preparation of a new class of charge-transfer salts.[17]

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for 2 and 3 (8 pages); tables of observed and calculated structure factors for 2 and 3 (23 pages). Ordering information is given on any current masthead page.

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13C NMR and Polarized IR Spectra of Vicinally Labeled [13C2]Cyclobutadiene in an Argon Matrix: Interconversion of Valence Tautomers

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We report the polarized IR spectrum of cyclobutadiene (1) aligned by photoselection and the static 13C NMR spectrum of vicinally 13C-dilabeled 1 in argon matrix. The rate of interconversion between [1,2-13C2]-1 (1A) and [1,4-13C2]-1 (1B) exceeds 10^3 s^{-1} at ~25 K.
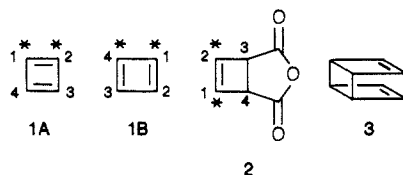
Cyclobutadiene[2] was initially assigned D_{4h} symmetry on the basis of its matrix-isolation IR spectrum,[3,4] in disagreement with most early[5-8] and all recent[9-12] calculations which predict a D_{2h} singlet ground state. Additional IR experiments led to the conclusion that the ground state is in fact rectangular.[13]

Heavy-atom tunneling has been proposed[14] to rationalize the activation parameters for valence tautomerization deduced from

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Table I. Typical Orientation Factors of IR Transitions of Photoaligned Rare-Gas Matrix-Isolated Cyclobutadiene (1)

sym	pol[a]	argon (10 K)		neon (2.8 K)	
		$\bar{v}$ (cm^{-1})	$K_u{}^b$	$\bar{v}$ (cm^{-1})	$K_u{}^b$
b_{3u}	x	576	0.379	576	0.365
b_{2u}	y	721	0.297		
b_{2u}	y	1245	0.298	1244	0.311
b_{1u}	z	1526	0.290	1527	0.310
$b_{2u}{}^c$	y	3107	0.294		
$b_{1u}{}^c$	z	3124	0.292		

^{a} x is the out-of-plane axis, and y is the short and z the long inplane axis. $^b K_u = \langle \cos^2 \bar{u} \rangle$, where $u = x, y,$ or $z,$ $\bar{u}$ is the angle between the molecular axis u and the laboratory axis Z, and the pointed brackets indicate ensemble averaging. The accuracy of the experimental determination from $K_u = d_u/(d_u + 2)$ was about ±0.01; $d_u = E_Z/E_Y$, where E_Z (E_Y) is the absorbance of light polarized along Z (Y).[21] ^{c} Assigned on the basis of calculated intensities.
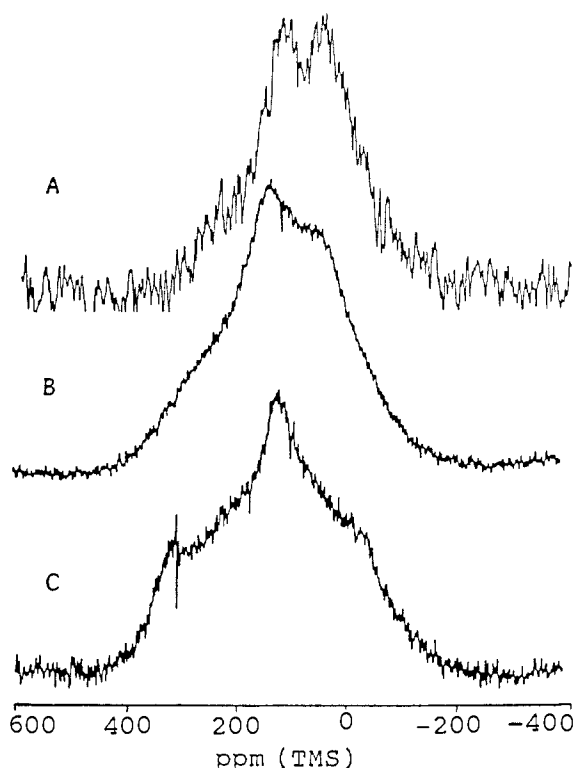

Figure 1. Experimental 13C NMR spectra of (A) cyclobutadiene (1) 13C-labeled in vicinal positions, (B) mixture of isotopomeric labeled cyclobutadiene dimers (3), and (C) [1,2-13C2]cyclobutene-3,4-dicarboxylic anhydride (2).

solution-trapping experiments[15,16] on vicinally dideuteriated 1. Calculations[17,18] have yielded tunneling rates of 10^5–10^{11} s^{-1} at –10 °C.

We have used the anhydride 2[19] as a photochemical source[20] of rare-gas matrix-isolated 1. UV irradiation with linearly polarized light produced persistent linear dichroism in the IR bands of argon matrix-isolated 1 and of its overirradiation product, C_2H_2. Persistent partial alignment was also observed for CO_2 produced from 2 with linearly polarized light. In neon matrices, alignment was observed only for 1. Under a variety of conditions, including temperatures as low as 2.8 K in Ne and 3.2 K in Ar, and a

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selection of UV wavelengths, the transition moment of the out-of-plane (x) polarized b_{3u} vibration at 576 cm^{-1} was partially aligned along the light polarization direction Z, while that of the short-axis in-plane (y) polarized b_{2u} vibrations at 1245 and 3107 cm^{-1} and of the long-axis in-plane (z) polarized b_{1u} vibrations at 721, 1526, and 3124 cm^{-1} all showed an identical degree of alignment away from Z (Table I). These are the results expected[21] under one or more of three sets of circumstances: (i) accidentally equal y-polarized and z-polarized fractions of UV absorption at all wavelengths tried, (ii) in-plane rotation of 1, either spontaneous or after excitation, but no rotation of CO_2 and C_2H_2 in argon, and (iii) interconversion of the valence tautomers.[22]

Argon matrix isolation dipolar ^{13}C NMR spectra of vicinally ^{13}C-labeled 1 demonstrated that (iii) applies. IR spectra showed that UV irradiation of 99% enriched $[1,2^{-13}C_2]$-2 produced 1A and 1B in an ~1:1 ratio. For the NMR measurement, the matrix was irradiated during the deposition of $[1,2^{-13}C_2]$-2 with argon (1:100) on a sapphire plate cooled to ~25 K by contact with a copper rod attached to the cold tip of an Air Products closed-cycle refrigerator inserted into the coils of a low-pressure mercury arc. The deposition was performed in eight portions, each followed by a 40-min irradiation without deposition. An NMR spectrum was obtained at a ^{13}C frequency of 20.12 MHz with cross-polarization.[24] Over many hours, the initial spectrum (Figure 1A) developed into that of an authentic sample of a mixture of isotopomeric dimers 3 (Figure 1B). The spectra of 1 and 3 were quite different from the spectrum of 2 (Figure 1C). By using a CsI substrate, IR measurements confirmed that at a 1:100 matrix ratio the dimerization of 1 is detectable after several hours at 25 K and complete after 4 h at 30 K.

The observed NMR spectrum of 1 (Figure 2A) was compared with simulations for a static noninterconverting 1:1 mixture of 1A and 1B (Figure 2B), for the case of very rapid interconversion between nonrotating 1A and 1B (Figure 2C), and for the two cases of rapid rotation:[25] Figure 2D, noninterconverting (1:1), and Figure 2E, rapidly interconverting 1A and 1B. The requisite ^{13}C chemical shielding tensor was computed by using the IGLO method[26,27] at the optimized[10] geometry. With a double-ζ basis set[28] the principal values were $\sigma_{11} = 349$, $\sigma_{22} = 83$, and $\sigma_{33} = 65$ ppm with respect to CH_4, with σ_{33} along x, σ_{11} 6° from z, and σ_{22} 6° from y. With the (951/51) basis set[28] contracted to (51111,311,1/311,1), the principal values were $\sigma_{11} = 324$, $\sigma_{22} = 87$, and $\sigma_{33} = 73$ ppm, and the tensor orientation was the same. Previous experience with this method of calculation on olefinic carbons[28,29] suggests that σ_{11} is not nearly as far downfield as calculated. From a correlation of computed and measured values[29] the true values were estimated to be $\sigma_{11} = 267 \pm 12$, $\sigma_{22} = 92 \pm 5$, and $\sigma_{33} = 78 \pm 9$ ppm. The results of the simulations are fairly insensitive to the values chosen.

The experimental spectrum is clearly different from the two simulated spectra which include rapid in-plane rotation (Figure
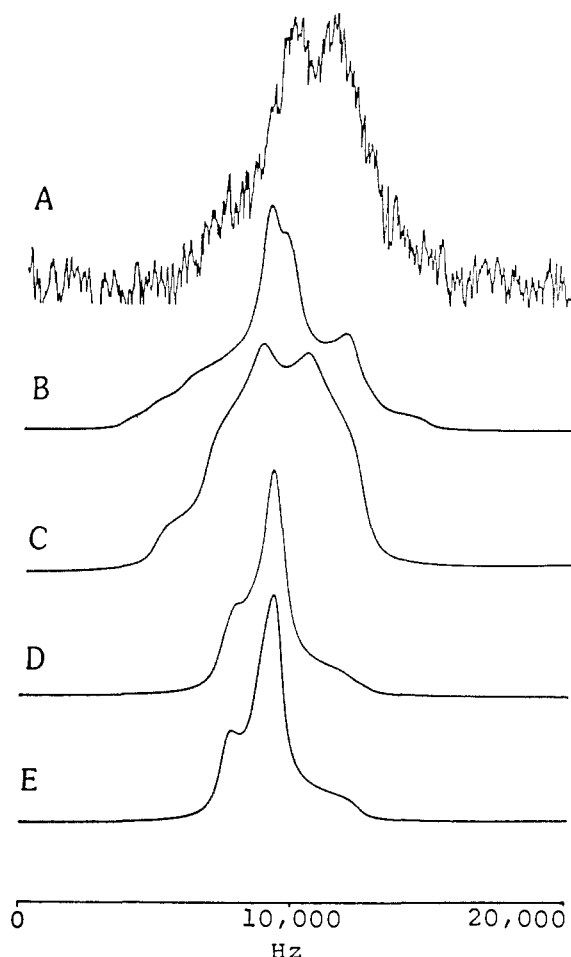

Figure 2. Observed ^{13}C NMR spectrum of cyclobutadiene (1) ^{13}C-labeled in vicinal positions (A) and simulated spectra expected for a static 1:1 mixture of 1A and 1B (B), nonrotating 1 rapidly interconverting between 1A and 1B (C), 1:1 mixture of rapidly rotating noninterconverting 1A and 1B (D), and rapidly rotating 1 rapidly interconverting between 1A and 1B (E).

2 (parts D and E)) and from that of a mixture of nonrotating and noninterconverting 1A and 1B (Figure 2B). It is close to the simulated spectrum of nonrotating rapidly interconverting 1A and 1B (Figure 2C).

Even a free adjustment of all fitting parameters did not produce a perfect simulation. Perhaps the interconversion rate is not quite in the fast limit, or some 2 or 3 is present, or the Simplex optimizing routine is not able to handle the large number of variables.

We conclude that matrix-isolated 1 interconverts rapidly ($>10^3$ s^{-1}) between its two valence tautometric forms at ~25 K, but we cannot differentiate between thermally activated and tunneling interconversion. However, if the interconversion barrier is 10–15 kcal/mol, as currently believed,[2,14] the interconversion in argon matrix must be due to tunneling at a rate of at least 10^3 s^{-1}, in qualitative agreement with calculations for the free molecule,[14,17,18] which should tunnel faster.

The results illustrate the power of rare-gas matrix-isolation ^{13}C NMR spectroscopy in deriving information about reactive intermediates. It should be noted that ^{13}C NMR spectra of somewhat unstable materials in an organic glass (methylketene[30]), in an argon matrix (ketene[28]), and of a highly reactive singlet biradical in an organic glass[31] have been reported previously.

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Methylaluminum Bis(2,6-di-tert-butyl-4-methylphenoxide) as a Protecting Group for Multifunctional Molecules: Synthetic Utility in Selective Carbonyl Reductions

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Selective reduction of one out of two different carbonyl moieties is an important synthetic operation.[1] The selectivity is commonly achievable by using modified hydride reagents formed by the replacement of hydride with sterically bulky substituents or electron-withdrawing groups in order to discriminate the structural or electronical environment of the carbonyl group, in which the sterically less hindered or electronically more labile carbonyl substrate is more easily reduced.[1,2] However, the opposite selectivity, i.e., selective reduction of the sterically more hindered or electronically less labile carbonyl substrate has never been attained.[3,4] Here we wish to disclose a conceptionally new approach to this problem. Our study began with experiments to test discrimination between two different carbonyl compounds by first complexing the less hindered carbonyl selectively with methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD)[5] and subsequent reduction of the more hindered carbonyl with nucleophilic hydride reagent as illustrated in Scheme I.

Treatment of a mixture of 1 equiv each of acetophenone and pivalophenone in CH_2Cl_2 with diisobutylaluminum hydride (DIBAH) (1 equiv) at -78 °C for 1 h gave 1-phenylethanol and 2,2-dimethyl-1-phenyl-1-propanol in 99% combined yield (ratio, 2.6:1). However, initial treatment of the two carbonyl substrates with MAD (1 equiv)[6] followed by reduction with DIBAH (1 equiv) at -78 °C resulted in the reversal of selectivity, producing

Scheme I

Hydride Attack at the Less Hindered Site

Hydride Attack at the More Hindered Site
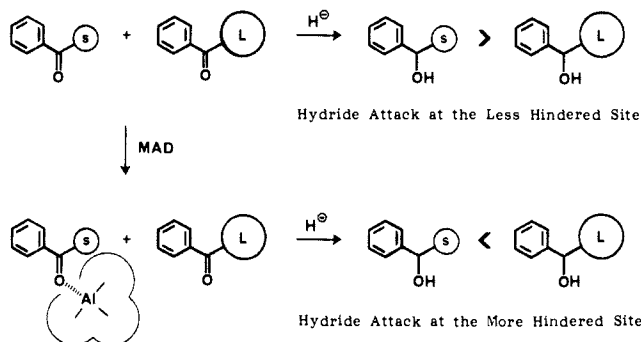
the corresponding alcohols (66% combined yield) in a ratio of 1:10. Although selective complexation between two different carbonyl groups with MAD is consistent with the above experiments, more direct evidence was obtained by low-temperature ^{13}C NMR spectroscopy. The 67.8 MHz ^{13}C NMR measurement of a mixture of 1 equiv each of MAD, acetophenone, and pivalophenone in CD_2Cl_2 at -70 °C showed that the original signal of acetophenone carbonyl at δ 198.3 shifted downfield to δ 213.6, whereas the signal of pivalophenone carbonyl remained unchanged.[7] Treatment of these ketones with excess MAD (2 equiv) and subsequent addition of DIBAH (1 equiv) resulted in greater selectivity (ratio = 1:16; 51% yield). Furthermore, use of 2 equiv each of MAD/DIBAH gave a satisfactory result in both selectivity and chemical yield (ratio = 1:16; 85% yield), suggesting that decomplexation of the more hindered pivalophenone and MAD is more readily facilitated by the action of DIBAH.[8] The effect of various aluminum hydride reagents was then examined by using a mixture of acetophenone and isobutyrophenone; Br_2AlH^9 was found to be more satisfactory in the case of aromatic ketones as illustrated in Table I. Other selected examples included in Table I clearly indicate the effectiveness of our approach in selective carbonyl reduction. The good selectivity is observed by pairing acetophenone with propiophenone, isobutyrophenone, and pivalophenone (entries 1-10). An electronic effect of substituents on the aromatic ring of acetophenone is also seen (entries 14 and 15). The strong resistance in camphor reduction should be interpreted in terms of the higher Lewis basicity of camphor combined with the sterically hindered camphor-MAD complex (entries 22 and 23). Discrimination between an aldehyde and a ketone with MAD was unsuccessful in view of the high reactivity of an aldehyde-MAD complex-to-hydride attack.

On the basis of data in Table I in combination with additional ketone discrimination experiments, the order of reducing susceptibility for various ketones is as follows[10]
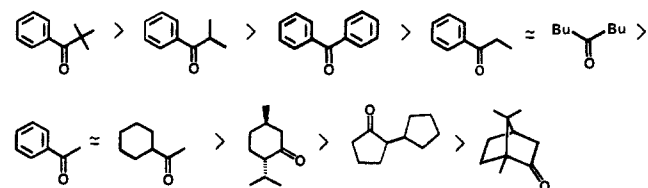
It is often required to reduce specific carbonyl groups in a regioselective manner in complex multifunctional molecules. A

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(6) MAD was prepared from 2,6-di-tert-butyl-4-methylphenol (2 equiv) and Me_3Al in hexane at room temperature and purified before use by crystallization from hexane followed by filtration in an argon box. Attempted use of unpurified MAD significantly lowered the selectivity.

(7) The signal of pivalophenone carbonyl appears at δ 209.2 compared to the original peak at δ 208.9. In contrast, the signal of pivalophenone-MAD complex appears at δ 232.6. For details, see Supplementary Material.

(8) Initial decomplexation of the more hindered ketone and MAD by the action of DIBAH followed by reduction of the resulting free ketone with DIBAH seems to be plausible, since the cis/trans ratio in the reduction of menthone or camphor are similar in the presence or absence of MAD.

(9) Prepared from $LiAlH_4$ and anhydrous $AlBr_3$ (3 equiv) in ether at 0 °C for 20 min.

(10) The order of reducing susceptibility in aliphatic ketone systems might be interpreted by the electronic effect of carbonyl groups which is correlated to the strength of the carbonyl absorption frequencies: cyclohexyl methyl ketone, 1709 cm^{-1} (C=O); menthone, 1710 cm^{-1}; 2-cyclopentylcyclopentanone, 1740 cm^{-1}; camphor, 1746 cm^{-1}.