

most easily obtained by bromination–dehydrobromination of the [4 + 2] adducts of conjugated dienes with SO_2 .¹⁶ To date, the only aminofulvenes we have studied introduce a hydrogen, a methyl, or a dimethylamino substituent into the azulene 4 position. Other substituents should be readily introduced at C-4 by a similar sequence, and substituted cyclopentadienes can be used to introduce substituents on the five-membered ring. Thus, a variety of seven-membered ring substituted azulenes may be obtained from cyclopentadiene, an amide, and a butadiene in six steps with typical overall yields of 5–40%.

As with any cycloaddition, three possible mechanisms can be considered. Although the data are limited, the lack of pronounced rate or yield differences observed when these reactions are carried out in benzene, chloroform, and methanol suggest that no zwitterionic intermediates are formed. Nevertheless, the pronounced nucleophilicity of the 2 position of the aminofulvene should cause bond formation between this position and the thiophene dioxide 2 position to proceed faster than bond formation between the fulvene 6 and thiophene dioxide 2' positions.

A qualitative pattern can be gleaned from the reaction times and yields reported in Table I. Alkyl substitution on the thiophene dioxide slows the reaction, while phenyl or chloro substitution accelerates the reaction. This is fully compatible with the idea that the electrophilicity of the thiophene dioxide determines its reactivity toward an aminofulvene. In terms of frontier orbital interactions, alkyl substitution lowers the thiophene dioxide electron affinity and lowers reactivity toward nucleophilic species, while chloro or phenyl substitution increases the electron affinity of the thiophene dioxide, and increases its reactivity toward nucleophilic species.¹⁷

Substitution of a 6-methyl or a 6-dimethylamino substituent on 6-dimethylaminofulvene should increase the nucleophilicity of the fulvene. Experimentally, a rate increase is not observed, probably because the addition of a 6 substituent sterically prevents the amino group lone pair from overlapping optimally with the fulvene π system. Thus, the ionization potentials of these 6,6-disubstituted fulvenes may be greater than that of 6-dimethylaminofulvene.⁴

For reactions of the unsymmetrical thiophene dioxides, two regioisomers can be formed, as shown in Scheme 11. We suggest naming these in analogy to the regioisomers which can be formed in the Diels–Alder reaction. The dimethylamino substituent is considered the dominant substituent on the fulvene. The pseudo-meta-regioselectivity observed for the 3-alkyl- or arylthiophene dioxides (formation of 6-substituted azulene) is precisely that expected on the basis of frontier orbital predictions for reactions involving two addends, both of whose electronic asymmetry is caused by electron-releasing substituents.^{17,18} Similarly, the 2,4-dimethylthiophene dioxide gives the predicted bis pseudo-meta regioisomer. However, the pseudo-para-regioselectivity observed for the reaction of 2-methylthiophene dioxide with 6-dimethylaminofulvene is opposite to the frontier orbital prediction, fitting better with a diradical-intermediate prediction. A satisfying explanation of the high regioselectivity observed must await further experimental and theoretical studies, but, in the examples now available, the attack of the nucleophilic fulvene occurs preferentially at the less substituted thiophene dioxide double bond, as is the case for Diels–Alder reactions of electron-rich dienes with benzoquinones.¹⁹

We are currently probing the general utility of this synthesis by studying the reactions of ring-substituted aminofulvenes and thiophene dioxides with other substituents and substitution patterns.

Preparation of 6-Methylazulene. 3-Methyl-3,4-dibromotetrahydrothiophene dioxide (3.0 g, 10 mmol) was dissolved in 75 mL of benzene. The solution was chilled to 0–5 °C, and triethylamine (3 mL, 20 mmol) was added. This solution was

stirred for 2 h, the triethylammonium bromide was filtered off, and the resulting solution was added to dimethylaminofulvene (1.5 g, 12.5 mmol). This solution was stirred at room temperature under a gentle stream of nitrogen for 72 h. The reaction mixture was evaporated to dryness, and the crude product was dissolved in 20% chloroform–petroleum ether. Insoluble material was filtered off, and the solution was chromatographed on alumina with petroleum ether eluent. The first fraction consisted of 6-methylazulene (0.36 g, 25% yield, based on dibromotetrahydrothiophene dioxide).

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Hydrogenation of 1,3-Butadiene with 1,3-Cyclohexadiene and D_2 over ZrO_2 Catalysts

Sir:

Recent evidence indicates that the *molecular* identity of hydrogen is conserved during hydrogenation of unsaturated hydrocarbons over certain metal oxide catalysts.¹ We have extended these observations to a more complex system involving the competitive hydrogenation of 1,3-butadiene both directly with dihydrogen and indirectly via the hydrogen donor

Table I. Comparison of Catalysts in Hydrogenation of 1,3-Butadiene

	Catalyst				
	ZrO ₂ ^a	ZnO ^{1d}	MoS ₂ ^{1e}	MgO ^{1f}	Co(CN) _x ³
Reaction temp, °C	0	29	Room Temp.	0	
Major product	<i>trans</i> -2-C ₄ '	1-C ₄ '	1-C ₄ '	<i>cis</i> -2-C ₄ '	<i>trans</i> (<i>x</i> ≤ 5.5) <i>cis</i> (<i>x</i> ≥ 6.0)
H ₂ -D ₂ Equilm	No	Yes	Yes	No	
Isotope effect	1.4	1.0-1.4	1.4-1.8		

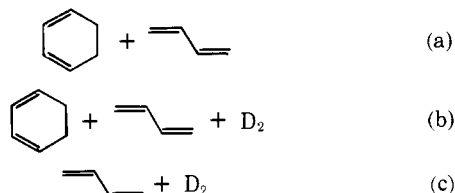
^a This work.**Table II.** Product Distributions

Reaction ^a	% convn ^b	Product distribution, %			
		1-C ₄ '	<i>trans</i> -2-C ₄ '	<i>cis</i> -2-C ₄ '	
a	6.7	75	5	20	
b	5.8	<i>d</i> ₀	74	8	18
		<i>d</i> ₂	68	15	17
c	6.0	<i>d</i> ₀	18	76	6
		<i>d</i> ₂	16	78	6

^a At 50 °C. ^b Based on 1,3-butadiene to butenes. ^c Product distribution including both *d*₀ and *d*₂ species.

molecule 1,3-cyclohexadiene over a ZrO₂ catalyst. Direct hydrogenation with H₂ gives primarily 2-butenes, whereas hydrogenation via the hydrogen donor molecule yields mainly 1-butene as the product. Reactions of this type are becoming important since hydrogen donor molecules can effect removal of sulfur and nitrogen from synthetic crude oil that has been derived from coal.²

The catalyst (50-m²/g surface area) was prepared by hydrolysis of ZrOCl₂ with aqueous ammonia to form an insoluble hydroxide which was dried and calcined in air at 500 °C. Three sets of reactions were examined separately between 0 and 75 °C in a closed recirculation reactor containing 0.40 g of catalyst, viz.,



Typical reaction mixtures contained 40 Torr of each component; no inerts were present in any experiment. The hydrocarbons were separated by gas chromatography, and the deuterium content of each component was measured mass spectrometrically. ¹³C NMR analysis was used to locate the position of the two D atoms in *trans*-2-butene-*d*₂.

When mixtures of D₂ and an olefin (such as propylene, isobutene, *n*-butene, or 1,3-butadiene) are passed over ZrO₂ between 0 and 75 °C, *d*₂ species are obtained exclusively as hydrogenated (deuterogenated) products over a wide range of conversion. Neither olefin D₂ exchange nor H₂-D₂ equilibration takes place.

Table I shows a comparison of the characteristics of several materials which catalyze the hydrogenation of 1,3-butadiene.

In attempting to explain these results, we discounted the possibility of *simultaneous* 1,2 addition of D₂ to the unsaturated compound because such an addition would violate the Woodward-Hoffmann rules for symmetry conservation. Although simultaneous 1,4 addition is *not* forbidden, steric factors make it unlikely that the observed *trans*-2-butene product could be formed by a simultaneous addition mechanism. It is

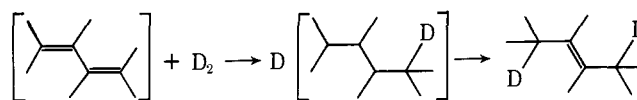
Table III. Isotopic Composition of *n*-Butenes in Reaction b

Product	% of product ^a	Isotopic Composition, %		
		<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂
1-C ₄ '	68	97	0	3
<i>trans</i> -C ₄ '	15	44	0	56
<i>cis</i> -C ₄ '	17	96	0	4

^a At 5.8% conversion of 1,3-butadiene to *n*-butenes.

much more likely that the reaction involves a *series* of surface reaction steps. A Langmuir-Hinshelwood mechanism (D and butadiene adsorbed on neighboring sites) is also unlikely, because rapid migration of dissociatively adsorbed H atoms would result in the scrambling of H and D atoms in the product molecules, which was not observed. If the adsorbed D (or H) atoms were bound so tightly to the surface that they do not migrate, there should then be a substantial, temperature dependent isotope effect, which also was not observed.

We believe the reaction probably involves a mechanism with H₂ (or D₂) reacting from the gas phase with a diolefin adsorbed strongly on isolated single sites, viz.,

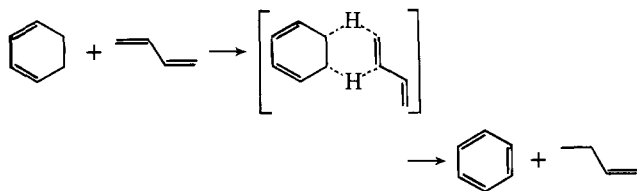


One D adds to form a methyl group, while the other D remains associated with the surface complex until becoming covalently added to the hydrocarbon. This mechanism will explain the observed reaction orders, the retention of molecular identity during hydrogenation, the absence of H₂-D₂ equilibration, and the temperature-independent isotope effect of ~1.4 which reflects the relative probability of collision of H₂ or D₂ (proportional to $\sqrt{M_{D_2}/M_{H_2}}$). This implies that the difference in zero point energies between H₂ or D₂ and their corresponding transition states must be the same.

The hydrogenation of 1,3-butadiene over ZrO₂ also takes place with the hydrogen being supplied directly from a hydrogen donor molecule such as 1,3-cyclohexadiene. Product distributions in reactions a, b, and c along with the isotopic distribution in reaction b are summarized in Tables II and III, respectively. Product distributions of *d*₀ and *d*₂ species for reaction b were calculated from Table III. Surprisingly, reactions a and c take place *independently* when both hydrogen sources are present in reaction b, reaction a being ~8 times faster than reaction c at 50 °C.

Since the deuterium content of 1-butene formed in reaction b remained constant (~97%) until most of the 1,3-cyclohexadiene was consumed, mixing of hydrogen and deuterium could not have occurred even though there was a small evolution of H₂ from the 1,3-cyclohexadiene. Hydrogenation by gaseous D₂ gives mainly *trans*-2-butene (78%), while hydrogen from the hydrogen donor gives predominately 1-butene (74%). The selectivity differences on various catalysts shown in Table I probably reflect the predominance of different surface inter-

mediate species, as Kwiatek³ has postulated, i.e., a σ -bonded intermediate gives 1-butene, while π -adsorbed intermediates give 2-butenes. However, this may not be the case in reaction b. The only factor that could account for the different products is the source of hydrogen. Thus, favorable formation of 1-butene in reactions a and b suggests the possible formation of an intermediate of the form



in which two H atoms are transported *simultaneously* to one end of the diolefin, which is an allowed process according to the Woodward-Hoffmann rules. In reaction c, which yields predominately 2-butenes, the process may occur via the reactive adsorption of dihydrogen from the gas phase directly onto adsorbed 1,3-butadiene.¹ ¹³C NMR analysis revealed that the two D atoms from D₂ are located almost exclusively on the 1 and 4 carbon atoms of *trans*-2-butene.

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Site of Protonation in Aromatic and Acyclic Amines and Acyclic Amides Revealed by N_{1s} Core Level Electron Spectroscopy

Sir:

Considerable gas phase proton affinity data has been collected in recent years by means of high pressure mass spectrometry and ICR techniques¹ and the data indicates that the behavior of the free molecule is frequently quite different from that in solution. Neither of the principally used proton affinity methods is capable of directly identifying the site of protonation in the molecule and those methods traditionally used to deduce this information (e.g., NMR) are done in solution in which the compound may behave differently. Alternatively, theoretical calculations² may be used to determine the most probable site of protonation.

A recent excellent correlation³ of the proton affinity of aniline and other substituted benzenes (C₆H₅X, X = F, Cl, H, CH₃, C₂H₅, NH₂) with STO-3G calculated shifts and Hammett σ^+ values in this series suggested that aniline might suffer protonation on the ring rather than at nitrogen, although a recent chemical ionization study⁴ and solution pK trends⁵ suggest preferential nitrogen protonation in this molecule.

We have measured the N_{1s} core ionization energy for a

Table I

Compd	$E_B(N_{1s}), eV$		Proton affinity, kcal
	This work, ^a	Other work	
Et ₃ N (1)	404.36	404.3 ^b	231.3 ^e
Et ₂ NH (2)	404.58	404.54 ^b	225.2 ^e
EtNH ₂ (3)	404.93	404.95 ^b	217.2 ^e
Me ₃ N (4)		404.79 ^{b,c}	225.6 ^f
Me ₂ NH (5)		404.90 ^{b,c}	220.6 ^f
MeNH ₂ (6)		405.14 ^{b,c}	213.1 ^f
NH ₃ (7)		405.6 ^b	202.3 ^g
Pyrrole (8)	406.18	406.1 ^d	209.45 ^f
Piperidine (9)	404.58		226.8 ^f
Pyrrrolidine (10)	404.60		223.3 ^e
Pyridine (11)	404.82		220.9 ^f
Aniline (12)	405.31		211.2 ^f
N-Monomethylaniline (13)	405.01		217.4 ^f
N,N-Dimethylaniline (14)	405.06		224.0 ^f
Cyclohexylamine (15)	404.72		222.0 ^f
Formamide (16)	406.30		
N-Monomethylformamide (17)	405.8		204.0 ^h
N,N-Dimethylformamide (18)	405.8		209.9 ^h

^a Relative to Ar_{2p(3/2)} 248.62 eV.⁹ ^b Reference 7. ^c Reference 6. ^d Reference 8. ^e Value given in ref 13 has been corrected to a PA(NH₃) of 202.3 kcal.¹² ^f Value given in ref 10 has been corrected to a PA(NH₃) of 202.3 kcal.¹² ^g Reference 12. ^h Reference 14 converted to PA(NH₃) of 202.3 kcal.¹²

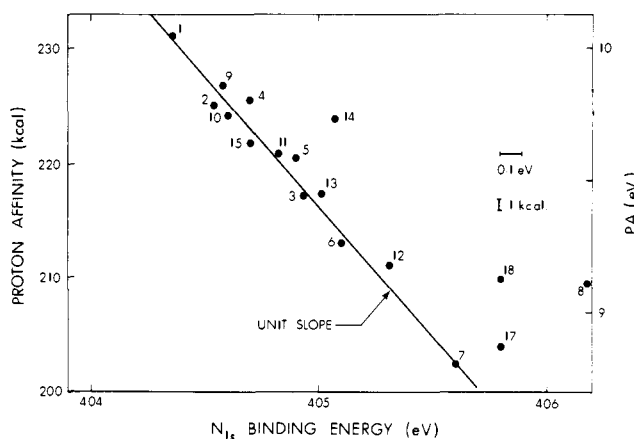


Figure 1. Correlation of N_{1s} binding energy with proton affinity of various amines and amides. The numbers refer to the compounds in Table I. The straight line has unit slope (23.1 kcal/eV) and is arbitrarily drawn through the NH₃ data point (compound 7).

number of gaseous amines extending previous data⁶⁻⁸ to these systems wherein the site of protonation may be ambiguous. The data (Table I) were obtained with a McPherson ESCA-36 instrument on gaseous samples of the amines at ~ 100 - μ pressure intimately mixed with similar amounts of Ar for calibration.⁹ The Mg K α x ray was used for excitation. Gas phase proton affinity data for the amines given primarily by Kebarle and coworkers^{10,11} has been corrected to the present prevailing value of 202.3 kcal for NH₃¹² as were the few other values taken from other work.^{13,14} The proton affinity data (Table I) correlated well with the N_{1s} binding energies as has been established for similar and related systems,^{7,15,16} as illustrated in Figure 1, especially if we assign generous limits of accuracy of ± 1.0 kcal to the proton affinities (although, if the differences have been obtained by constructing a "ladder",¹⁰⁻¹⁴ they are probably better than this) and ± 0.1 eV to the $E_B(N_{1s})$ values. The straight line is an arbitrary unit slope