the pK gap even further, so that ΔpK_0 in **1** would probably be much less than 20,[21] and ΔpK^* could easily become zero, since substituent electronic effects are generally more pronounced in excited states.[22] In addition, we have already shown that external proton transfers to carbon in S_1 can be quite fast ($k_{H^+} \sim 10^6-10^7$ M^{-1} s^{-1}).[6]

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(21) Using available ρ and σ values (Jones, R. A. Y. "Physical and Mechanistic Organic Chemistry"; Cambridge Univ Press: Cambridge, 1979. Hammett, L. P., "Physical Organic Chemistry"; McGraw-Hill: New York, 1970. Noyce, D. S.; Schiavelli, M. D., *J. Am. Chem. Soc.* **1968**, *90*, 1020) and assuming $\sigma_0 \cong \sigma_p$, we can estimate that for **1**, the ground-state pK gap between pK_a (phenol) and pK_{BH^+} (phenylacetylene) would be reduced by approximately 4 log units.

(22) Baldry, P. J. *J. Chem. Soc., Perkin Trans.* **1979**, *2* 951.

Selective Cyclobutane Adduct Formation in Competition with Diels–Alder Addition in Cation Radical Cycloadditions

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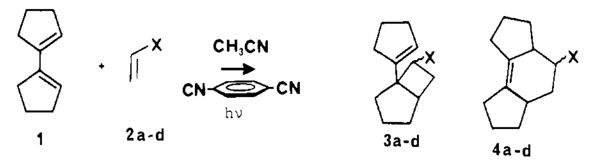
Although cyclodimerization of conjugated dienes could, a priori, yield adducts of three distinct types (vinylcyclohexenes, divinylcyclobutanes, and cyclooctadienes), in reality essentially only Diels–Alder adducts are obtained in the cation radical catalyzed cyclodimerizations of dienes,[1-3] in accord with formal selection rules.[4] More detailed theoretical considerations, however, suggest that irrespective of their formal symmetry status cation radical pericyclic reactions quite generally have extraordinarily low activation barriers.[4] Indeed, the symmetry-forbidden cation radical cyclodimerization of alkenes to give cyclobutanes has recently been shown to proceed efficiently under conditions identical with those of the (allowed) cation radical Diels–Alder.[5] Consequently, though the preference for the Diels–Alder mode in diene/diene cycloadditions is synthetically useful, it appears unlikely to be overwhelmingly large, so that competitive or even selective cyclobutane formation might be feasible in some cycloadditions. We wish to record the initial observations of selective cyclobutane formation in competition with the Diels–Alder mode in the cycloaddition of electron-rich alkenes and styrenes to certain conjugated dienes. In addition to the theoretical interest in this novel chemoselection mode and its basis, the reaction represents an attractive synthetic approach to selective construction of functionalized vinylcyclobutanes. Efficient transformation of the latter into cyclohexenes is found to provide the further option of convenient, indirect access to the formal Diels–Alder adducts.

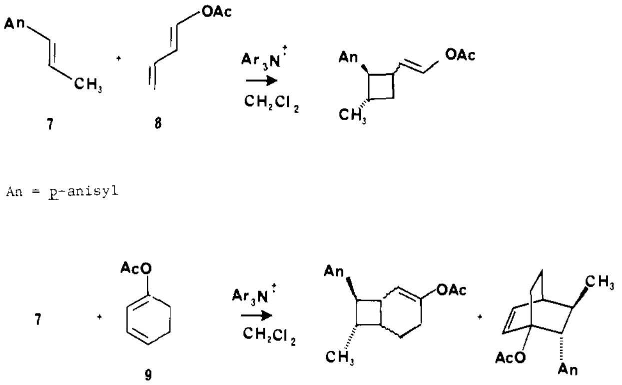
Reaction of 1,1′-dicyclopentenyl (**1**) with ethyl vinyl ether (**2a**) under photosensitized electron-transfer (ET) conditions[3] was observed to yield the cyclobutane adduct **3a** (Scheme I) in 71% yield with high chemoselection (98.1%) relative to **4a** (1.9%). The latter, synthesized independently, proved to be stable under the ET reaction conditions. Cycloadducts **3a** and **4a** were not formed in control irradiations in the absence of the ET sensitizer. Owing to the instability of **3a** toward tris(*p*-bromophenyl)aminium hexachlorostibnate (**5**, $Ar_3N^{+}\cdot$) in methylene chloride, this reaction could not be effected by aminium salt catalysis, but all of the remainder of the reactions discussed herein except that of **2d** were carried out by both types of cation radical procedures (ET and $Ar_3N^{+}\cdot$), similar results being obtained from each method. Reaction of **1** with two other electron-rich alkenes (**2b,c**) also yielded primarily the cyclobutane adducts (**3b,c**) along with minor amounts of **4b,c** (Scheme I). Reaction of **2a** with 1,1′-dicyclohexeneyl proceeded likewise, giving only 2.4% of the Diels–Alder adduct. These results contrast sharply with the cation radical diene/diene cycloadditions and more directly with the additions of **2b,c** to 1,3-cyclohexadiene (**6**),[3] all of which show high Diels–Alder chemoselection (**2a** failed to add to **6**). The disparate behavior of **1** and **6** cannot derive solely from the relative s-cis populations of these dienes, since dienes like **1** are known to be relatively cis rich, whereas the additions to **1** are capable of very high cyclobutane chemoselection.

Scheme I



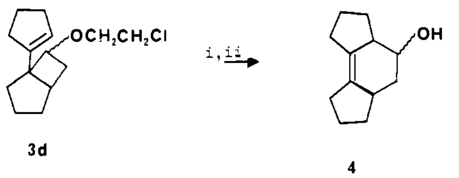
Cpd	X	%	%
a	OEt	98.1	1.9
b	OPh	82.5	17.5
c	SPh	68.7	31.3
d	OCH_2CH_2Cl	96.9	3.1

Scheme II



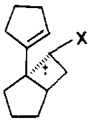
An = p-anisyl

Scheme III



i = $\underline{n}$-BuLi,Et_2O,HMPA

ii = KH,THF,Δ



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The ability of electron-rich styrenes to give similarly high cyclobutane chemoselection is illustrated (Scheme II) in the cation radical addition of *trans*-anethole (**7**) to 1-acetoxybutadiene (**8**) and 1-acetoxy-1,3-cyclohexadienbe (**9**). The former reaction was carried out under both ET (40% yield) and aminium salt (23%) conditions. In both cases only the cyclobutane adduct was obtained (3.8:1 t:c isomer ratio). The reaction with **9** was carried out by aminium catalysis only (28%) and gave the cyclobutane and

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(1) Bellville, D. J.; Wirth, D. W.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

(2) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665.

(3) Bauld, N. L.; Bellville, D. J.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 5158.

(4) Bauld, N. L.; Bellville, D. J.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(5) Bauld, N. L.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 633. For the photosensitized electron-transfer dimerization of olefins, see: Neunteufel, R. A.; Arnold, D. R. *Ibid.* **1973**, *95*, 4080. Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677.

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Diels–Alder adducts in a 2:1 ratio.

The propensity for cyclobutane chemoselection in cation radical cycloadditions of electron-rich alkenes and styrenes to some dienes, though by no means universal, contrasts with the consistent cyclohexane chemoselection observed in diene/diene cycloadditions. This divergent behavior, though not yet completely understood, is considered to derive, at least in part, from the fact that, whereas Diels–Alder addition to electron-rich alkenes and styrenes requires complete deconjugation of the donor substituent from the cation radical site in the adduct, the cyclobutane-forming process does not. This unusual circumstance is engendered by the fact that the adduct cyclobutane cation radicals almost certainly have a "long-bond" structure (e.g., **10**), in which the donor substituent is still highly stabilizing, rather than a fully closed cyclobutane structure. Both theoretical[6,7] and experimental[5] studies have strongly implicated long-bond structures as the sole minimum for σ cyclobutane cation radicals, and this is especially true when donor substituents such as alkoxy are attached. In contrast, the π cyclohexene cation radical moiety in the Diels–Alder adducts is expected (and has been calculated[8]) to have a normal (i.e., closed) π cation radical structure. It is, consequently, not implausible to suggest that cyclobutane cation radical adducts (with retained substituent stabilization and considerable relief of cyclobutane ring strain as a result of the long-bond structure) can, in many cases, achieve stability greater than the corresponding cyclohexene cation radical adduct. This order of product stabilities could then be reflected in the transition states for cyclization as product development control. Extended basis set (3-21G) ab initio reaction-path calculations now in progress as well as further experimental studies should shed further light on the basis for the novel cyclobutane chemoselection.

Thermal rearrangement of vinylcyclobutanes is well-known to give cyclohexenes, providing an indirect route to the Diels–Alder adducts as an additional synthetic option.[9] However, in view of the special facility of the "anionic oxy" vinylcyclobutane rearrangement,[10] the cycloaddition of **1** to β-chloroethyl vinyl ether (**2d**) was performed under ET conditions.[11] Treatment of **3d** with *n*-butyllithium in ether/HMPA gave **3** (X = OH) in 70% yield.[12] Rearrangement of the latter afforded the Diels–Alder adduct **4** (X = OH) in 60% unoptimized yield (Scheme III).[10]

The conversion of **1** and **2a** to **3a** on a preparative scale is illustrative of the general procedure for selective cyclobutane formation:

A solution of 10 g of **1** (74 mmol) and 64 g of **2a** (887 mmol) dissolved in anhydrous acetonitrile (120 mL) containing 26 mol % (2.5 g) of 1,4-dicyanobenzene (ET) was irradiated through a Pyrex filter under argon atmosphere for 56 h at room temperature by a 450-W Hanovia medium-pressure mercury vapor lamp housed in a water-cooled immersion jacket. Evaporation of the solvent, removal of the ET by extraction of the crude into pentane, and column chromatography (silica gel, pentane) yielded 10.9 g (71%) of **3a** as an oil.[13]

Acknowledgment. We thank the National Science Foundation (NSF CHE-8121700) for support.

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(6) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 5700.

(7) Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145. Ab initio (3-21G; 6-31G*) calculations of the cation radical olefin cycloaddition path are described.

(8) Bauld, N. L., unpublished research. The cyclohexene cation radical structure was fully optimized at the 3-21G level.

(9) Ellis, R. J.; Frey, H. M. *Trans. Faraday Soc.* **1963**, *59*, 2076.

(10) Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 520.

(11) This particular cation radical cycloaddition was much more efficient in methylene chloride than acetonitrile.

(12) Danheiser, R. L.; Davila, C. M.; Morin, J. M. *J. Org. Chem.* **1980**, *45*, 1340.

(13) This product and all others mentioned in this paper were fully characterized by GC/MS, high-resolution MS, and ^{1}H and ^{13}C magnetic resonance spectroscopy. Wherever carbonyl or hydroxyl groups are present, infrared spectral data also support the assignment. All products were obtained as diastereomeric mixtures, but these were not separated, except in the case of **4** (X = OH), where careful silica gel chromatography yielded both isomers cleanly.

Carbon Dioxide Chemistry. The Synthesis and Properties of *trans*-[Mo(CO$_2$)$_2$(PMe$_3$)$_4$]: The First Stable Bis(carbon dioxide) Adduct of a Transition Metal

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The coordination of a CO$_2$ molecule to a transition-metal center is considered to be the first step in its activation,[1] since it is through coordination that the electronic structure and the reactivity of the molecule are modified. We have recently reported[2] that the reaction of *cis*-[Mo(N$_2$)$_2$(PMe$_3$)$_4$] (**1**) with CO$_2$ yields a carbon dioxide complex of composition [Mo(CO$_2$)$_2$(PMe$_3$)$_4$] (**2**) in addition to the disproportionation products [Mo(CO$_3$)(CO)(PMe$_3$)$_4$] (**3**) and [Mo(CO$_3$)(CO)(PMe$_3$)$_3$]$_2$ (**4**). For **2** no clear distinction could be made between the two structural possibilities envisaged, namely a bis CO$_2$ adduct [Mo(CO$_2$)$_2$(PMe$_3$)$_4$] and a head-to-tail dimer [Mo(C$_2$O$_4$)(PMe$_3$)$_4$]. In this paper we report a straightforward high-yield preparation[3] of **2** and present chemical and spectroscopic evidence that demonstrate this compound is the first stable bis CO$_2$ adduct of a transition metal, *trans*-[Mo(CO$_2$)$_2$(PMe$_3$)$_4$].

Complex **2** is a yellow, moderately air-stable solid[4] that can be heated in vacuo at ca. 50 °C for 4–5 h without decomposition, although it decomposes quickly at higher temperatures (70–80 °C). In solution it is only moderately stable, decomposing slowly at 25 °C, even under N$_2$, although decomposition is prevented by addition of PMe$_3$. Since we have been unable to obtain crystals suitable for X-ray analysis, a detailed investigation of its chemical and spectroscopic properties has been undertaken.

While the addition of MeI or I$_2$ to solutions of **2** produces CO$_2$ (detected by GC), the coordinated CO$_2$ cannot be displaced by N$_2$ or C$_2$H$_4$. Interaction with CO, however, affords *cis*-[Mo(CO)$_2$(PMe$_3$)$_4$] and CO$_2$, and reaction with COS yields [Mo(S$_2$CO)(CO)$_2$(PMe$_3$)$_2$], which can also be obtained from *cis*-Mo(N$_2$)$_2$(PMe$_3$)$_4$ and COS. This strongly favors formulation of **2** as a Mo(0) species, a proposal also supported by spectroscopic data. Thus the ^{31}P NMR spectrum consists at 20 °C of a broad unresolved signal which becomes a sharp singlet at 50 °C and converts at −60 °C into a pattern of lines characteristic of an AA′BB′ spectrum (δ_A 1.88, δ_B −3.25; $^2J_{AB} = 144.4$, $^2J_{AB'} = -17.8$, $^2J_{AA'} = 14.5$, $^2J_{BB'} = 23.3$ Hz). From these data a trans geometry, A, similar to that found for the ethylene complex analogue *trans*-[Mo(C$_2$H$_4$)$_2$(PMe$_3$)$_4$],[5] can be proposed for this compound.[6] In agreement with this, the room-temperature ^{13}C NMR spectrum of **2*** (50% enriched in ^{13}C) shows a quintet at δ 206.1 ($^2J_{PC} = 17.9$ Hz) in the region expected for coordinated carbon dioxide.[7] Furthermore, the ^{31}P NMR of **2*** recorded at 60 °C clearly shows

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(1) Sneeden, R. P. A. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford, 1982; Vol. 8. For other recent reviews on CO$_2$ chemistry see ref 1 of ref 2, this paper.

(2) Carmona, E.; Gonzâlez, F.; Poveda, M. L.; Marin, J. M.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3365.

(3) Compound **2** has been independently prepared by M. L. H. Green.

(4) In a typical preparation a solution of 0.68 g (ca. 1.5 mmol) of **1** in 150 cm^3 of petroleum ether was pressurized in a 250 cm^3 capacity Fischer-Porter vessel, with 5 atm of CO$_2$. The mixture was left aside for ca. 12–18 h and the resulting yellow solid filtered off and washed with petroleum and diethyl ether (yield 0.57 g, 80%). The compound can be recrystallized from toluene or tetrahydrofuran.

(5) Carmona, E.; Marin, J. M.; Poveda, M. L.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3014.

(6) A similar structure with the bonded C–O groups eclipsed with respect to one another but staggered with respect to the *trans*-P–Mo–P vectors would also be consistent with these data.

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