molecule. In contrast, the Ga₃⁺ complex of the proline binder
4 showed a single set of signals with a pattern close to that of the
Fe³⁺ complex but amenable to NMR measurement (trace d) in CDC₁₃ solution (10 mM), 298 K. Residual signals of 3 in
trace d (ca. 20%) indicate slow exchange under these conditions.

[n-BuOCH₂CH₂CONHCH(−Bu)COOH]₃ showed almost identical chemical shifts for its diastereotopic protons in the NMR (Figure 1). This establishes the isomeric purity of
1. A priori, H bonds may involve equivalent or nonequivalent
amides of adjacent chains. In order to distinguish between these
two possibilities compound 2 with only one type of amide group
was examined. The IR spectrum of ester 2 showed two NH
absorptions (3435 and 3371 cm⁻¹, 0.65 mM CHCl₃) and its NMR
spectrum (Figure 1a) single signals for the diastereotopic protons
that do not impair the molecule’s conformational freedom. The H
bonds in amide 1 thus involve nonequivalent amides. This
ulti-
mately causes a tilt of the side chain to generate a propellerlike
arrangement.

Replacement of the isoproplamine 1 by methyl hydroxyl-
amine provided the Fe³⁺ binder 3. 3 adopted a bonded propellerlike conformation like the parent molecule 1 according to
its bonded NH (3284 cm⁻¹ in CDC₁₃) in the IR spectrum and the nonequivalence of its diastereotopic protons in the NMR (Figure 1e). Titration showed a 1:1 stoichiometry for Fe³⁺ binding, and CD
(Δε = +3.4 at 450 nm and −6.8 at 365 nm in MeOH) es-

tablished predominance of the A-cis isomer (trace d) in CDC₁₃, indicating weak H bonds that do not impair the molecule’s conformational freedom. The H
bonds in amide 1 thus involve nonequivalent amides. This
ulti-
mately causes a tilt of the side chain to generate a propellerlike
arrangement.

NMR analysis of the Ga⁺⁺ complex of 3 (which is structurally close to the Fe⁺⁺ complex but amenable to NMR measurement)
showed a single set of signals with a pattern close to that of the
free ligand (Figure 1d). This establishes the isomeric purity of the complex and its structural similarity to the uncomplexed
molecule. In contrast, the Ga⁺⁺ complex of the proline binder
4 showed a complex NMR pattern, indicative of isomeric mixtures.

These biomimetic tripodlike binders functioned as growth promoters of Arthrobacter flavescens. This mutant still contains
ferrichrome receptors but lacks the capability to produce ferrichrome. Therefore, its growth depends on externally added siderophores. Although the activity observed for some of these compounds described above was only around 1% of that of ferrichrome, this result is significant and suggestive of specific recognition. No synthetic compound tested so far on this very system, except for synthetic retrohydroxamate ferrichrome, has shown any activity. If and to which extent the chemistry of the natural ferrichromes is governed by some preorientation of con-
formation that favors certain pathways of complexation, as in
the artificial carriers, remains a topic of future research.

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The First [4 + 3] Cycloaddition of a 1,3-Dipole with a
1,3-Diene

Janusz Baran and Herbert Mayr

Institut für Chemie, Medizinische Universität zu
Lübeck, Ratzeburger Allee 160, D-2400 Lübeck 1
Federal Republic of Germany
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1,3-Dipolar cycloaddition reactions are usually considered to
proceed via concerted [4, + 2] mechanisms though arguments
for the stepwise nature have been presented. The nonstereo-

specific cycloaddition of an electron rich thioacyclohexyldride
with dimethyl dicyanofumarate, an electron deficient dipolarophile,
has just been reported as the first unequivocal example of a
nonconcerted 1,3-dipolar cycloaddition.

In accordance with the orbital symmetry rules, 1,3-dipoles have
been found to react with 1,3-dienes to give vinyl-substituted


cycloadditions have only been observed in the ozonation of an-
thracenes and in one case as an intramolecular variant.

Figure 2. Schematic representation of the A-cis Fe⁺⁺ complex of 3.

Figure 1. 270 MHz ¹H NMR traces of compound 2 (R = OMe, trace a), 1 (R = NH-i-Pr, trace b), 3 (R = N(Me)OH, trace c), and 3-Ga⁺⁺ (trace d) in CDC₁₃ solution (10 mM), 298 K. Residual signals of 3 in
trace d (ca. 20%) indicate slow exchange under these conditions.


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NMR, IR, MS, and elemental analysis (see Supplementary Material).


reactivity also toward a nitrone.

products nonterminal positions of the 1,3-diene fragment in 2519.

hexamethylcyclopentane with magnesium in THF, exhibits 1,4-
the diastereomeric for the unusually high percentage of 1,4-adducts formed from

Figure 1. Formation of 3a,b and 7 from 1 (0.456 mol/L) and 2 (0.453 mol/L) in toluene at 80.0 °C (5 and 6 could not be determined by the HPLC method used).

Scheme I

We have reported recently that the steric shielding of the nonterminal positions of the 1,3-diene fragment in 1 is responsible for the unusually high percentage of 1,4-adducts formed from 1 and dibromoaromatics. We report now that the diene 1, which was prepared by treatment of 1,2-(bisbromomethyl)-3,3,4,4,5,5-hexamethylcyclopentene9 with magnesium in THF, exhibits 1,4-reactivity also toward a nitrone.

C,N-Diphenylnitron (2) and 1,2-bis(methylene)-3,3,4,4,5,5-hexamethylcyclopentene (1) react in benzene at 80 °C to give the diastereomeric [3 + 2] cycloadducts 3a (28%) and 3b (4%), the [4 + 3] cycloadduct 7 (18%), and the partially oxidized products 8 (8%) and 9 (2%).10 Main evidence for the structure of 7 comes from the 13C NMR spectrum (triplets at δ = 31.46


(10) All new compounds have been completely characterized by 1H, 13C NMR, IR, MS, and elemental analysis (see Supplementary Material).

Figure 2. Schematic energy profiles for concerted and nonconcerted cycloaddition reactions of nitrones with ordinary 1,3-dienes.

Scheme II

and 74.59) and the catalytic hydrogenation of 7 to give 1-(hydroxymethyl)-3,3,4,4,5,5-hexamethyl-2-(2-phenylethyl)cyclopentene (10).

The constant ratio 3a:3b:7, which was observed at different degrees of conversion, excludes mutual interconversions of these compounds under the conditions of the cycloaddition (Figure 1). This conclusion is in accord with the observation that isolated samples of 3a, 3b, and 7 remained unchanged when heated in benzene for 2 days at 80 °C.

As shown in Scheme I, the [3 + 2] cycloadducts 3a,b may be formed by a concerted cycloaddition reaction or, like the other products, via the intermediate diradical 4. An alternative pathway for the formation of the [4 + 3] cycloadduct, generation of 12 via [4 + 2] cycloaddition12 of 1 and 2 and successive Meisenheimer rearrangement13 to give 7, has been ruled out by the experiments described in Scheme II. Compound 11 was oxidized to give the amine oxide 12, which can be assumed to have the same stereochernistry (phenyl groups trans) as the potential Diels–Alder adduct of 1 with 2. When 12 was heated in toluene at 80 °C in presence and absence of 2, compound 13 was formed, while 7 was not detectable.

If the applicability of the orbital symmetry rules is taken for granted, i.e., if a concerted [4 + 4] process cannot account for the formation of 7, the diradical 4 must be formed as an intermediate. The nonobservance of [4 + 3] cycloadducts in reactions of nitrones with ordinary 1,3-dienes may be explained in two different ways: (a) Nitron cycloadditions are concerted processes, and only the [3 + 2] cycloaddition is orbital-symmetry allowed (Figure 2a). (b) Nitron cycloadditions proceed stepwise, but cyclization to five-membered rings is normally preferred (Figure 2b).

If situation (a) were true, the formation of 7 from 1 and 2 would imply that the special steric situation in 1 increased the barrier of the concerted [3 + 2] process to the same height or above the barrier of the stepwise process. In this case, compound 1 should react more slowly than normal dienes. If Figure 2b were true,


the steric bulk in 1 might give rise to the formation of the [4 + 3] cycloadduct 7 at the expense of the [3 + 2] cycloadducts without affecting the overall addition rate. The rate constant for the 1,3-dipolar cycloaddition of 2 with 1-methyl-3-methylene-1-cyclohexene (14), a model compound which reacts at the exocyclic double bond exclusively, is of the same order of magnitude \( k_2 = 4.4 \times 10^{-5} \text{ L mol}^{-1} \text{s}^{-1} \), toluene, 80 °C, determined by HPLC as the corresponding value reported for the reaction of 2 with ethyl crotonate \( k_2 = 14 \times 10^{-5} \). A slightly smaller value \( k_2' = 1.1 \times 10^{-5} \) is derived for the reaction of 1 with 2 from Figure 1. As a consequence of the discussion related to Figure 2, the close similarity of the reactivities of 1 and 14 implies that in reactions of 2 with normal 1,3-dienes, generally a stepwise mechanism should be accessible, the activation energy of which is at most 2–3 kcal/mol greater than that of the concerted process.

The intermediate diradical 4 profits from allylic resonance, which would not be the case for intermediates formed from nitrones and alkylethylenes. Therefore, the mechanistic considerations on those cycloadditions are not affected by this work.

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Supplementary Material Available: Analytical data (mp/bp, 'H NMR, 13C NMR, IR, mass spectrum) for 3a, 3b, and 7–13 (4 pages). Ordering information is given on any current masthead page.

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Gaseous Negative Ions from Neutral Molecules and Positive Ions: New Information for Neutralization–Reionization Mass Spectrometry

Rong Feng, Chrysostomos Wesdemiotis, and Fred W. McLafferty

Chemistry Department, Baker Laboratory Cornell University, Ithaca, New York 14853-1301 Received July 6, 1987

Collisional activation of fast gaseous ions can lead to dissociation and/or charge permutation processes. \(^2\) \(^3\) Combinations of these are used in neutralization–reionization mass spectrometry (NRMS) \(^2\) to prepare fast gaseous neutrals from mass-selected multikilovolt ions. A further collision can dissociate the neutrals into structurally indicative fragments which are collisionally reionized into positive ions for mass analysis. \(^4\) In this way NRMS has been used recently to study unusual structures such as \( \text{H}_2\text{C}=\text{CHCH}_2' \), \( \text{H}_2\text{Cl} \), and \( \text{H}_2\text{C}(\text{HO})_2 \). \(^5\) We consider here the alternative reionization to negative ions, which previously has been applied only to \( \text{D}_2^+ \), \( \text{D}_3^+ \), \( \text{H}_2^+ \), \( \text{H}_3^+ \), \( \text{H}_4^+ \), \( \text{H}_5^+ \), and \( \text{C}_2\text{H}_4^+ \) molecules. Collisional charge reversal of positive ion mixtures (not subjected to mass analysis) has been used to prepare negative ions such as \( \text{C}_1^-, \text{HO}^-, \text{N}^- \). \(^6\) Gaseous anions have also been generated directly by electron impact, flowing afterglow, and chemical ionization techniques. \(^9\) We report here that collisional electron transfer to mass-selected cations or neutrals provides an alternative route to negative ions; the resulting mass spectra contain novel information on the structures and chemistry of the precursor cations and neutrals, as well as the product anions.

Generation of Negative Ions. The appropriate multikilovolt precursor ions are generated and mass-selected in the first mass spectrometer (MS-I) of the tandem mass spectrometer described previously \(^6\) to yield neutral molecules by charge-exchange neutralization or dissociation. \(^3\) These fast neutrals are reionized by collision to produce anions which, together with their anionic dissociation products, are measured by scanning MS-II. The spectrum obtained by Hg neutralization of allyl cations in the first collision region followed by deflection of the residual ions and subsequent Xe reionization in the second collision region \( \text{Hg}/\text{Xe NR}^- \) spectrum is shown in Figure 1A. Alternatively, a single target can effect the two-electron transfer; \(^7\) \(^8\) Figure 1B shows the resulting charge-reversal spectrum with Hg \( \text{Hg}^+ \) neutralization of \( \text{CH}_2=\text{CHCH}_2^+ \) produced 1.8% \( \text{CH}_2=\text{CHCH}_2^+ \).

Figure 1. (A) Hg (70%)/Xe (70% T), (B) Hg (15% T), and (C) Xe (15% T) NR spectra of \( \text{CH}_2=\text{CHCH}_2^+ \) from propene. Absolute abundance of \( \text{CH}_2=\text{CHCH}_2^+ \) in percent of the unattenuated \( \text{CH}_2=\text{CHCH}_2^+ \) main-beam abundance: (A) 0.00012; (B) 0.00095; (C) 0.00038. Hg \( 70\% \) neutralization of \( \text{CH}_2=\text{CHCH}_2^+ \) produces 1.8% \( \text{CH}_2=\text{CHCH}_2^+ \).
