Intramolecular Cycloaddition Reactions of Diazoalkenes. A Theoretical Prognosis of Nitrene Type Behavior

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Abstract: Thermolysis of the sodium salt of allyl-substituted tosylhydrazones leads to diazoalkenes. These reactive 1,3-dipoles undergo intramolecular 1,1 cycloaddition to produce 1,2-diazabicyclo[3.1.0]hex-2-enes in high yield. The results with (*E*)- and (*Z*)-1-phenyl-3-penten-1-one *N*-tosylhydrazone indicate that the intramolecular 1,1 cycloaddition reaction is highly stereospecific. Inspection of molecular models of the allyl-substituted diazoalkene system indicates that the normal "two-plane" orientation approach of the diazo group and allyl π system is impossible as a result of the geometric restrictions imposed on the system. Consequently the normal mode of 1,3-dipolar addition does not occur here. Instead, attack of the terminal nitrogen atom of the diazo group on the neighboring double bond occurs to generate the 1,2-diazabicyclohexene ring system. The fact that the 1,1 cycloaddition is limited to the phenyldiazo derivatives has been rationalized by theoretical studies in terms of the potential nitrene character of the terminal nitrogen atom of phenyldiazomethane. The energetics and the shapes of the highest occupied molecular orbital of the delocalized π system and the orthogonal, unoccupied, 2π orbital are such that phenyldiazomethane could undergo concerted 1,1 cycloaddition to electron-rich olefins provided steric requirements are favorable for the process. It is further suggested that the in-plane 2π system also plays an important role in both the 1,3 cycloaddition and diazo coupling reactions of electron-deficient diazo compounds.

The cycloaddition of 1,3-dipoles has become an important method for the preparation of five-membered heterocyclic rings[1,2] and has recently had a significant impact on the synthesis of natural products.[3-5] Numerous possibilities for variation are available by changing the structure of both the dipole and dipolarophile. Diazoalkanes are a long known and thoroughly investigated class of 1,3-dipoles.[6] In fact, dipolar cycloadditions of diazoalkanes to olefins are among the most thoroughly studied examples.[7-12] The cycloadditions of simple diazoalkanes are HO(1,3-dipole)–LU(dipolarophile) controlled.[13,14] Both conjugating and electron-attracting groups accelerate reactions of dipolarophiles with diazoalkanes as compared to ethylene. With these dipolarophiles, 3-substituted Δ^1-pyrazolines are favored, a result of the union of the larger diazoalkane HO coefficient on carbon with that of the larger dipolarophile LU coefficient on the unsubstituted carbon.[13] Simple diazoalkanes and alkylethylenes are rather unreactive as a result of the large energy gap between the frontier molecular orbitals. Recently, it has been shown that 3-substituted pyrazolines are formed as the major products in the 1,3-dipolar cycloaddition of diazomethane with 1-alkenes.[15,16] With these systems, the difference between the two frontier orbital interactions is quite small, but the nearly equal magnitude of the terminal coefficients in the diazomethane LU suggests that the diazomethane HO determines product regiochemistry.

In spite of the copious literature dealing with bimolecular cycloaddition reactions of diazoalkanes, intramolecular examples, have only started to receive attention.[17-25] The fact that a double bond can participate in an intramolecular 1,3-dipolar cycloaddition reaction with a suitably placed 1,3-dipole has been known for a long time. The first example of such a process was reported by LeBel and Whang in 1959.[26] Since their initial report, many papers dealing with intramolecular 1,3-dipolar cycloadditions have been published and considerable use has been made of this reaction for organic synthesis.[27,28]

Recent results from our laboratory have shown that there are two pathways by which certain 1,3-dipoles can react with multiple π bonds.[29] The most frequently encountered path involves a "parallel plane approach of addends" and can be considered to be an orbital symmetry allowed [4 + 2] concerted process.[1] The other path, designated as 1,1 cycloaddition, was first encountered with nitrilium betaines and operates only in certain intramolecular cases.[29-32] It occurs when the p orbitals of the dipolarophile have been deliberately constrained to attack perpendicular to the ni-

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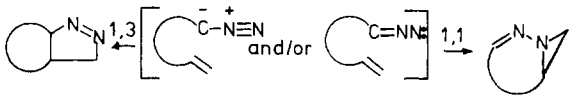
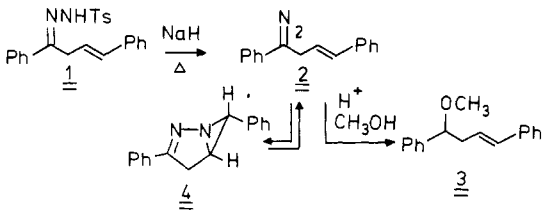
trilium betaine plane. Work in our laboratory[33,34] as well as studies by Miyashi and Mukai[35] have shown that intramolecular 1,1 cycloaddition of diazoalkenes can also occur. Thus, various allyl-substituted diazomethanes have been found to undergo a formal nitrene type 1,1 cycloaddition to give 1,2-diazabicyclo[3.1.0]-hex-2-enes on heating.[33-35]



As a further consequence of our interest in this area, we thought it worthwhile to determine whether additional examples of nitrene behavior of diazoalkanes could be uncovered. In this paper we describe some of our efforts involving the generation and chemistry of a number of diazoalkanes containing unsaturation two atoms away from the dipole center.

Results

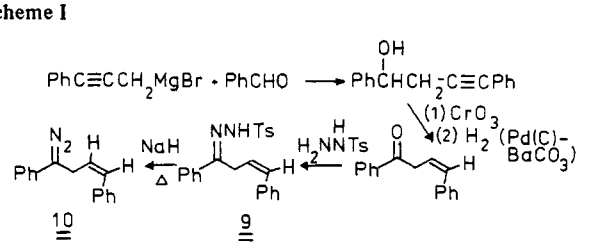
As our first model we chose to investigate the intramolecular dipolar cycloaddition reaction of the diazoalkene derived from the tosylhydrazone of (*E*)-1,4-diphenyl-3-buten-1-one (**1**).



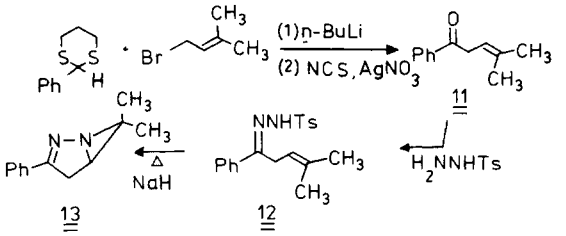
Heating the tosyl salt of **1** in benzene at 80 °C for 20 min resulted in a deep red coloration which gradually faded on extended heating. The initially formed diazo compound **2** was characterized by a strong band in the IR spectrum at 1984 cm^{-1} and by NMR absorptions at δ 3.58 (d, 2 H, J = 5.0 Hz) for the methylene protons and 6.44 (dt, 1 H, J = 16.0 and 5.0 Hz) and 6.84 (d, 1 H, J = 16.0 Hz) for the vinyl protons. This assignment was confirmed by treatment of the red solution with methanolic hydrochloric acid, which resulted in the isolation of 1,4-diphenyl-1-methoxy-3-butene (**3**). The structure of **3** was unambiguously established by comparison with an independently synthesized sample. When a solution of the diazo compound **2** in benzene was allowed to stand at room temperature for 48 h, a single product **4**, mp 145–146 °C, whose molecular formula corresponds to $C_{16}H_{14}N_2$, could be isolated by careful fractional crystallization. This material exhibits a band in the infrared at 1558 cm^{-1} (C=N). The assignment of the 3,6-diphenyl-1,2-diazabicyclo[3.1.0]hexene structure to compound **4** is supported by its ultraviolet spectrum (max 257 nm (ϵ 11 400)) which is similar to that reported for related azabicyclo[3.1.0]hexenes.[36] The NMR of **4** showed a doublet at δ 2.44 (1 H, J = 4.0 Hz), a doublet of doublet of doublets at 3.05 (1 H, J = 7.0, 4.0, and 2.0 Hz), a pair of doublet of doublets at 3.50 (1 H, J = 18.0 and 7.0 Hz) and 3.58 (1 H, J = 18.0 and 2.0 Hz), and a multiplet at 7.2–8.16 (10 H). In support of the diazabicyclo[3.1.0]hexene assignment is the observation of other workers that the magnitude of trans C(4)–C(5) vicinal coupling of bicyclo[3.1.0]hex-2-enes is close to zero,[37-39] while that for cis vicinal coupling is ca. 7 Hz.[40] This is to be expected since molecular models show that the dihedral angle for the trans C(4)–C(5) protons is about 110°, while that for the cis protons is approximately 0°.

The reversibility of the 1,1 cycloaddition between **2** and **4** was directly observed by NMR analysis. Thus, heating a solution of

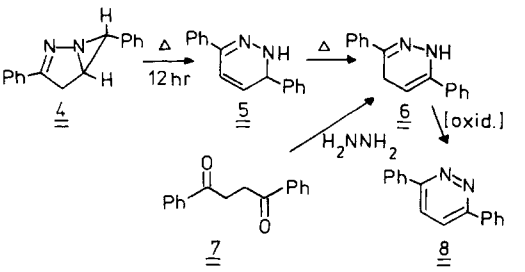
Scheme I



Scheme II



4 in $CDCl_3$ at 80 °C for 15 min in a NMR tube gave rise to diazoalkene **2**. The absorptions due to **2** disappeared upon cooling to room temperature, cleanly reproducing the spectrum of **4**. When the thermolysis of **4** was carried out in benzene at 80 °C



for 12 h, it was initially converted to dihydropyridazine **5** (NMR, 60 MHz) δ 6.02 (dd, 1 H, J = 10.0 and 4.0 Hz), 6.34 (s, 1 H), 6.52 (dd, 1 H, J = 10.0 and 2.0 Hz), 6.75 (dd, 1 H, J = 4.0 and 2.0 Hz), and 7.0–8.0 (m, 10 H). Further heating of **5** resulted in the formation of the isomeric dihydropyridazine **6**. Structure **6** was unequivocally established by comparison with an independently synthesized sample prepared by treating 1,2-dibenzoylethane (**7**) with hydrazine. Finally, compound **6** was slowly oxidized to 3,6-diphenylpyridazine (**8**) on heating in the presence of oxygen.

In an attempt to probe the stereochemical aspects of the intramolecular 1,1 cycloaddition, we synthesized the related *Z* stereoisomer **9** according to the route outlined in Scheme I. Heating the sodium salt of **9** at 80 °C for 20 min resulted in the formation of the cis diazoalkene **10**: IR 2000 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 3.40 (dd, 2 H, J = 7.0 and 2.0 Hz), 5.80 (dt, 1 H, J = 11.0 and 7.0 Hz), and 6.80–7.50 (m, 11 H). Unfortunately, we were unable to isolate any characterizable material from the further reaction of this diazoalkene, and we decided to abandon further work with this system.

As a result of the above observations, we decided to study a number of related systems in order to determine the generality of the 1,1 cycloaddition. 1-Phenyl-4-methyl-3-penten-1-one (**11**) was synthesized from phenyldithiane and 1-bromo-3-methyl-2-butene according to the general procedure of Corey and Seebach.[41] This β,γ-unsaturated ketone was converted to tosylhydrazone **12** in good yield by heating with *p*-toluenesulfonylhydrazine. Thermolysis of the sodium salt of tosylhydrazone **12** at 90 °C gave 3-phenyl-6,6-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**13**) in 60% as a crystalline solid, mp 52–53 °C (Scheme II). This material was identified on the basis of its characteristic NMR spectrum ($CDCl_3$) which showed a pair of singlets at δ 0.92 (3

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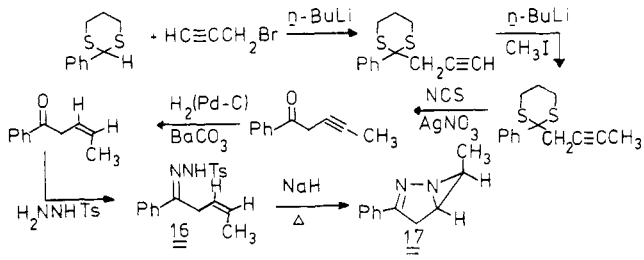
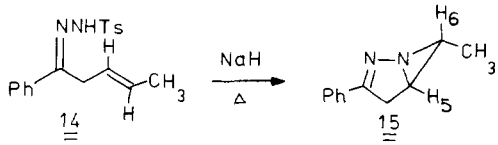
Scheme III



H) and 1.35 (3 H), a doublet of doublets at 2.50 (1 H, J = 8.0 and 4.0 Hz), 2.87 (1 H, J = 18.0 and 4.0 Hz), and 3.08 (1 H, J = 18.0 and 8.0 Hz), and a multiplet at 7.2–8.0 (5 H). In addition, the ^{13}C NMR spectrum of **13** revealed a series of peaks at 11.85 (*endo*-CH_3) 25.89 (*exo*-CH_3), 35.30 (C_4), 47.08 (C_6), 50.09 (C_5), and 171.03 (C_3) ppm.

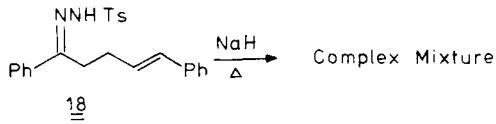
Attention was next turned to the intramolecular cycloaddition reaction of (*E*)-1-phenylpent-3-en-1-one *N*-tosylhydrazone (**14**). The synthesis of this isomer was straightforward and involved treating the anion of phenyldithiane with crotyl chloride followed by hydrolysis and tosylhydrazone formation. Heating a benzene solution of the sodium salt of the *E* isomer **14** at 80 °C for 1 h



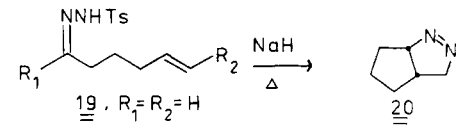
followed by allowing the mixture to stand at room temperature for 48 h gave *exo*-3-phenyl-6-methyl-1,2-diazabicyclo[3.1.0]-hex-2-ene (**15**), mp 53–54 °C, in 53% isolated yield as the exclusive 1,1-cycloadduct. Spectral data and elemental analysis were in complete agreement with structure **15** and are summarized in the Experimental Section. The stereochemistry of cycloadduct **15** was easily assigned on the basis of its characteristic NMR spectrum. Spin decoupling experiments indicate that protons H_5 and H_6 in structure **15** are coupled by 4.0 Hz.

In order to probe the stereochemical course of the internal cycloaddition reaction, we studied the thermolysis of the sodium salt of the isomeric *Z* isomer **16**. The synthesis of this compound is outlined in Scheme III. Details of the synthesis are given in the Experimental Section. When the sodium salt of the (*Z*)-tosylhydrazone **16** was heated at 90 °C, the major product obtained was *endo*-3-phenyl-6-methyl-1,2-diazabicyclo[3.1.0]hex-3-ene (**17**). This product was identified on the basis of its characteristic 90-MHz NMR spectrum (CCl_4) which showed a doublet at δ 0.98 (3 H, J = 6.0 Hz), a multiplet at 2.4–2.9 (2 H), a set of doublet of doublets at 3.01 (1 H, J = 18.0 and 3.0 Hz) and 3.20 (1 H, J = 18.0 and 8.0 Hz), and a multiplet at 7.2–7.8 (5 H) and was further supported by its ^{13}C NMR spectrum ($CDCl_3$) 5.7 (CH_3), 34.3 (C_4), 41.6 (C_5) and 42.2 (C_6). NMR analysis of the crude reaction mixture showed that the corresponding exo isomer **15** was present in less than 5% yield. These results clearly indicate that the intramolecular 1,1 cycloaddition reaction of the allyl-substituted diazoalkene system is highly stereoselective.

At this stage of our studies we decided to investigate the intramolecular cycloaddition reaction of the diazoalkane derived from the next higher homologue. Whereas the sodium salt of tosylhydrazone **1** was smoothly converted to 1,2-diazabicyclohexene **4** on heating, thermolysis of 1,5-diphenyl-4-penten-1-one *N*-tosylhydrazone (**18**) resulted in the formation of a complex mixture of products which resisted all attempts at purification.



The crude NMR spectrum of the reaction mixture showed that the vinyl protons were still present. Apparently, with the diazoalkane derived from tosylhydrazone **18**, the methylene chain is not of sufficient length to allow the dipole and double bond to approach each other in parallel planes. Consequently, intramolecular 1,3-dipolar cycloaddition does not occur. The situation here is very different from that observed with the tosylhydrazone of 5-hexenal (**19**).[42] With tosylhydrazone **19**, the transition state

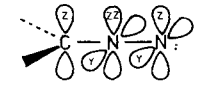


for cycloaddition allows easy attainment of the "parallel-plane approach", and thus intramolecular 1,3-dipolar cycloaddition of the initially generated diazoalkane readily occurs to give 3,3a,4,5,6,6a-hexahydrocyclopentapyrazole **20**. From these results it is clear that the spatial relationship of the diazoalkane and double bond p orbitals plays an extremely important role in controlling the mode of intramolecular cycloaddition.

Discussion

The primary spatial requirement for intramolecular dipolar cycloaddition is that the distance between the two reacting centers should be sufficiently close so that effective overlap of the 1,3-dipole with the dipolarophile occurs. For concerted 1,3-dipolar cycloaddition to take place, the atoms of the dipolarophile should be arranged in such a way as to allow their p orbitals to lie in a plane parallel to the plane of the 1,3-dipole. Inspection of molecular models of the allyl-substituted diazoalkane system indicates that the normal "two-plane" orientation approach of the diazo group and allyl π system is impossible as a result of the geometric restrictions imposed on the system. Consequently, the normal mode of 1,3-dipolar addition does not occur here. Instead, attack of the terminal nitrogen atom of the diazo group on the neighboring double bond occurs to generate the 1,2-diazabicyclohexene ring system. The experimental observations indicate that the intramolecular 1,1 cycloaddition reaction of allyl-substituted diazoalkenes is highly stereoselective, and the results parallel the stereospecific addition of singlet nitrenes[43] and the intramolecular 1,1 cycloaddition of nitrile ylides[29,30] and nitrile imines.[31,32] Such geometric restriction alone, however, is not sufficient for the 1,1 cycloaddition process to occur. Thus, no 1,1 cycloaddition[44] has been reported for allyldiazomethane[45] and its derivatives bearing α-alkyl-[46] and π-electron-withdrawing groups.[47] Formation of the 1,2-diazabicyclohexene ring seems to be limited to α-phenyl substituted derivatives.[33-35]

Mechanistically, the concerted 1,1 cycloaddition reaction of singlet nitrenes can be attributed to an electronic sextet on nitrogen. The diazo group possesses two mutually perpendicular π systems. One of these (πz) is delocalized over the entire π



framework and, like the allyl anion, contains four electrons (z).

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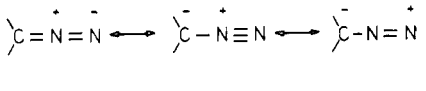
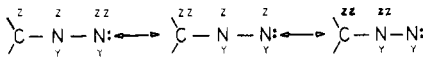
Table I. Total and Orbital Energies and Total Gross Population (4-31G) for RCH=N=N

	R							
		C_6H_5		P-HO-C_6H_4		CHO		
	H	planar	perpend	planar	perpend	syn	anti	perpend
energy								
total hartree	−147.6000	−376.8104	−376.8021	−451.5523	−451.5461	−260.1470	−260.1441	−260.1135
ΔE, kcal		0	5.18	0	3.90	0	1.84	21.04
πz, eV	−8.760	−7.392	−8.351	−7.232	−8.416	−9.439	−0.528	−9.224
πz^*, eV	4.685	3.250	3.998	3.324	3.695	2.414	2.355	4.141
πy^*, eV	3.427	3.656	3.601	3.649	3.686	2.807	2.600	2.721[a]
$\Delta E(\pi y^* - \pi z)$	12.19	11.05	11.95	10.56	12.10	12.25	12.13	11.95
gross population								
C	6.319	6.184	6.204	6.182	6.205	6.273	6.234	6.262
N_2	6.912	6.904	6.901	6.909	6.901	6.845	6.878	6.891
N_1	7.035	7.012	7.032	7.015	7.032	6.920	6.947	6.990

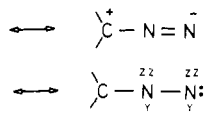
[a] Another πy^* orbital at 3.839 eV.

The other π system (i.e., πy) is localized on the two nitrogen atoms, each of which furnishes an electron (y). The terminal nitrogen atom also bears a lone pair of electrons which is sp hybridized. The canonical forms **21a** and **21b**, which are commonly considered





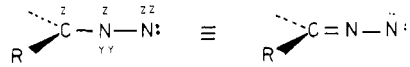
21a 21b 21c



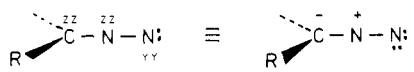
21d

to be appropriate representations, involve electron redistribution in the πz system. Structures **21c** and **21d** are generally regarded to be of lesser importance. In these resonance structures, the πy system remains unpolarized.

The sextet structure on the other hand, requires additional polarization in the πy system. Polarization of the πy system away from the terminal nitrogen (N_1) in **21a** formally generates the πy electron-deficient nitrene sextet (**22**), whereas πy polarization

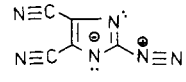


22



23

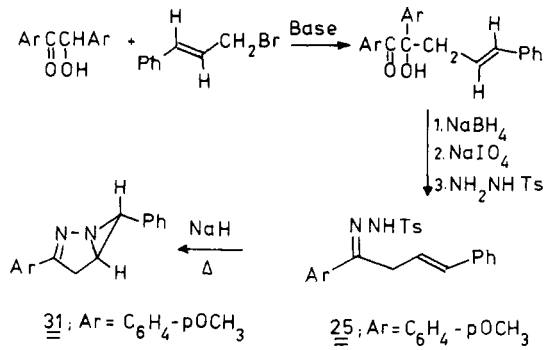
onto N_1 in **21c** gives rise to the πz-deficient nitrene **23**. The latter representation could become significant if the substituent R is simultaneously πz withdrawing and πy donating. 2-Diazo-4,5-dicyanoimidazole (**24**)[44] may represent such an example, in which



24

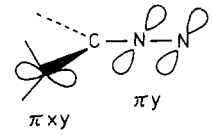
the dicyanoimidazole ring is a strong electron acceptor while the ring nitrogen lone pairs may donate electrons into the diazo πy system.

Scheme IV



31; Ar = C_6H_4-pOCH$_3$ 25; Ar = C_6H_4-pOCH$_3$

The nitrene form **22** could become quite important if the R group is π donating and σ withdrawing. It is interesting to note that a phenyl group has such characteristics (i.e., $\sigma_R = -0.11$ and $\sigma_I = 0.10$). If the πy-deficient nitrene **22** is important in the 1,1 cycloadditions that we have encountered, then derivatives such as *p*-methoxyphenylallyldiazomethane should undergo intramolecular 1,1 cycloaddition, whereas those like the *p*-nitrophenyl derivative would not. Another possibility, though less likely, is that the reactive species is in a perpendicular form in which the phenyl π orbitals homoconjugatively withdraw electrons from the diazo πy system.



πxy πy

In this case, the *p*-methoxyphenyl derivative will not be expected to undergo the 1,1 cycloaddition, since the substituent operates on the diazo πy system as a π donor and a σ acceptor. Although the *p*-nitro derivative might be a candidate for structure **22**, the perpendicular form is expected to be much less stable relative to the planar form and energetically inaccessible.

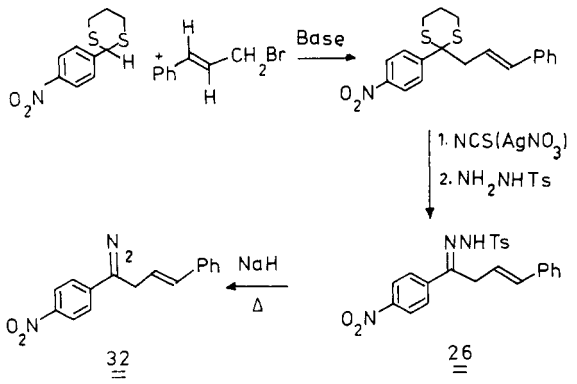
In order to provide additional information concerning the course of the 1,1 cycloaddition, we have prepared the *p*-methoxy and *p*-nitro derivatives, **25** and **26**, according to the routes outlined in Schemes IV and V. The *p*-methoxy-substituted tosylhydrazone **25** was found to cyclize cleanly and quickly to give a 1,1-cycloadduct in very high yield. On the other hand, we could find no detectable signs of a 1,1-cycloadduct from the *p*-nitro-substituted tosylhydrazone. The diazo compound **32** was easily generated but did not undergo internal cycloaddition. Extended heating resulted in a complex mixture of products.

Theoretical Studies. We have also undertaken a theoretical exploration of the 1,1 cycloaddition in order to better understand the substituent and conformational effects. Because semiempirical calculations of diazo compounds were found to be somewhat method dependent, we have performed ab initio calculations at the 4-31G level[48] using the program GAMESS[49a] and standard

Table II. 4-31G Frontier Orbial Coefficients, C(i) and C(o), for Diazo Compounds, RCH=N^2=N_1

compd		πz			πz^*			πy^*		
		C_{N_1}	C_{N_2}	C_C	C_{N_1}	C_{N_2}	C_C	C_{N_1}	C_{N_2}	C_C
R = H	C(i)	−0.400	0.114	0.401	−0.324	0.461	−0.289	−0.444	0.365	0.046
	C(o)	−0.385	0.117	0.430	−0.532	0.715	−0.612	−0.636	0.457	0.286
R = C_6H_5										
planar	C(i)	−0.295	0.127	0.301	−0.269	0.323	−0.134	−0.444	0.394	0.000
	C(o)	−0.308	0.139	0.346	−0.410	0.478	−0.217	−0.656	0.511	0.343
perpend	C(i)	−0.380	0.109	0.413	−0.078	0.085	−0.066	−0.289	0.230	−0.005
	C(o)	−0.374	0.122	0.457	−0.131	0.177	−0.147	−0.417	0.304	0.203
R = 4-HOC_6H_5										
planar	C(i)	−0.284	0.129	0.283	−0.264	0.316	−0.143	−0.443	0.392	0.002
	C(o)	−0.299	0.141	0.329	−0.405	0.479	−0.237	−0.655	0.508	0.351
perpend	C(i)	−0.379	0.108	0.413	−0.062	0.063	−0.052	−0.334	0.274	0.004
	C(o)	−0.373	0.121	0.458	−0.105	0.143	−0.120	−0.486	0.359	0.241
R = CHO										
syn	C(i)	−0.327	0.078	0.398	−0.332	0.374	−0.107	−0.459	0.405	−0.008
	C(o)	−0.306	0.067	0.442	−0.494	0.552	−0.199	−0.652	0.512	0.274
anti	C(i)	−0.340	0.086	0.390	−0.323	0.389	−0.127	−0.461	0.402	−0.016
	C(o)	−0.328	0.098	0.420	−0.483	0.544	−0.217	−0.665	0.526	0.207
perpend	C(i)	−0.376	0.096	0.423	−0.341	0.459	−0.286	−0.314	0.234	−0.016
	C(o)	−0.362	0.107	0.448	−0.555	0.698	−0.500	−0.442	0.323	0.190

Scheme V



geometries.[49b] The results obtained are summarized in Figure 1 and Tables I and II. *p*-Hydroxyphenyl- and formyldiazomethane have been used as models for *p*-methoxyphenyl- and *p*-nitrophenyldiazomethane, respectively. The 4-31G basis set describes the core orbitals by a linear combination of four Gaussian functions, while each valence orbital is represented by a total of four Gaussians split into two functions. One of these is a three-term Gaussian expansion with a relatively high exponent for the inner (e.g., p_z(i)) part while the other is a single more diffuse Gaussian for the outer (e.g., p_z(o)) part. In highly bonding MO's, the contribution of inner parts is more important than outer and primarily accounts for the bond strength. It should be noted, on the other hand, that with frontier (and virtual) MO's, outer orbitals generally have larger coefficients than inner (C(o) > C(i)). The ratio of outer and inner parts provides for the diffuseness[50] of the orbital. It is this diffuseness that governs the regiochemistry of orbital controlled interactions.

Diazomethane. In accord with previous calculations[51] and experimental results,[52] diazomethane is expected to be a 1,3-dipole

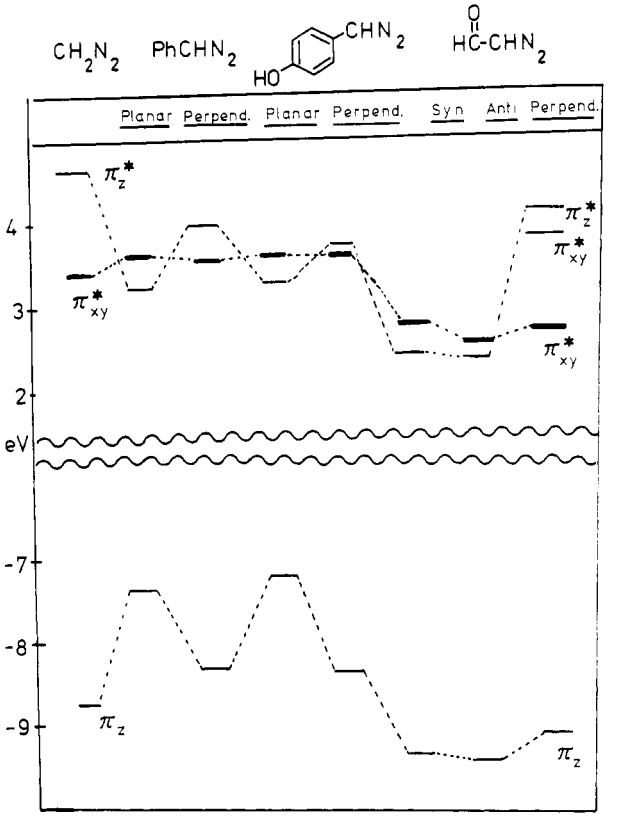


Figure 1. 4-31G Frontier orbital energies for diazomethane, phenyldiazomethane, *p*-hydroxyphenyldiazomethane, and formyldiazomethane.

of the type I class.[53] The πz HO (ϵ −8.76 eV, IP 3.99 eV)[54] is relatively high lying and reactive, whereas the πz^* orbital lies too high (ϵ 4.69 eV) to be reactive. The relatively low-lying πy^* LU (ϵ 3.43 eV) has the largest eigenvector on N_1 and must be responsible for the reactions of diazoalkanes toward nucleophiles such as phosphines.[55] Although the reactivity of the πy^* orbital suggests that diazoalkanes should be a potential 2π component

(48) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

(49) (a) Du Puis, M.; Spangler, D.; Wendoloski, J. J. NRCC Program QG01. We thank Dr. J. J. Wendoloski for running calculations reported herein. (b) The following geometries were used for the diazo groups: N-N 1.114 Å, C-N 1.313 Å, C-H 1.020 Å, HCN 116.5°. For CHO: C-C 1.418 Å, C-O 1.222 Å, C-H 1.000 Å, CCO 120°. For phenyl ring: C-C (diazo) 1.450 Å, C-C 1.378 Å, C-H 1.050 Å. For phenol ring, OH was placed in the *xy* plane: C-O 1.370 Å, O-H 0.960 Å, COH 104.5°.

(50) Streitwieser, A.; Berk, C. M.; Schriver, G. W.; Grier, D.; Collins, J. B. *Tetrahedron* **1981**, *37*, 345.

(51) (a) Sorriso, S. "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley-Interscience: New York, 1978; p 95. (b) Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287 and references therein. (c) Leroy, G.; Sana, M. *Theor. Chim. Acta* **1974**, *33*, 329.

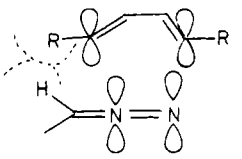
(52) (a) Geittner, J.; Huisgen, R.; Reissig, H.-U. *Heterocycles* **1978**, *11*, 109. (b) Huisgen, R.; Geittner, J. *Ibid.* **1978**, *11*, 105. (c) Bihlmaier, W.; Huisgen, R.; Reissig, H.-U.; Voss, S. *Tetrahedron Lett.* **1979**, 2621.

(53) Geittner, J.; Huisgen, R.; Sustmann, R. *Tetrahedron Lett.* **1977**, 881.

(54) Herzberg, G. "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules"; Van Nostrand: Toronto, Canada, 1967.

(55) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 619. Wittig, G.; Haag, W. *Chem. Ber.* **1955**, *88*, 1654.

for [2 + 4] cycloadditions with electron-rich dienes, severe nonbonded interactions between the diazo and diene substituents appear to prevent such reactions.



Phenyl- and *p*-(Hydroxyphenyl)diazomethane. Calculations with the aryldiazomethanes predict that the perpendicular form is thermodynamically less stable (by 4–5 kcal/mol) but kinetically less reactive than the corresponding planar form. The frontier molecular orbital (FMO) energy profiles of the perpendicular forms are similar to that of diazomethane (Figure 1). The only difference is that the πz^* orbitals are lowered in energy and are mainly localized in the aryl π framework.

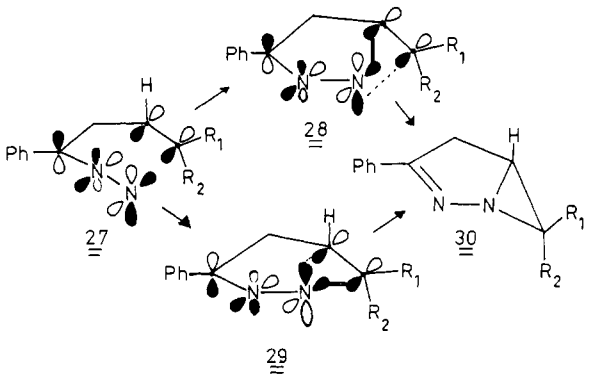
With the planar aryldiazomethanes, the πz and πz^* orbitals lie much closer to the nonbonding level (i.e., more reactive) due to the conjugation between the two π systems. The higher reactivity relative to diazomethane resulting from the activated πz HO, however, is tempered somewhat by the diminished eigenvectors on the critical terminal atoms of the 1,3-dipole. Although no bimolecular 1,3-dipolar cycloaddition of phenyl-substituted allyldiazomethanes leading to dimers and oligomers has been observed, the usual 1,3-dipolar adduct has been isolated with dimethyl fumarate.[35]

The πy^* orbital of these planar aryldiazoalkanes lies slightly above the πz^* LU and is similar to the πy^* of diazomethane in both energy and shape. Like other diazoalkanes, this orbital is responsible for the reaction with nucleophiles such as phosphines[55,57] and carbanions.[57] No [2 + 4] cycloaddition is observed, however, even with electron-rich dienes.[56] This is probably the result of steric factors (vide supra).

Let us now consider the potential nitrene character of the diazo moiety. The nitrene character of the diazo group, like a carbene, is derived from the mutually perpendicular frontier molecular orbitals which are energetically accessible and possess sizable eigenvectors at the atomic center. In the case of diazo compounds, this means that the πz and πy^* orbitals should have sizable eigenvectors on N_1 and that the $\pi z - \pi y^*$ energy gap should be small. It is interesting to note that the energy gap calculated for the aryldiazomethanes (ca. 11 eV) is about 1 eV smaller than the other diazo species we have examined (see Figure 1 and Table I). This is not due to a lowering of the πy^* but rather is the result of the activated πz HO. One can attribute the diminished $\pi y - \pi y^*$ energy gap, the shapes of the orbital, as well as the intramolecularity of the reaction to the observed nitrene-type reactivity of the phenyl-substituted allyldiazomethanes.

Inspection of molecular models indicates that the olefin π orbitals of allyldiazomethanes can interact with the diazo πy orbital but not very well with the πz orbital. The π(olefin)–πy interaction will be increased substantially if the diazo terminal nitrogen is bent toward the allyl group in the xy plane. The energy surface with respect to such deformation is quite soft,[58] essentially since the πz conjugation remains undisturbed. Furthermore, this deformation lowers the πy^* orbital, thereby making the system more electrophilic and nitrene-like. The following sequence of events would be expected to promote the intramolecular 1,1 cycloaddition. First, the terminal nitrogen atom interacts through the πy^* orbital with the π HO of an electron-rich olefin.[59] This process will be aided by the soft in-plane bending of the diazo group and also by the intramolecular nature of the reaction. The initial interaction is followed by a reaction pathway similar to the now familiar route in which methylene adds to ethylene.[61] For this process to proceed effectively, it is necessary that the diazo group possess a high-lying occupied πz orbital with a sizable coefficient on N_1. Our calculations indicate that phenyl- and *p*-methoxyphenyl-substituted allyldiazomethanes fulfill these requirements and further suggest that the perturbation of in-plane π orbitals of other 1,3 dipoles and related compounds may result in some novel reactivity patterns.

The experimental results are totally consistent with the concerted 1,1 cycloaddition process. Nevertheless, it is possible that bond formation at one carbon of the olefinic double bond is more advanced than that at the other carbon in the transition state. In an extreme case of nonsynchroneity, nucleophilic attack of the olefin double bond on the terminal nitrogen atom of the in-plane bent diazo group will generate a five- and/or a six-membered ring dipole (i.e., **28** or **29**) which contains an azaallylic carbanion as



well as a carbonium ion. Collapse of the new cyclized dipole gives rise to the diazabicyclohexene ring system. As long as the closure step is fast relative to exo $C-C^+R_1R_2$ bond rotation in **28** or ring flipping in **29**, the 1,1 cycloaddition will proceed with retention of configuration. The preference for cyclization to give either **28** or **29** will be determined by various factors such as carbonium ion stability, ring strain, and FMO shapes of the olefin. Although this stepwise process cannot be rigorously ruled out, the stereospecificity and reversibility[33–35] of the reaction as well as the fact that allyldiazomethanes bearing electron-withdrawing groups such as *p*-nitrophenyl, ester, and phosphoryl do not undergo the 1,1 cycloaddition may be collectively taken as strong evidence for concertedness.

Formyldiazomethane. MO calculations dealing with formyldiazomethane reveal some interesting aspects which should also hold for *p*-nitrophenyldiazomethane. The relative thermodynamic stabilities calculated for the syn, anti, and perpendicular forms are in qualitative agreement with the experimental results[51,52] and previous calculations.[51] The perpendicular form is not readily accessible and its chemical reactivity is expected to be uneventful. As expected for the planar forms, both the πz and πz^* orbitals are substantially lowered in energy. The πz HO has a shape which is appropriate for a concerted 1,3 cycloaddition, but because of its energy level it will only interact strongly with the π^* orbital of electron-deficient dipolarophiles. As with the diazo compounds discussed previously, the πz^* LU has a very small coefficient on the diazo carbon atom and is not expected to undergo concerted 1,3 cycloaddition of the type III[53] variety even with electron-rich dipolarophiles (vide infra).

The πy^* orbital of planar formyldiazomethane is highly stabilized relative to diazomethane and has a large coefficient on N_1. The $\pi z - \pi y^*$ energy gap, however, is about 1 eV greater than that of phenyldiazomethane. This gap is expected to be even greater for *p*-nitrophenyldiazomethane since the πy^* orbital will not be so well stabilized. According to our hypothesis, allyl-

(56) Fisera, L.; Geittner, J.; Huisgen, R.; Reissig, H.-U. *Heterocycles* **1978**, *10*, 153.

(57) McGarriety, J. F. "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley-Interscience: New York, 1978; p 179.

(58) The deformation of 10° and 20° require 1.6 and 5.6 kcal, respectively, by CNDO/2.

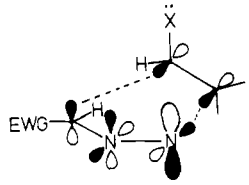
(59) The styryl group in **10** is most likely nonplanar[60] and not as nucleophilic as the *E* stereoisomer **2**.

(60) Mixer, R. Y.; Heck, R. F.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1953**, *75*, 4094.

(61) Hoffmann, R.; Hayes, D. M.; Skell, P. S. *J. Phys. Chem.* **1972**, *76*, 664. Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

diazomethanes which are substituted with electron-withdrawing groups would not be expected to give 1,1-cycloadducts. As with the previous cases, nucleophilic attack on N_1 should lead to diazo coupling,[57,62] but no [2 + 4] cycloaddition with electron-rich dienes is to be expected.

It is conceivable that the πy^* orbital of the diazo group is also involved in the observed 1,3-dipolar cycloaddition[62] of this type III[53] dipole. These reactions are known to be often complicated by side reactions such as diazo coupling[57,62] as well as by the rapid disappearance of the diazo moiety which is unrelated to the formation of 1,3-cycloadducts.[62] Interestingly, an intramolecular version of the 1,3-cycloreversion process is also known[47] which generates allyldiazomethanes bearing electron-withdrawing α substituents. As was mentioned earlier, the πz^* LU does not have the appropriate shape for concerted 1,3 cycloaddition even though it is low lying. There is no other πz^* orbital below 6 eV. It should be pointed out that if the π HO of an electron-rich dipolarophile attacks the πy^* orbital in the 1,1 addition and if this is followed by a πz HO (diazo) interaction at the diazo carbon atom, 1,3-dipolar cycloaddition will result.



This "non-least-motion" approach is somewhat reminiscent of ketene cycloadditions to double bonds and will experience similar stereoselections as the skewed transition state proposed by Houk.[63] The πz HO of formyldiazomethane has the largest pz coefficient on the diazo carbon. Moreover, in the presence of steric factors which hinder πz HO participation, the reaction path will be directed toward diazo coupling.

Summary and Conclusion

Diazo compounds show diverse reactivities even without losing nitrogen. In addition to the well-established 1,3-dipolar cycloadditions of the type I class, diazo compounds can undergo intramolecular 1,1 cycloaddition, diazo coupling, and 1,3 cycloaddition of the type III variety. The experimental and theoretical studies described in this paper suggest that for the latter class of reactions, the πy^* orbital of the diazo group plays an important role. The $\pi z - \pi y^*$ energy gap, the shape of the πz orbital, as well as steric effects which control the relative orientation of nucleophiles will collectively dictate the ultimate outcome of the reaction.

Experimental Section[64]

Preparation of (*E*)-1,4-Diphenyl-3-buten-1-one *N*-Tosylhydrazone (1). A solution containing 2.20 g of 1,4-diphenyl-3-buten-1-one[65] and 2.05 g of *p*-toluenesulfonylhydrazine in 100 mL of anhydrous ether was stirred at room temperature for 7 days. The ether layer was concentrated under reduced pressure and the resulting solid was collected by filtration. Recrystallization of the solid from chloroform–hexane gave 3.15 g (81%) of (*E*)-1,4-diphenyl-3-buten-1-one *N*-tosylhydrazone (**1**) as a white crystalline solid: mp 143–144 °C; IR (KBr) 3230, 1600, 1480, 1440, 1160, 1060, 1040, 975, 960, 895, 805, 725, 715, and 660 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.40 (s, 3 H), 3.55 (d, 2 H), 6.0–6.3 (m, 2 H), 7.20–8.30 (m, 14 H); UV (methanol) 255 nm (ϵ 29 800); mass spectrum, *m/e* 264, 219, 169, 164, 150, 145, 132, 131 (base), 130, 119, 114, 113, 105, 100, 93, 91.

Anal. Calcd for $C_{23}H_{22}N_2O_2S$: C, 70.74; H, 5.68; N, 7.18; S, 8.20. Found: C, 70.90; H, 5.75; N, 7.09; S, 3.08.

Pyrolysis of the Sodium Salt of (*E*)-1,4-Diphenyl-3-buten-1-one *N*-Tosylhydrazone (1). To a solution containing 390 mg of the above hydrazone (**1**) in 5 mL of dry tetrahydrofuran was added 72 mg (50% oil dispersion) of sodium hydride under a nitrogen atmosphere. The mixture was allowed to stir at room temperature for 20 min and then 40 mL of pentane was added. The resulting precipitate was filtered and dried under vacuum to give 400 mg (100%) of a white solid. This material was taken up in 25 mL of benzene and heated at reflux under a nitrogen atmosphere for 20 min. The precipitate that formed was filtered and the solvent was removed under reduced pressure to give 90 mg of an oily red liquid whose structure was assigned as *trans*-1,4-diphenyl-4-diazobut-1-ene (**2**): IR (CCl_4) 3070, 3040, 2970, 2930, 1984, 1682, 1600, 1480, 1440, 1345, 1240, 1060, 1000, 944, and 665 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 3.58 (d, 2 H, J = 5.0 Hz), 6.44 (dt, 1 H, J = 16.0 and 5.0 Hz) 6.84 (d, 1 H, J = 16.0 Hz), 7.24–8.00 (m, 10 H).

A 90-mg sample of diazoalkene **2** was allowed to stir at room temperature for 2 days. Removal of the solvent left a yellow solid which was recrystallized from ether to give 69 mg (77%) of a white solid, mp 144–145 °C, whose structure was assigned as *exo*-3,6-diphenyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**4**) on the basis of the following data: IR (KBr) 3450, 3050, 2930, 1558, 1485, 1440, 1380, 1340, 1065, 748, 730, and 680 cm^{-1}; NMR ($CDCl_3$, 400 MHz) δ 2.44 (d, 1 H, J = 4.0 Hz), 3.05 (ddd, 1 H, J = 7.0, 4.0, and 2.0 Hz), 3.56 (dd, 1 H, J = 18.0 and 7.0 Hz), 3.58 (dd, 1 H, J = 18.0 and 2.0 Hz), 7.24–8.16 (m, 10 H); UV (methanol) 257 nm (ϵ 11 400); mass spectrum, *m/e* 234 (M^+) 233, 205, 203, 202, 157, 149, 131, 130, 129, 128, 127, 117, 115, 105, 104, 103, 102, 100, and 77 (base).

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.97; H, 6.05; N, 11.94.

Treatment of *trans*-1,4-Diphenyl-4-diazobut-1-ene (2) with Acidic Methanol. To a solution containing 50 mg of diazo compound **2** in 10 mL of methanol was added one drop of hydrochloric acid. The reaction mixture was allowed to stir at room temperature for 10 min and was then poured into 50 mL of water and extracted with ether. The ether extracts were washed with a 5% sodium bicarbonate solution and then water. The ethereal layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to leave behind a pale yellow oil which was purified by chromatography on a thick-layer plate using a 1:1 ether–hexane mixture as the eluent. The resulting pale yellow oil was identified as *trans*-1,4-diphenyl-4-methoxy-1-butene (**3**) on the basis of the following spectral data: IR (neat) 3040, 2950, 2830, 1600, 1480, 1440, 1100, 960, 730, and 685 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.60 (dd, 1 H, J = 6.0 and 4.0 Hz), 2.70 (dd, 1 H, J = 7.0 and 4.0 Hz), 3.35 (s, 3 H), 4.25 (t, 1 H, J = 7.0 Hz), 6.15 (td, 1 H, J = 16.0 and 6.0 Hz), 6.45 (d, 1 H, J = 16.0 Hz), 7.15–7.50 (m, 10 H); UV (methanol) 252 nm (ϵ 19 700; mass spectrum, *m/e* 238 (M^+), 121 (base) 117, 116, 115, 105, 91, 77.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.58; H, 7.65.

The structure of methoxy ether **3** was further verified by comparison with an independently synthesized sample. To a solution containing 222 mg of *trans*-1,4-diphenyl-3-buten-1-one in 5 mL of methanol was added 50 mg of sodium borohydride. The reaction mixture was allowed to stir at room temperature for 10 h and was then poured into 20 mL of water. The solution was acidified with aqueous hydrochloric acid and extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent gave 202 mg (89%) of *trans*-1,4-diphenyl-4-hydroxy-1-butene as a white crystalline solid: mp 89–90 °C; IR (KBr) 3400, 3020, 2880, 1480, 1438, 1370, 1020, 940, 720, and 680 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.20 (bs, 1 H), 2.60 (t, 2 H, J = 6.0 Hz), 4.60–4.80 (bt, 1 H, J = 7.0 Hz), 6.05 (dt, 1 H, J = 16.0 and 6.0 Hz), 6.50 (d, 1 H, J = 16.0 Hz) 7.00–7.45 (m, 10 H).

To a solution containing 100 mg of the above alcohol in 5 mL of dimethyl sulfoxide and 3 mL of methyl iodide was added 5 mL of 10% sodium hydroxide solution. The reaction mixture was allowed to stir at room temperature for 6 h and was then poured into 20 mL of water and extracted with ether. The ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give 90 mg of *trans*-1,4-diphenyl-5-methoxy-1-butene (**3**) as a pale yellow oil which was identical in every detail with that of a sample obtained from the acid treatment of diazo compound **2**.

Thermolysis of *exo*-3,6-Diphenyl-1,2-diazabicyclo[3.1.0]hex-2-ene (4). A 200-mg sample of diazabicyclo[3.1.0]hex-2-ene **4** in 0.2 mL of deuteriochloroform was heated at 80 °C for 15 min. The crude NMR

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(63) Houk, K. N.; Sims, J.; Watts, C. R.; Luskas, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.

(64) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by the Atlantic Microanalytical Laboratory. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear resonance spectra were determined at 60 MHz with a Varian T-60 spectrometer, at 100 MHz with a Varian XL-100 spectrometer, and at 90 MHz with a Varian Em-390 spectrometer.

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spectrum indicated it to contain a mixture of diazabicyclohexene **4** and *trans*-1,4-diphenyl-4-diazobut-1-ene (**2**). The solution was heated for an additional 12 h and then the solvent was removed under reduced pressure to leave behind a yellow solid. Recrystallization of this material from an ether–hexane mixture afforded 192 mg of a yellow crystalline solid; mp 142–143 °C, which was identified as 3,6-diphenyl-1,4-dihydropyridazine (**6**) on the basis of its spectral properties: IR (KBr) 3440, 1482, 1460, 1440, 1380, 730, and 675 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 3.35 (d, 2 H, J = 4.0 Hz), 4.95 (dt, 1 H, J = 4.0 and 2.0 Hz), 7.40–8.10 (m, 10 H); UV (methanol) 245 nm (ϵ 18 000); mass spectrum, m/e 234, 233, 205, 203, 202, 157, 149, 131, 130, 129, 128, 127, 117, 115, 104, 103, 102, 100, and 77 (base). The structure of this compound was further verified by comparison with an independently synthesized sample prepared according to the method of Baddar and co-workers.[66] To a solution containing 500 mg of dibenzoylethane (**7**) in 5 mL of *n*-butanol was added 0.5 mL of 85% hydrazine hydrate. The mixture was heated at reflux for 3 h under a nitrogen atmosphere. The precipitate that formed (250 mg) was collected and shown to be 3,6-diphenyl-1,4-dihydropyridazine (**6**). This material was identical in every detail with the sample obtained from the thermolysis of **4**.

A 100-mg sample of dihydropyridazine **6** in 10 mL of ethanol was heated at reflux for 5 min. The precipitate that formed was collected and shown to be 3,6-diphenylpyridazine (**8**) by comparison with an independently synthesized sample:[66] mp 219–220 °C; IR (KBr) 3450, 3100, 2930, 1575, 1540, 1480, 1440, 1400, 1375, 1150, 1000, 850, 750, and 680 cm^{-1}; UV (methanol) 280 nm (ϵ 28 000) and 230 nm (ϵ 6100); NMR ($CDCl_3$, 60 MHz) δ 7.55–8.55 (m, 12 H).

Preparation of (*Z*)-1,4-Diphenyl-3-buten-1-one *N*-Tosylhydrazone (9). Phenylpropargyl bromide[67] was prepared from phenylpropargyl alcohol by treatment with phosphorus tribromide and pyridine in ether. The product was purified by distillation at 110–120 °C (8 mm). To a solution of the Grignard reagent prepared from 7.0 g of magnesium and 16.8 g of phenylpropargyl bromide in 200 mL of anhydrous ether was added slowly and with stirring 9.1 g of benzaldehyde in 50 mL of ether. After stirring for 10 h, the mixture was decomposed by ice and a saturated solution of ammonium chloride. The ether layer was separated, washed with water, dried over anhydrous sodium carbonate, and fractionated through a 6-in. Vigreux column. The product was obtained by distillation at 145–147 °C (0.05 mm). Recrystallization of the oil from a 10% ether–hexane mixture gave 6.3 g of 1,4-diphenyl-3-butyn-1-ol as a white solid, mp 55–56 °C; NMR ($CDCl_3$, 60 MHz) δ 2.70 (bs, 1 H), 3.00 (d, 2 H, J = 6.0 Hz), 5.10 (t, 1 H, J = 6.0 Hz), 7.20–7.70 (m, 10 H).

To a solution containing 5.0 g of the above alcohol in 50 mL of acetone was added 2.2 g of chromium trioxide in 12 mL of a 23% sulfuric acid solution at 0 °C. The reaction mixture was stirred for 20 min at 0 °C and was then poured into 200 mL of ice water. The aqueous layer was extracted with ether, and the ethereal extracts were washed with aqueous sodium carbonate and aqueous potassium iodide and twice with water and dried over magnesium sulfate. Removal of the solvent left a yellow solid which was recrystallized from a 10% ethyl acetate–hexane mixture to give 3.0 g of 1,4-diphenyl-3-butyn-1-one as a white crystalline solid: mp 76–77 °C; NMR ($CDCl_3$, 60 MHz) δ 4.10 (s, 2 H), 7.10–7.50 (m, 10 H).

A 1.0-g sample of 1,4-diphenyl-3-butyn-1-one was hydrogenated with 50 mg of palladium on barium carbonate in 25 mL of ethyl acetate to which was added 1 drop of quinoline. One equivalent of hydrogen was taken up over a period of 2 h. The solution was filtered free of the catalyst and the solvent was removed under reduced pressure in the cold. The resulting yellow oil was taken up in 50 mL of pentane. This solution was then cooled to −78 °C and the resulting light yellow solid was filtered. Recrystallization from 25 mL of pentane gave 500 mg of *cis*-1,4-diphenyl-3-buten-1-one as a white solid,[68] mp 54–55 °C; NMR ($CDCl_3$, 60 MHz) δ 4.15 (dd, 2 H, J = 6.0 and 2.0 Hz), 6.20 (dt, 1 H, J = 12.0 and 6.0 Hz), 6.85 (td, 1 H, J = 12.0 and 2.0 Hz), 7.25–8.10 (m, 10 H).

A solution containing 1.10 g of *cis*-1,4-diphenyl-3-buten-1-one and 1.05 g *p*-toluenesulfonylhydrazine in 40 mL of anhydrous ether was stirred at room temperature for 7 days. The ether layer was concentrated under reduced pressure and the resulting solid was collected by filtration. Recrystallization of the solid from a 10% chloroform–hexane mixture gave 870 mg (42%) of (*Z*)-1,4-diphenyl-3-buten-1-one *N*-tosylhydrazone (**9**) as a white solid: mp 125–126 °C; IR (KBr) 3450, 3203, 1590, 1440, 1380, 1350, 1340, 1318, 1160, 1070, 790, 760, 680, and 660 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.36 (s, 3 H), 3.56 (dd, 2 H, J = 6.0 Hz and 2.0 Hz), 5.38 (dt, 1 H, J = 12.0 and 6.0 Hz), 6.60 (d, 1 H, J = 12.0 Hz), 7.10-7.90 (m, 17 H); UV (methanol) 250 nm (ϵ 22 700).

Anal. Calcd for $C_{23}H_{22}N_2O_2S$: C, 70.74; H, 5.68; N, 7.18; S, 8.20. Found: C, 70.68; H, 5.63; N, 7.21, S, 8.14.

Thermolysis of the Sodium Salt of (*Z*)-1,4-Diphenyl-3-buten-1-one *N*-Tosylhydrazone (9). To a solution containing 250 mg of the above *cis*-hydrazone (**9**) in 3 mL of dry tetrahydrofuran was added 45 mg (50% oil dispersion) of sodium hydride under a nitrogen atmosphere. The mixture was allowed to stir at room temperature for 20 min and then 40 mL of pentane was added. The resulting precipitate was filtered and dried under reduced pressure to give 250 mg (100%) of a white solid which was immediately used in the next step. A 250-mg sample of the above salt was taken up in 25 mL of dry benzene and was heated at reflux under a nitrogen atmosphere for 20 min. The precipitate that formed was filtered and the solvent was removed under reduced pressure to give *cis*-1,4-diphenyl-4-diazobut-1-ene (**10**) as a red oil: IR (CCl_4) 3100, 3050, 2000, 1530, 1470, 1220, 1120, 1070, 1020, and 660 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 3.40 (dd, 2 H, J = 7.0 and 2.0 Hz), 5.80 (dt, 1 H, J = 11.0 and 7.0 Hz), 6.80–7.50 (m, 11 H). A 60-mg sample of diazoalkene **10** was allowed to stir at room temperature for 5 days. Removal of the solvent under reduced pressure left a dark yellow oil. Unfortunately, all attempts to isolate any characterizable compounds from the reaction mixture failed and we abandoned further work with this system.

Preparation of 1-Phenyl-4-methyl-3-penten-1-one *N*-Tosylhydrazone (12). In a 250-mL round-bottom flask was added 15.0 g of phenyldithiane followed by 150 mL of dry tetrahydrofuran. This solution was cooled to −78 °C and 75 mL of a 1.4 N *n*-butyllithium solution in hexane was slowly added.[69] The reaction mixture was stirred at −78 °C for 6 h and then 12.5 g of 1-bromo-3-methyl-2-butene was added. The mixture was allowed to warm to 25 °C and was stirred at this temperature for 18 h. Aqueous acidic workup followed by drying over magnesium sulfate afforded 1-phenyl-1-(4-methyl-3-butenyl)dithiane (85%) as a pale yellow oil which slowly crystallized on standing. Recrystallization from methanol gave a white crystalline solid: mp 49–50 °C; IR (neat) 3050, 2900, 1640, 1600, 1430, 1420, and 1020 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.40 (s, 3 H), 1.60 (s, 3 H), 1.8–2.0 (m, 2 H), 2.4–2.7 (m, 6 H), 4.91 (t, 1 H, J = 7.0 Hz), 7.1–7.4 (m, 3 H), and 7.7–7.9 (m, 2 H).

To a mixture containing 10.5 g of *N*-chlorosuccinimide and 15.0 g of silver nitrate in 100 mL of a 80% acetonitrile solution was added 5.0 g of the above dithiane in 10 mL of acetonitrile.[70] The mixture was allowed to stir at 25 °C for 1 h, and then 10 mL of a saturated sodium sulfite solution, 10 mL of a sodium carbonate solution, and 10 mL of a saturated sodium chloride solution were added in 1-min intervals. The mixture was extracted with ether and the ethereal extracts were filtered through Celite and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a clear oil (65% yield) whose structure was assigned as 1-phenyl-4-methyl-3-penten-1-one (**11**):[71] bp 118–119 °C (0.08 mm); IR (neat) 3050, 2900, 2850, 1690, 1600, 1210, and 980 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.61 (s, 3 H), 1.70 (s, 3 H), 3.60 (d, 2 H, J = 7.0 Hz), 5.40 (t, 1 H, J = 7.0 Hz), 7.1–7.7 (m, 3 H), and 7.9–8.1 (m, 2 H).

To a 500-mg sample of the above ketone in 1 mL of a 60% aqueous methanol solution was added 534 mg of *N*-tosylhydrazine. The mixture was heated to 60 °C for 10 min and then 1 drop of glacial acetic acid was added and heating was then continued for an additional 15 min. The mixture was allowed to cool to 0 °C and the resulting solid that precipitated was collected and recrystallized from methanol to give 1-phenyl-4-methyl-3-penten-1-one *N*-tosylhydrazone (**12**) (50%) as a white solid: mp 105–106 °C; IR (neat) 3200, 3100, 2950, 2800, 1600, and 1380 cm^{-1}; UV (95% ethanol) 265 nm (ϵ 13 600); NMR ($CDCl_3$, 90 MHz) δ 1.60 (s, 3 H), 1.70 (s, 3 H), 2.30 (s, 3 H), 3.21 (d, 2 H, J = 7.0 Hz), 4.82 (t, 1 H, J = 7.0 Hz), 7.2–7.4 (m, 5 H), and 7.5–7.8 (m, 4 H).

Anal. Calcd for $C_{19}H_{22}N_2SO_2$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.47; H, 6.45; N, 8.09.

Thermolysis of 1-Phenyl-4-methyl-3-penten-1-one *N*-Tosylhydrazone (12). A solution containing 250 mg of **12** was treated with an excess of sodium hydride. After stirring for 20 min, the solution was filtered and the filtrate was concentrated under reduced pressure. The sodium salt that was obtained was dried under vacuum and then 5 mL of carbon tetrachloride was added to the flask. The tube was heated at 90 °C for 30 min. The solution was filtered and the solvent was removed under reduced pressure. The resulting residue was purified by preparative thick-layer chromatography giving 3-phenyl-6,6-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**13**) as a crystalline solid: mp 52–53 °C (60% yield); IR (neat) 3080, 3010, 2950, 1565, 1500, 1440, 1350, and 760

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cm^{-1}; UV (95% ethanol) 256 nm (ϵ 14000); NMR ($CDCl_3$, 60 MHz) δ 0.92 (s, 3 H), 1.35 (s, 3 H) 2.50 (dd, 1 H, J = 8.0 and 4.0 Hz) 2.87 (dd, 1 H, J = 18.0 and 4.0 Hz), 3.08 (dd, 1 H, J = 18.0 and 8.0 Hz), and 7.2–8.1 (m, 5 H); ^{13}C NMR (20 MHz, $CDCl_3$) 11.85 (*endo*-CH_3) 25.89 (*exo*-CH_3), 35.30 (C_4), 47.08 (C_6), 50.09 (C_5), and 171.03 (C_3); mass spectrum, *m/e* 186 (M^+), 158, 143 (base), 128, and 115.

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.26; H, 7.46; N, 14.93.

Preparation of (*E*)-1-Phenyl-3-penten-1-one *N*-Tosylhydrazone (14). In a 2-necked round-bottom flask was added 10 g of phenyldithane followed by 100 mL of dry tetrahydrofuran. This solution was cooled to −78 °C and 40 mL of a 1.5 N *n*-butyllithium solution in hexane was slowly added.[69] The solution was kept at −78 °C for 6 h after which 5.0 g of crotyl chloride was added. The reaction was then slowly warmed to room temperature and left stirring for 18 h. Aqueous workup gave (*E*)-1-phenyl-1-(2-butenyl)dithiane as a clear oil in 91% yield. This material was sufficiently pure that it could be used in the next step without further purification: NMR (60 MHz, $CDCl_3$) δ 1.50 (d, 3 H, J = 6.0 Hz), 1.6–2.0 (m, 2 H), 2.4–2.7 (m, 6 H), 5.0–5.2 (m, 2 H), 6.9–7.5 (m, 5 H); IR (neat) 3025, 2990, 2850, 1600, 1420, and 1360 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}S_2$: C, 67.18; H, 7.19. Found: C, 67.07; H, 7.25.

In a 500-mL round-bottom flask was added 9.36 g of *N*-chlorosuccinimide, 18.3 g of silver nitrate, and 240 mL of a 80% acetonitrile water mixture.[70] To this mixture was added 6.0 g of (*E*)-1-phenyl-1-(2-butenyl)dithiane in 24 mL of acetonitrile. The reaction was left stirring at room temperature for 1 h after which 24 mL of a saturated aqueous sodium sulfite solution, 24 mL of a saturated sodium carbonate solution, and finally 24 mL of a saturated sodium chloride solution were added. The organic solution was dried over magnesium sulfate and concentrated under reduced pressure. The residue was then distilled under reduced pressure (bp 88–90 °C (0.4 mm)) to give *trans*-1-phenyl-3-penten-1-one[72] in 44% yield: IR (neat) 3050, 2990, 2800, 1690, 1440, 1350, 900 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.7–1.9 (m, 3 H), 3.6–3.8 (m, 2 H), 5.6–5.8 (m, 2 H), 7.2–8.0 (m, 5 H).

The *trans*-tosylhydrazone was prepared by reacting 1.0 g of *trans*-1-phenyl-3-penten-1-one with 1.17 g to tosylhydrazine in 2 mL of a 60% ethanol–water solution. This mixture was heated to 60 °C for 5 min, and then 1 drop of glacial acetic acid was added and the mixture was heated for an additional 5 min. The reaction mixture was then cooled to −20 °C whereupon the *trans*-tosylhydrazone crystallized. The white crystals obtained were recrystallized from 95% ethanol to give 854 mg (41%) of (*E*)-1-phenyl-3-penten-1-one *N*-tosylhydrazone (**14**) as a crystalline solid: mp 128–129 °C; NMR (90 MHz, $CDCl_3$) δ 1.50 (dd, 3 H, J = 6.0 and 3.0 Hz), 2.35 (s, 3 H), 3.15–3.35 (m, 2 H), 5.2–5.4 (m, 2 H), 7.2–7.9 (m, 9 H); IR (KBr) 3200, 3000, 2900, 1600, 1460, 1440, 1380 cm^{-1}; UV (95% ethanol) 265 nm (ϵ 13200); mass spectrum *m/e* 328, 173, 129.

Anal. Calcd for $C_{18}H_{20}N_2SO_2$: C, 65.85; H, 6.09; N, 8.53. Found: C, 65.75; H, 6.14; N, 8.51.

Thermolysis of (*E*)-1-Phenyl-3-penten-1-one *N*-Tosylhydrazone (14). A solution containing 10 mL of ether and 750 mg of (*E*)-1-phenyl-3-penten-1-one *N*-tosylhydrazone (**14**) was treated with an excess of sodium hydride. After 20 min, the solution was filtered and the filtrate was concentrated under reduced pressure. The yellow sodium salt that was obtained (800 mg) was dried under vacuum for an additional 2 h. After this time, 10 mL of carbon tetrachloride was added to a 100-mg sample of the salt and the mixture was transferred to a thick-wall thermolysis tube. The tube was heated under an argon atmosphere at 90 °C for 30 min after which a reddish pink solution appeared along with a white flocculent precipitate. The solution was filtered under argon and the solvent was removed under reduced pressure. The residue was purified by preparative thick-layer chromatography (silica gel, 50% ethyl acetate/hexane) giving *exo*-6-methyl-3-phenyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**15**) as a crystalline solid: mp 53–54 °C (54% yield); H NMR ($CDCl_3$, 400 MHz) δ 1.36 (d, 3 H, J = 6.0 Hz), 1.52 (dq, 1 H, J = 6.0 and 4.0 Hz), 2.74 (ddd, 1 H, J = 6.0, 4.0 and 3.0 Hz), 3.36 (dd, 1 H, J = 18.0 and 6.0 Hz), 3.44 (dd, 1 H, J = 18.0 and 3.0 Hz), and 7.2–8.1 (m, 5 H); ^{13}C NMR (20 MHz, $CDCl_3$) 168.32 (C=N), 131.76, 130.62, 128.62, 127.40 (aromatic), 48.85 (C_6), 46.74 (C_5), 37.99 (CH_2), 16.89 (*exo*-CH_3); UV (95% ethanol) 255 nm (ϵ 12100); IR (neat) 3090, 3000, 2950, 1560, 1500, 1440, 1340, 760 cm^{-1}; mass spectrum, *m/e* 173, 172, 143, 144, 130, 129, 128 (base peak).

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71, H, 7.02; N, 16.27. Found: C, 76.75, H, 7.08; N, 16.17.

Preparation of (*Z*)-1-Phenyl-3-penten-1-one *N*-Tosylhydrazone (16). In a 250-mL round-bottom flask was added 11.9 g of phenyldithane followed by 150 mL of dry tetrahydrofuran. The flask was cooled to −78 °C and 40 mL of a 1.4 *N* *n*-butyllithium solution in hexane was slowly added over a 25-min period. The reaction was kept at −78 °C for 6 h whereupon 7.0 g of propargyl bromide was added in one portion. The reaction was allowed to warm up to room temperature and was left stirring under nitrogen for 18 h. Aqueous workup followed by magnesium sulfate drying gave the expected acetylenic dithiane in 62% yield. The oil was recrystallized from methanol to give a white crystalline solid: mp 78–79 °C; IR (neat) 3300, 3000, 2900, 1600, 1400, 900 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.9–8.1 (m, 3 H), 2.7–2.9 (m, 3 H), 3.0 (d, 2 H, J = 3.0 Hz), 7.3–7.6 (m, 3 H), 7.2–8.0 (m, 2 H); mass spectrum, *m/e* 234, 196, and 195 (base).

Anal. Calcd for $C_{13}H_{14}S_2$: C, 66.65; H, 5.91. Found: C, 66.48; H, 6.03.

In a 250-mL round-bottom flask was added 6.43 g of 1-phenyl-1-(2-propynyl)dithane followed by 200 mL of dry tetrahydrofuran. This solution was cooled to −78 °C and 25 mL of a 1.4 N *n*-butyllithium solution in hexane was slowly added. The reaction was kept at −78 °C for 1 h and then 1 mL of freshly distilled dimethyl sulfate was added at −78 °C. After 20 min, the reaction was cooled to 0 °C and 4 mL of dimethyl sulfate was added again.[73] The reaction was kept at 0 °C for 1 h and at room temperature for 2 h. After aqueous workup, 4.62 g of a yellow oil was obtained, which when diluted with 10% hexane–acetone crystallized to 1-phenyl-1-(2-butynyl)dithiane as a white solid: mp 68–69 °C (72% yield); IR (neat) 3060, 2960, 2900, 2400, 1595, 1480, 1445, 1410, 700 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.65 (t, 3 H, J = 3.0 Hz), 1.8–2.0 (m, 2 H), 2.6–2.7 (m, 4 H), 2.85 (q, 2 H, J = 3.0 Hz), 7.8–8.1 (m, 2 H), and 7.2–7.5 (m, 3 H); mass spectrum, *m/e* 248, 197, 141, 122, and 115.

Anal. Calcd for $C_{14}H_{16}S_2$: C, 67.72; H, 6.44. Found: C, 67.51; H, 6.53.

In a 500-mL round-bottom flask was added 8.6 g of *N*-chlorosuccinimide, 12.2 g of silver nitrate, and 240 mL of a 80% acetnitrile–water mixture. To this solution was added 4.0 g of 1-phenyl-1-(2-butynyl)-dithiane in 10 mL of acetonitrile. A white precipitate was immediately formed and the solution turned yellow. The reaction was left stirring for 1 h at room temperature, and then 10 mL of a saturated sodium sulfite solution, 10 mL of a sodium carbonate solution, and 10 mL of a saturated chloride solution were added in 1-min intervals. Filtration through Celite followed by magneisum sulfate drying gave 1-phenyl-3-pentyn-1-one in 38% yield: bp 70–71 °C (0.04 mm); NMR (90 MHz, $CDCl_3$) δ 1.95 (t, 3 H, J = 3.0 Hz), 3.95 (q, 2 H, J = 3.0 Hz), 7.6–7.9 (m, 3 H), and 8.2–8.4 (m, 2 H); IR (neat) 3050, 2950, 2800, 1700, 1600, 1550, 1450, 900 cm^{-1}; mass spectrum, *m/e* 248, 205, 197 (base), 194, 141.

Anal. calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.46, H, 6.29.

In an atmospheric pressure hydrogenation apparatus was hydrogenated 0.5 g of 1-phenyl-3-pentyn-1-one in 50 mL of ethyl acetate, using 5% palladium on barium carbonate as the catalyst and adding 1 drop of quinoline as the poison.[74] This solution was hydrogenated for 18 h. The *cis*-ketone formed was filtered and the solvent was removed under reduced pressure. The residue was distilled to give *cis*-1-phenyl-3-penten-1-one: bp 75–76 °C (0.15 mm) (49% yield); NMR (90 MHz, $CDCl_3$) δ 1.7 (dd, 3 H, J = 6.0 and 1.5 Hz), 3.6–3.8 (m, 2 H), 5.6–5.8 (m, 2 H), and 7.3–8.1 (m, 5 H); IR (neat) 3050, 2900, 1690, 1600, 1450, 1360, 1260, 1200 cm^{-1}. This material was used without further purification in the next step.

In a 10-mL flask was added 208 mg of *cis*-1-phenyl-3-penten-1-one, 1 mL of a 60% methanol water mixture, and 294 mg of tosylhydrazine. This mixture was heated to 60 °C for 10 min, and then 1 drop of glacial acetic acid was added and the resulting mixture was heated for an additional 15 min.[75,76] The flask was then placed in the freezer upon which the product crystallized. The resulting solid was recrystallized from methanol to give 170 mg (24% yield) of *cis*-1-phenyl-3-penten-1-one *N*-tosylhydrazone (**16**) as colorless crystals: mp 117–118 °C; IR (neat) 3250, 3090, 2980, 2800, 1600, 1380, 900 cm^{-1}; UV (95% ethanol) 265 nm (ϵ 11500); mass spectrum, *m/e* 328, 173, 129; NMR (90 MHz, $CDCl_3$) δ 1.70 (dd, 3 H, J = 6.0 and 1.5 Hz), 2.40 (s, 3 H), 3.3–3.6 (m, 2 H), 5.0–5.4 (m, 1 H), 5.5–5.9 (m, 1 H), and 7.2–8.0 (m, 9 H).

Anal. Calcd for $C_{18}H_{20}N_2SO_2$: C, 65.85; H, 6.09; N, 8.53. Found: C, 65.77; H, 6.16; N, 8.36.

Thermolysis of (*Z*)-1-Phenyl-3-penten-1-one *N*-Tosylhydrazone (16). In a 10-mL round-bottom flask was added 101 mg of the above *cis*-tosylhydrazone followed by 5 mL of dry tetrahydrofuran and 100 mg of solid sodium hydride. This solution was stirred for 20 min and was then

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filtered and the solvent was removed under reduced pressure. The solid sodium salt obtained was dried under a vacuum for 2 h. The salt was diluted with 10 mL of carbon tetrachloride and this solution was transferred to a thermolysis tube. The solution was heated to 90 °C for 45 min and filtered under argon and the filtrate concentrated under reduced pressure. The residue was immediately diluted with fresh carbon tetrachloride and its spectral properties were recorded; NMR (90 MHz, CCl_4) δ 0.98 (d, 3 H, J = 6.0 Hz), 2.42–2.90 (m, 2 H), 3.01 (dd, 1 H, J = 18.0 and 3.0 Hz), 3.20 (dd, 1 H, J = 18.0 and 8.0 Hz), and 7.2–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) 130.64, 128.57, 127.41 (aromatic), 42.18 (C_6), 41.63 (C_5), 34.30 (CH_2), 5.71 (CH_3). The spectral data for the diazoalkane that was also formed are as follows: IR (neat) 2025 cm^{-1}; NMR (90 MHz, $CDCl_3$) 5.70–5.80 (m, J = 10.5 Hz), 1.70 (d, J = 6.0 Hz, 3 H). All attempts to isolate a pure sample of the *endo*-diazabicyclohexene **17** failed as a result of its high reactivity.

Preparation of (*E*)-1-*p*-Anisyl-4-phenyl-3-buten-1-one *N*-Tosylhydrazone (25). To a solution containing 13.61 g of anisoin and 9.1 g of cinnamyl bromide in 100 mL of dimethyl sulfoxide was added 25 mL of a 10% aqueous sodium hydroxide solution. The mixture was stirred overnight at room temperature and the solution was poured onto ice water. The precipitate that formed was filtered and recrystallized from ethanol to give 1,2-di-*p*-anisyl-2-hydroxy-5-phenyl-4-penten-1-one: mp 102–103 °C; NMR ($CDCl_3$, 90 MHz) δ 3.21 (dd, 2 H, J = 7.0 and 3.0 Hz), 3.82 (s, 6 H), 4.55 (s, 1 H), 5.9–6.5 (m, 2 H), 6.85 (d, 2 H, J = 9.0 Hz), 6.94 (d, 2 H, J = 9.0 Hz), 7.23 (s, 5 H), 7.45 (d, 2 H, J = 9.0 Hz), and 7.80 (d, 2 H, J = 9.0 Hz); IR (KBr) 3450, 1650, 1600, 1500, 1240, 1170, and 1050 cm^{-1}.

To a solution containing 12.0 g of the above compound in 100 mL of methanol at 0 °C was added 2.0 g of sodium borohydride. The mixture was stirred at 25 °C for 5 h and was then poured into water. A 10% hydrogen chloride solution was added to the aqueous solution until the pH of the mixutre was neutral to litmus. The solution was extracted with ether, dried over magnesium sulfate, and evaporated under reduced pressure to give 1,2-di-*p*-anisyl-5-phenyl-4-penten-1,2-diol as a diastereomeric mixture: mp 178–184 °C (11.65 g, 96%); NMR ($CDCl_3$, 90 MHz) δ 2.6–2.8 (m, 2 H), 2.9 (m, 2 H), 3.79 (s, 6 H), 4.78 (s, 1 H), 5.7–6.40 (m, 2 H), and 6.6–7.4 (m, 14 H); IR (KBr) 3500, 2950, 1600, 1500, 1440, and 1240 cm^{-1}.

To a solution containing 9.0 g of the above diol in 500 mL of methanol was added 200 mL of a solution containing 6.0 g of sodium metaperiodate in a 1:1 methanol–water mixture. The resulting solution was stirred at 25 °C for 10 h and was then diluted with water and extracted with ether. Concentration of the solvent under reduced pressure left 3.4 g (65%) of (*E*)-1-*p*-anisyl-4-phenyl-3-buten-1-one as a white solid: mp 109–110 °C; NMR ($CDCl_3$, 90 MHz) δ 3.80 (m, 5 H), 6.3–6.7 (m, 2 H), 6.98 (d, 2 H, J = 9.0 Hz), 7.20–7.50 (m, 5 H), and 8.10 (d, 2 H, J = 9.0 Hz); IR (KBr) 1680, 1600, 1240, and 1170 cm^{-1}; UV (ethanol) 270 nm (ϵ 22 700); mass spectrum, m/e 252, 135 (base), and 117.

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.78; H, 6.47.

A solution containing 1.0 g of the above ketone and 0.9 g of *p*-toluene sulfonyl hydrazine in 20 mL of dry tetrahydrofuran was allowed to stir at 25 °C for 4 days. The solution was concentrated under reduced pressure and the resulting residue was collected by filtration. Recrystallization of the solid from chloroform–hexane gave 1.33 g (80%) of (*E*)-1-*p*-anisyl-4-phenyl-3-buten-1-one *N*-tosylhydrazone (**25**) as a white crystalline solid: mp 160–161 °C; NMR ($CDCl_3$, 90 MHz) δ 2.35 (s, 3 H), 3.50 (d, 2 H), 3.81 (s, 3 H), 5.8–6.2 (m, 2 H), 6.85 (d, 2 H, J = 9.0 Hz), 7.0–7.4 (m, 7 H), 7.60–7.90 (m, 4 H); IR (KBr) 3240, 1600, 1500, 1240, and 1170 cm^{-1}; UV (ethanol) 255 nm (ϵ 15 800); mass spectrum, m/e 420, 265 (base), 251, 238, and 198.

Anal. Calcd for $C_{24}H_{24}N_2O_3S$: C, 68.56; H, 5.75; N, 6.66; S, 7.61. Found: C, 68.12; H, 5.89; N, 6.52; S, 7.46.

Pyrolysis of the Sodium Salt of (*E*)-1-*p*-Anisyl-4-phenyl-3-buten-1-one *N*-Tosylhydrazone (25). To a solution containing 200 mg of hydrazone **25** in 5 mL of dry tetrahydrofuran was added 20 mg of a dry sodium hydride under a nitrogen atmosphere. The mixture was allowed to stir at room temperature for 20 min, and the resulting precipitate was filtered and dried under vacuum to give 210 mg (100%) of a white solid. This material was taken up in 25 mL of benzene and was heated at reflux under a nitrogen atmosphere for 45 min. The precipitate that formed was filtered, and the solvent was removed under reduced pressure to leave behind a yellow oil which was recrystallized from ether to give 50 mg (40%) of a white solid, mp 139–140 °C, whose structure was assigned as *exo*-6-phenyl-3-*p*-anisyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**31**) on the basis of the following data: NMR ($CDCl_3$, 90 MHz) δ 2.38 (d, 1 H, J = 4.0 Hz), 3.05 (dd, J = 6.0 and 4.0 Hz), 3.50 (dd, 1 H, J = 18.0 and 6.0 Hz), 3.52 (d, 1 H, J = 18.0 Hz), 3.81 (s, 3 H), 6.85 (d, 2 H, J = 9.0 Hz), 7.30 (s, 5 H), and 7.80 (d, 2 H, J = 9.0 Hz); IR (KBr) 1600, 1500, 1340, 1240, and 1170 cm^{-1}; UV (ethanol) 281 nm (ϵ 20 500); mass spectrum, m/e 236 (base), 222, and 206.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.18; H, 6.08; N, 10.60.

Preparation of (*E*)-1-(*p*-Nitrophenyl)-4-phenyl-3-buten-1-one *N*-Tosylhydrazone (26). A stream of dry hydrogen chloride gas was bubbled into an ice-colled solution of 10.0 g of 1,3-propanedithiol and 14.5 g of *p*-nitrobenzaldehyde in 250 mL of chloroform for 15 min. The reaction mixture was stirred at room temperature for 12 h and was then washed with water, a 1% potassium hydroxide solution, and then a saturated salt solution. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting yellow solid was recrystallized from ethyl acetate to give 15 g (65%) of 1-(*p*-nitrophenyl)-1,1-dithiane as a yellow solid: mp 139–140 °C; IR (KBr) 1600, 1510, and 1340 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.10 (m, 2 H), 3.15 (m, 4 H), 5.28 (s, 1 H), 7.70 (d, 2 H, J = 9.0 Hz), and 8.20 (d, 2 H, J = 9.0 Hz).

To a solution containing 7.0 g of the above dithiane in 150 mL of dry xylene was added 3.36 g of potassium *tert*-butoxide. The mixture was stirred for 1 h at 25 °C and then 6.0 g of cinnamyl bromide was added in one portion. The reaction mixture was heated at reflux for 24 h and was then quenched with water. The organic layer was concentrated under reduced pressure, and the dark oil that was obtained was subjected to silica medium-pressure column chromatography using a 4% ethyl acetate–hexane mixture as the eluent. The second fraction isolated from the column contained 300 mg (6%) of 1-(*p*-nitrophenyl)-4-phenyl-3-buten-1,1-dithiane as a yellow solid: mp 109–110 °C; IR (KBr) 2900, 1600, 1510, 1340, and 950 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.8–2.2 (m, 2 H), 2.6–2.8 (m, 4 H), 2.90 (d, 2 H, J = 7.0 Hz), 6.05 (dt, 1 H, J = 17.0 and 7.0 Hz), 6.38 (d, 1 H, J = 17.0 Hz), 7.2–7.4 (m, 5 H), and 8.20 (m, 4 H); mass spectrum, m/e 240 (base), 194, and 166.

Anal. Calcd for $C_{19}H_{19}NO_2S_2$: C, 63.86; H, 5.36; N, 3.92. Found: C, 63.81; H, 5.29; N, 3.84.

To a solution containing 0.6 g of *N*-chlorosuccinimide and 0.86 g of silver nitrate in 5 mL of a 80% acetonitrile–water mixutre was added 400 mg of the above dithiane in 20 mL of acetonitrile. A white precipitate appeared immediately and the solution turned yellow. The mixture was stirred for 5 min at 25 °C, and 1 mL of a saturated sodium sulfite solution, 1 mL of a sodium carbonate solution, and 1 mL of a saturated sodium chloride solution were added in 1-min intervals. The organic layer was separated and the solvent was removed under reduced pressure to give 85 mg (30%) of (*E*)-1-(*p*-nitrophenyl)-4-phenyl-3-buten-1-one as a yellow solid: mp 129–130 °C; IR (KBr) 1690, 1600, 1510, 1340, and 950 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 4.00 (d, 2 H, J = 6.0 Hz), 6.3–6.7 (m, 2 H), 7.2–7.7 (m, 5 H), 8.20 (d, 2 H, J = 9.0 Hz), and 8.50 (d, 2 H, J = 9.0 Hz); UV (ethanol) 255 nm (ϵ 12 900); mass spectrum, m/e 267, 150, 117, and 77.

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.87; H, 4.87; N, 5.32.

To a 160-mg sample of the above ketone in 5 mL of dry tetrahydrofuran was added 140 mg of *p*-toluenesulfonylhydrazine. The mixture was stirred at room temperature for 4 days and was then concentrated under reduced pressure. The resulting oil was purified by flash chromatography using a 3% ethyl acetate–hexane mixture as the eluent to give 190 mg of (*E*)-1-(*p*-nitrophenyl)-4-phenyl-3-buten-1-one *N*-tosylhydrazone (**26**) as a yellow oil: IR (neat) 3230, 1600, 1500, and 1320 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.38 (s, 3 H), 3.52 (d, 2 H), 6.1–6.3 (m, 2 H), 7.20–8.30 (m, 13 H); UV (ethanol) 265 nm (ϵ 14 900).

Anal. Calcd for $C_{23}H_{21}N_3O_4S$: m/e 435.4882 (P^+). Found: m/e 435.4882 (P^+).

Pyrolysis of the Sodium Salt of (*E*)-1-(*p*-Nitrophenyl)-4-phenyl-3-buten-1-one *N*-Tosylhydrazone (26). To a solution containing 150 mg of the above hydrazone in 5 mL of dry tetrahydrofuran was added 34 mg (50% oil dispersion) of sodium hydride under a nitrogen atmosphere. The mixture was allowed to stir at 25 °C for 20 min and then 20 mL of pentane was added. The resulting precipitate was filtered and dried under vacuum. The white solid that remained was taken up in 10 mL of benzene and heated at reflux under a nitrogen atmosphere for 20 min. The precipitate that formed was filtered and the solvent was removed under reduced pressure to give 40 mg of a red oil whose structure was assigned as *trans*-1-phenyl-4-(*p*-nitrophenyl)-4-diazobut-1-ene (**32**) on the basis of its spectral properties: IR (neat) 1985, 1600, 1500, and 1320 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 3.52 (d, 2 H, J = 5.0 Hz), 6.0–6.4 (m, 2 H), 7.20–8.38 (m, 9 H). Further heating of this material produced a complex mixture of products which could not be separated even on extended chromatography. There were no detectable signs of a 1,2-diazabicyclo[3.1.0]hexene in the crude reaction mixture.

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Registry No. 1, 74457-33-3; **1**·Na, 74457-34-4; **2**, 74457-35-5; **3**,

74457-36-6; **4**, 74457-37-7; **6**, 23990-17-2; **8**, 891-22-5; **9**, 77764-69-3; **9**·Na, 84066-52-4; **10**, 77764-71-7; **11**, 36597-09-8; **12**, 76620-32-1; **12**·Na, 84066-53-5; **13**, 76620-31-0; **14**, 77764-70-6; **14**·Na, 76620-26-3; **15**, 76633-73-3; **16**, 76620-27-4; **16**·Na, 84066-54-6; **17**, 76620-30-9; **25**, 84066-55-7; **25**·Na, 84066-56-8; **26**, 84066-57-9; **26**·Na, 84066-58-0; **31**, 84066-59-1; **32**, 84066-60-4; *p*-toluenesulfonylhydrazine, 1576-35-8; 1,4-diphenyl-3-buten-1-one, 32363-55-6; *trans*-1,4-diphenyl-4-hydroxy-1-butene, 84107-76-6; phenylpropargyl bromide, 1794-48-5; benzaldehyde, 100-52-7; 1,4-diphenyl-3-butyn-1-ol, 17572-78-0; 1,4-diphenyl-3-butyn-1-one, 17572-79-1; *cis*-1,4-diphenyl-3-buten-1-one, 17572-77-9; phenyldithiane, 5425-44-5; 1-bromo-3-methyl-2-butene, 870-63-3; 1-phenyl-1-(3-methyl-2-butenyl)dithiane, 84066-61-5; crotyl chloride, 591-97-9; (*E*)-1-phenyl-1-(2-butenyl)dithiane, 84066-62-6; *trans*-1-phenyl-3-penten-1-one, 74157-93-0; 1-phenyl-1-(2-propynyl)dithiane, 84066-63-7; 1-phenyl-1-(2-butynyl)dithiane, 84066-64-8; 1-phenyl-3-pentyn-1-one, 76620-28-5; *cis*-1-phenyl-3-penten-1-one, 61752-45-2; cinnamyl bromide, 4392-24-9; anisoin, 30587-18-9; 1,2-di-*p*-anisyl-2-hydroxy-5-phenyl-4-penten-1-one, 84066-65-9; 1,2-di-*p*-anisyl-5-phenyl-4-penten-1,2-diol (isomer 1), 84066-66-0; 1,2-di-*p*-anisyl-5-phenyl-4-penten-1,2-diol (isomer 2), 84066-67-1; (*E*)-1-*p*-anisyl-4-phenyl-3-buten-1-one, 84066-68-2; *p*-nitrobenzaldehyde, 555-16-8; 1,3-propanedithiol, 109-80-8; 1-(*p*-nitrophenyl)-1,1-dithiane, 24588-74-7; 1-(*p*-nitrophenyl)-1-(3-phenyl-2-propenyl)-1,1-dithiane, 84066-69-3; (*E*)-(*p*-nitrophenyl)-4-phenyl-3-buten-1-one, 84066-70-6; diazomethane, 334-88-3; phenyldiazomethane, 766-91-6; *p*-hydroxyphenyldiazomethane, 84066-71-7; formyldiazomethane, 6832-13-9.

Palladium-Catalyzed Acylation of Unsaturated Halides by Anions of Enol Ethers

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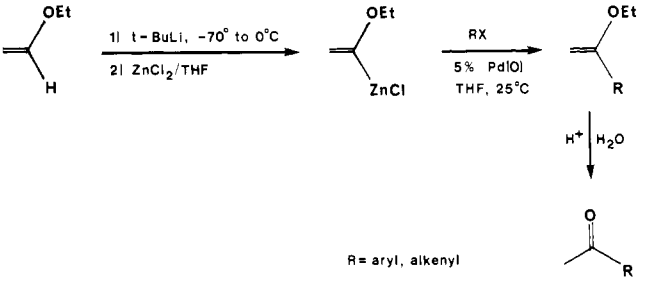
Abstract: Zinc salts of enol ether anions are coupled to aryl and alkenyl halides by using palladium catalysts, effecting a direct acetylation of aryl and alkenyl halides. Zinc salts of allenic ethers are coupled with aryl and alkenyl halides under similar conditions to give α,β-unsaturated ketones, the allenic ether serving as a source of the acryloyl group. Allenic ethers were γ arylated in a palladium-catalyzed coupling with aryl halides to give β,β-diaryl-α,β-unsaturated aldehydes.

Direct nucleophilic alkylation and acylation of unsaturated organic halides would be a useful procedure in synthesis, but, until recently, such reactions were rare. Recently developed organometallic processes include nickel- and palladium-catalyzed coupling of alkenyl halides with Grignard reagents[1] and the acylation of alkenyl halides by acylnickel carbonylates.[2] A major advance in this area was the result of Negishi's elegant and important work on transmetallation reactions, which resulted in very efficient procedures for the coupling of main-group organometallics to aryl, alkenyl, and allylic halides, using palladium catalysis.[3] Thus, alkenyl alanes have been coupled with aryl[4] and alkenyl[5] halides. Zirconium alkenes have also been coupled with aryl[6] and alkenyl[7] halides, and aluminum and zirconium alkenes have been coupled with alkenyl, alkynyl, and aryl halides by using $ZnCl_2$ as cocatalyst.[8] Alkynyl zincs have been coupled with alkenyl[9] and acyl halides,[10] aryl and benzyl zincs have been coupled with aryl halides,[11] and homoallyl- and homopropargyl zincs have been coupled with alkenyl halides.[12] Finally, alkenyl alanes and various aryl metals (Al, Cd, Mg, Zn, Zr) have been coupled with a variety of allylic substrates.[13]

Scheme I



For a number of synthetic problems, we had the need to directly introduce acyl and α,β-unsaturated acyl groups into aryl and alkenyl halides. From the work of Negishi cited above, it appeared that palladium-catalyzed reactions of these substrates with carbanions of enol and allenic ethers should perform the desired transformation.[14] Herein we report the results of our studies.

Results and Discussion

Acylation of Aryl and Alkenyl Halides with Enol Ether Anions. Initial studies centered on the simple acetylation of aryl and alkenyl halides. The enol ether of acetaldehyde was lithiated with *tert*-

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