invoking rotation is a nonlinear Hammett correlation. For example, Roberts and his co-workers[13] studied the degenerate isomerization in hexafluoroacetone *N*-phenylimines **10** and found that, with the exception of the *p*-nitro compound, the rate constants gave a Hammett plot with a negative slope of –0.98. An inversion transition state **6** for the nitro derivative and rotation transition state **11** for the other five compounds were proposed. A similar proposal was made by one of the present authors[4] on pyrazolone and benzoylacetanilide azomethines and, recently, by Prosyanik et al.[15] on iminomalonates. For example, in **12**, a V-shaped Hammett plot was obtained in benzene, and a rotation mechanism was proposed for electron-donating substituents.



The inversion–rotation controversy has been active in *Z*–*E* isomerization of azobenzenes, too, and, as in the carbon–nitrogen double bond, inversion is believed to be the reasonable choice in most of the cases. The most convincing evidence for this mechanism is the facile isomerization of an azobenzene unit incorporated into a ring system[28,29] in which the rotation of the phenyl ring around the nitrogen–nitrogen bond is difficult for steric reasons. The decrease in polarity during activation[30–32] and the absence of an anisotropic solvent effect on the activation parameters[33] are also in accord with the inversion mechanism.

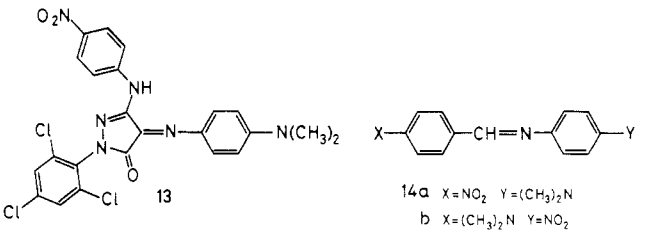
In 4-(diethylamino)-4′-nitroazobenzene, however, an increase in solvent polarity led to a large acceleration of the isomerization rate,[34] and, as a result, the rotation mechanism was proposed for push–pull substituted azobenzenes. Later, Asano and his co-worker[35,36] studied pressure effects on the isomerization of 4-(dimethylamino)-4′-nitroazobenzene and other related compounds in various solvents; they concluded that there are two independent rotation and inversion pathways and that the relative importance of each reaction depends upon the solvent polarity. This conclusion was further supported by determining that nonlinear Arrhenius plots are obtained from data measured with use of relatively nonpolar solvents and also that in these same solvents the activation volumes show unusual temperature dependences.[36]

Table I. First-Order Rate Constants (s^{-1}) and Activation Volumes ($cm^3\ mol^{-1}$) for Thermal *E*–*Z* Isomerization of 12c and 12d at 25 °C in Benzene and Methanol

	solvent			
	benzene		methanol	
P/MPa	**12c**	**12d**	**12c**	**12d**
0.1	2.48	7.55	5.46	4.12
20.0	3.03	6.85		
30.0			5.70	4.48
40.0	2.86	7.10		
60.0	2.50	6.12	5.23	3.39
70.0	2.63	6.74		
90.0			5.23	5.06
120.0			5.72	4.67
150.0			4.86	4.73
180.0			5.26	4.47
210.0			5.65	4.50
240.0			5.43	4.38
$\Delta V^{\ddagger}$	1.0 ± 4.3	5.0 ± 2.5	0.1 ± 0.6	–1.0 ± 1.2

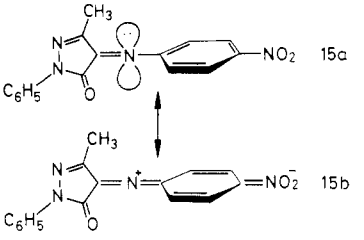
These pressure and solvent effects in azobenzenes can be summarized as follows. For isomerization by inversion, an increase in solvent polarity slightly retards the reaction, and pressure changes lead to only nominal kinetic effects ($\Delta V^{\ddagger} \approx 0$). For isomerization by rotation, by contrast, large solvent polarity and pressure-induced acceleration are observed because of the large polarity increase in the activation step.

The similarities in syn–anti and cis–trans isomerizations about carbon–nitrogen and nitrogen–nitrogen double bonds, respectively, are expected to include like responses to changes in pressure and solvent polarities. We decided to expand our investigations to include the following isomerizable compounds with carbon–nitrogen double bonds: pyrazolone azomethines **12a–d**, **13**, and *N*-benzylideneanilines **14a,b**.[37]



Results and Discussion

Pyrazolone Azomethines. Based on the substituent effect study mentioned above,[4] it is predicted that (*E*)-**12d** isomerizes via the inversion transition state **15**, where the pyrazolone and the phenyl rings are perpendicular to each other and the isomerization barrier is expected to be lowered by the contribution of resonance structure **15b**. Since



formal charges appear in **15b**, it might be expected that the polarity of the reactant should increase upon activa-

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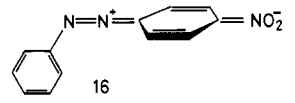
Table II. Rate Constants (s^{-1}) for Thermal *E–Z* Isomerization of 12a and 12b in Various Solvents at 25 °C

solvent	12a	12b
hexane	44.3	26.2
benzene	24.1	17.5
CCl_4	31.6	21.3
$CHCl_3$	15.2	10.3
CH_2ClCH_2Cl	16.5	11.9
acetone	24.8	17.1
cyclohexanone	22.8	16.0
DMF	21.5	15.4
$HCONH_2$	8.74	7.10
i-PrOH	31.4	23.1
EtOH	25.7	19.7
MeOH	19.5	14.4

tion. However, in 4-nitroazobenzene, which isomerizes about six times faster than azobenzene,[28,33] both the solvent and pressure effects were small, clearly indicating that the contribution of **16** does not result in a large polarity increase. Therefore, small pressure and solvent effects are



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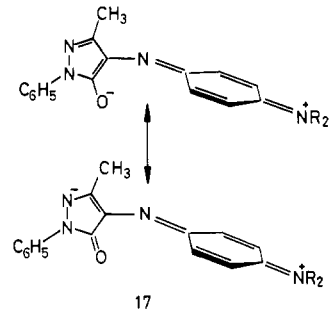

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expected for **12d**, also. Similarly, the isomerization in **12c** is not expected to be much influenced either by pressure or by solvent polarity because this compound is predicted to be a borderline case of inversion and rotation. The first-order rate constants obtained for **12c** and **12d** are given in Table I along with the activation volumes obtained by using eq 1 and 2.

$$\ln k = a + bP \quad (1)$$

$$\Delta V^{\ddagger} = -bRT \quad (2)$$

The rate constants change little with pressure. All of the activation volumes are small and should be considered to be close to zero because the experimental errors in the rate constants are relatively large (±10–25%) in these compounds. In addition, the reaction was not influenced by changing the solvent from benzene to methanol. These results are in accord with our expectation and support the inversion mechanism.

By contrast, substituent effect studies showing higher rates of isomerization for **12a** and **12b** predict the intervention of the rotation mechanism and the corresponding transition state **17**. The electronic structure of **17** is similar to the rotation transition state proposed for 4-(dialkylamino)-4′-nitroazobenzene. It seems reasonable, therefore, to expect a large acceleration by pressure and a solvent polarity increase for **12a** and **12b**. The experimental results for **12a** and **12b** were, however, totally unexpected. As can be seen from Table II, each isomerization reaction was influenced only slightly by solvent, and the rate constants *decreased* with increasing solvent polarity. Contrary to the results obtained for 4-(diethylamino)-4′-nitroazobenzene,[38] little acceleration by hydrogen bonding to the reactant was observed. These results leave little doubt that the transition state polarities of **12a** and **12b** are slightly smaller than the polarities of their respective starting *E* isomers.

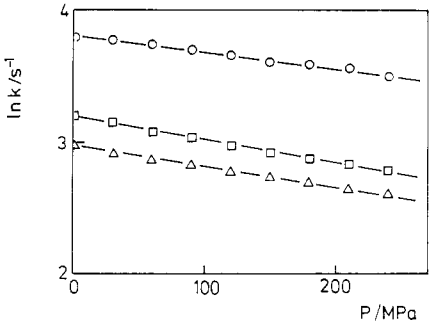

Figure 1. Pressure effects on the rates of thermal *E–Z* isomerization of **12a** at 25 °C. (○), hexane; (□), acetone; (△), methanol.

Table III. Activation Volumes ($cm^3\ mol^{-1}$) for Thermal *E–Z* Isomerization of 12a and 12b at 25 °C

	solvent			
	hexane	benzene	acetone	methanol
12a	3.0 ± 0.1	5.0 ± 0.1	4.5 ± 0.1	3.8 ± 0.1
12b	2.3 ± 0.1	4.2 ± 0.2	3.7 ± 0.1	3.6 ± 0.1

Pressure effect studies gave additional strong support to this conclusion. Figure 1 shows typical examples of the pressure dependence of the rate constants, and Table III presents the activation volumes. The values are small, but they are unmistakably positive. For example, in **12a**, the rate constant decreases from 19.54 ± 0.21 s^{-1} at 0.1 MPa to 13.43 ± 0.23 s^{-1} at 240 MPa in methanol.

The most reasonable way to explain all of these results is that isomerization in **12a** and **12b** also proceeds via inversion. Since no bond cleavage takes place, weaker electrostatic interactions caused by the rehybridization of the imino nitrogen[31] may be the reason for the positive activation volumes. It also must be pointed out that, although the Hammett plot is bent, **12c** isomerizes faster than **12d** in methanol. The higher reactivity of **12d** observed in benzene may not be a reflection of a fundamental change in the reaction mechanism.

We also studied presure effects on **13** in methanol to see whether the rotation mechanism would be realized by virtue of the nitro and chloro substituents on phenyl groups connected to the pyrazolone ring. The result was disappointing as the pressure effect was nil. The activation volume was 0.17 ± 0.74 $cm^3\ mol^{-1}$.

The foregoing results for the pyrazolone azomethines indicate that previous conclusions based solely on the influence of substituents on rates of isomerization must be corrected. It now appears that pyrazolone azomethines generally isomerize via the inversion route irrespective of the electronic nature of the substituent on the phenyl imino group.

***N*-Benzylideneanilines.** Although the rates of isomerization of various substituted (*Z*)-*N*-benzylideneanilines to their respective *E* isomers[1,2] do not suggest any mechanistic changes, the effect of push–pull substitution as studied in azobenzene has not yet been examined. Considering the structural similarities between *N*-benzylideneaniline and azobenzene, one might expect that the cooperative interactions of electron-donating and -attracting substituents in 4- and 4′-positions would be able

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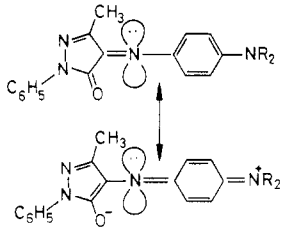
Table IV. First-Order Rate Constants (s^{-1}) and Activation Volumes (cm^3 mol^{-1}) at 25 °C and 0.1 MPa for Thermal *Z*-*E* Isomerization of 14a and 14b

	14a		14b	
solvent	k	$\Delta V^{\ddagger}$	k	$\Delta V^{\ddagger}$
hexane	0.511	0.3 ± 0.1	432	−1.2 ± 0.2
benzene	0.248	1.5 ± 0.9	694	−1.2 ± 0.3
THF			1076	−1.2 ± 0.1
C_6H_5Cl			1550	−0.8 ± 0.1
o-$C_6H_4Cl_2$			2202	−1.1 ± 0.2
acetone	0.245	1.2 ± 0.8		
MeOH	0.0684	3.1 ± 0.4		

to lower the energy of the rotation pathway to make it competitive with inversion.

To investigate this mechanistic hypothesis, measurements on **14a** and **14b** have been performed, and the results are shown in Table IV. The most important feature of Table IV is the high reactivity of **14b**. It reacts 850 and 2800 times faster than **14a** in hexane and benzene, respectively. This reminds us of the high reactivity for isomerization by rotation of 4-(dialkylamino)-4′-nitroazobenzenes. However, neither solvent polarity nor pressure shows the expected large influence on the reaction rate of **14b**. The reaction is only slightly accelerated by pressure. The activation volumes are independent of solvent, and they are −1.09 ± 0.18 cm^3 mol^{-1}. Although not measured in acetone or methanol due to high reactivity, the results listed in Table IV for **14b** are sufficient to conclude that the effect of solvent polarity is also much smaller than in 4-(dimethylamino)-4′-nitroazobenzene, which isomerized 344 times faster in *o*-dichlorobenzene than in hexane.[33] Therefore, we have to conclude that the polarity change in the activation step is small and that inversion dominates the mechanism for this compound. The reactivity of **14a** is about 1 order lower than the unsubstituted *N*-benzylideneaniline, which isomerizes with a rate constant of 4.60 s^{-1} at 25 °C in cyclohexane.[2] Although the reason for this stabilization of the *Z* isomer is not clear, the pressure and solvent effects are strikingly similar to those observed for **12a** and **12b**. Most likely **14a** also isomerizes by inversion.

Substituent Effects in 12 and 14. As discussed above, the evidence is that isomerization in **12** and **14** proceeds by inversion at the imino nitrogen. Therefore, similar substituent effects might be expected for these two classes of compounds. Contrary to this expectation, however, the effects were quite different. When a nitro group was introduced to the para position of the phenylimino group, it accelerated the isomerization of *N*-benzylideneaniline about 50 times[2] but decelerated the reaction of **12** in methanol (a small acceleration was observed in benzene). On the other hand, the introduction of a dimethylamino group to the same position resulted in deceleration in **14**,[1,2] but acceleration in **12**. There is no simple way to explain these substituent effects. For example, the higher reactivity of **12a** and **12b** might be explained by considering a *coplanar* inversion transition state, **18**. Nevertheless,



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the reason for the absence of similar acceleration in **14** and the absence of solvent polarity induced acceleration in **12a,b** remains a puzzle. What can be stated is that substituent effects show the electronic nature of the inversion transition state to be not necessarily the same in all compounds investigated here.

Experimental Section

Materials. The melting points are uncorrected. 4-[[4-(Diethylamino)phenyl]imino]-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one, **12a**, 4-[[4-(dimethylamino)phenyl]imino]-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one, **12b**, 2,4-dihydro-5-methyl-2-phenyl-4-(phenylimino)-3*H*-pyrazol-3-one, **12c**, 2,4-dihydro-5-methyl-4-[(4-nitrophenyl)imino]-2-phenyl-3*H*-pyrazol-3-one, **12d**, and 4-[[4-(dimethylamino)phenyl]imino]-2,4-dihydro-5-[(4-nitrophenyl)amino]-2-(2,4,6-trichlorophenyl)-3*H*-pyrazol-3-one, **13**, were synthesized as described.[39,40] **12a**: mp 120.5–121.2 °C (lit.[41] mp 117–118 °C. Anal. Calcd for $C_{20}H_{22}N_4O$: C, 71.87; H, 6.63; N, 16.76. Found: C, 71.91; H, 6.85; N, 16.77. **12b**: mp 190.9–191.4 °C (lit.[42] mp 187 °C). Anal. Calcd for $C_{18}H_{18}N_4O$: C, 70.57; H, 5.92; N, 18.29. Found: C, 70.36; H, 6.07; N, 18.35. **12c**: mp 103.5–104 °C (lit.[43] mp 106 °C). Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.80; H, 4.90; N, 15.99. **12d**: mp 176–176.5 °C; IR (KBr) 3400, 3100, 2920, 2830, 1714, 1583, 1509, 1337, 1148, 861, 822, 758, 738, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3), 7.16 (d, 2, J = 9), 7.21 (t, 1, J = 8), 7.39 (t, 2, J = 8), 7.81 (d, 2, J = 8), 8.29 (d, 2, J = 9); ^{13}C NMR (75.43 MHz, $CDCl_3$) δ 12.0, 118.1, 119.2, 124.6, 125.8, 128.9, 137.1, 145.9, 149.8, 150.4, 152.6, 154.4. Anal. Calcd for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17. Found: C, 61.98; H, 3.81; N, 18.17. **13**: mp 248.5–249.5 °C; IR (KBr) 3420, 3075, 2920, 2850, 1681, 1603, 1582, 1552, 1505, 1372, 1323, 1242, 1148, 1060, 905, 849, 824, 804, 748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (s, 6), 6.72 (d, 2, J = 9), 7.48 (s, 2), 7.57 (s, 1), 7.68 (d, 2, J = 9), 8.20 (d, 2, J = 9), 8.42 (d, 2, J = 9); ^{13}C NMR (75.43 MHz, $CDCl_3$) δ 40.3, 111.6, 117.1, 125.5, 128.8, 134.3, 135.4, 135.7, 136.4, 141.6, 144.8, 146.2, 153.3, 154.0. Anal. Calcd for $C_{23}H_{17}Cl_3N_6O_3$: C, 51.95; H, 3.22; Cl, 20.00; N, 15.80. Found: C, 51.56; H, 3.22; Cl, 20.56; N, 15.45. The mass spectra of **12c** and **12d** have been published elsewhere.[44] *N*,*N*-Dimethyl-*N*′-[(4-nitrophenyl)methylene]-1,4-benzenediamine, **14a**, and *N*-[[4-(dimethylamino)phenyl]-methylene]-4-nitrobenzenamine, **14b**, were prepared as described.[45] **14a**: mp 226–226.1 °C (lit.[45] mp 223–224 °C). Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60. Found: C, 67.04; H, 5.79; N, 15.48. **14b**: mp 208.5–209.5 °C (lit.[45] mp 207 °C). Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60. Found: C, 66.90; H, 5.59; N, 15.55.

Kinetic Measurements. All rate constants were measured by flash photolysis; details are described elsewhere.[46]

Conclusions

The kinetic effects of pressure, solvent, and substituent reported here demonstrate the versatility of the inversion mechanism in geometrical isomerization about the carbon–nitrogen double bond. Contrary to azobenzene, mere push–pull substitution is not enough to realize the rotation mechanism even in methanol. These results cast doubt about the validity of the rotation mechanism claimed for other compounds[13–15] on the basis of the substituent effects alone.[47] Furthermore, qualitatively different substituent effects in pyrazolone azomethines and *N*-benzylidene-

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anilines show subtle differences for the inversion mechanism in these two classes of compounds.

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Registry No. **12a**, 117985-07-6; **12b**, 117985-08-7; **12c**, 117985-05-4; **12d**, 117985-06-5; **14a**, 111955-89-6; **14b**, 117985-09-8.

Supplementary Material Available: Tables of rate constants for the isomerization of **12a**, **13**, and **14b** in various solvents and at various pressures (3 pages). Ordering information is given on any current masthead page.

Ozonolysis of Tetrasubstituted Ethylenes, Cycloolefins, and Conjugated Dienes on Polyethylene

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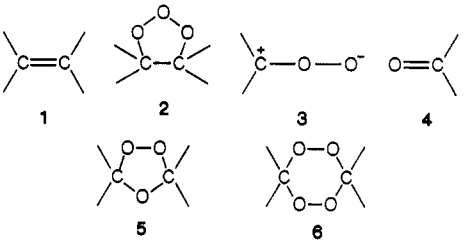
Ozonolyses of four tetrasubstituted ethylenes (**7a–d**), of two medium-sized cycloolefins (**10a,b**), and of norbornene (**14**) on polyethylene gave the corresponding ozonides, which could not be obtained by ozonolyses in solution. Ozonolyses of three conjugated dienes (**25a,b**, **28**) on polyethylene gave the corresponding diozonides, as the first examples of this class of ozonides. The thermal decomposition of some of the ozonides has been studied.

Introduction

Ozonides (**5**) can be prepared by ozone treatment of olefins, by oxygenation of olefins, oxiranes, or furans, and by oxygenation of diazoalkanes in the presence of aldehydes.[2] Since the scope of the application of oxygenation reactions is limited by certain structural prerequisites such as the presence of aromatic substituents in olefin or oxirane substrates, the ozonolysis of olefins (**1**) in aprotic solvents represents the most versatile method for the preparation of ozonides. Nevertheless, this method failed when applied to a variety of substrates such as most tetrasubstituted ethylenes, monocyclic olefins except for those having four- to six-membered rings, certain bicyclic olefins, and certain acyclic conjugated dienes. While such reactions do proceed according to the Criegee mechanism[3a] in the initial steps to give the primary ozonides **2** and the initial fragments of types **3** and **4**, the latter do not undergo [3 + 2]-cycloadditions to give ozonides **5**. The failure of tetrasubstituted ethylenes to afford the corresponding ozonides **5** has been attributed to the low reactivity of the ensuing ketone fragments **4**, as opposed to aldehyde fragments, in 1,3-dipolar cycloadditions;[3b] in the case of medium-sized cycloolefins, it has been argued that the chances for intramolecular ring closures are not as good with the Criegee intermediates of larger cycloolefins as with those derived from four-, five-, or six-membered cycloolefins.[3c] Hence, in either case, the carbonyl oxide fragments **3** undergo side reactions which often lead to peroxidic materials other than ozonides, particularly acyclic and cyclic oligomers of **3**, such as dimers of structure **6**.

In an attempt to prevent such side reactions, ozonolyses of olefins adsorbed on silica gel have been examined[4,5] with



the goal of immobilizing the primary fragments **3** and **4** at the places of their origin and thus favoring [3 + 2]-cycloadditions to give ozonides **5**. It was reported that this method provided higher yields of the ozonides of cyclopentene and of 2-pentene than ozonolysis in solution and that no cross-ozonides were formed from 2-pentene.[4] But to our knowledge, it was in no case possible to obtain an ozonide from a substrate that did not afford an ozonide in solution. In fact, it was reported that in the ozonolysis of 1-decene, *cis*-6-decene, and 1-methylcyclohexene on silica gel, "the results showed a marked similarity with ozonation in non-participating solvents".[5] In pursuit of this concept, we have carried out ozonolyses of olefins on solid organic polymers, and it was found that powdered polyethylene can be superior to silica gel. In the following, we report results from the application of this method to the ozonolysis of the tetrasubstituted ethylenes **7a–d**, the cycloolefins **10a,b** and **14**, and the conjugated dienes **25a,b** and **28**.

Results and Discussion

Tetrasubstituted Ethylenes (7a–d). Ozonolyses of **7a**,[3d] **7b**,[6] and **7d**[7] in aprotic solvents have been reported to give no or at best trace amounts (in the case of **7d**) of the corresponding ozonides **8**, whereas to our knowledge the ozonolysis of **7c** has not yet been examined. Nevertheless, ozonides **8c** and **8d** are known. They have been prepared via alternate routes, viz., **8c** from electron transfer

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