(7) Small impurity signals were present in this spectrum.

(8) Since traces of mercury vapor were present in this and the subsequently described experiments, the decomposition of **2** may have been mercury-sensitized in part. The anhydride shows substantial absorption at 2537 Å, however ($\lambda_{max}^{CH_3CN}$ 240 mm, ε 540), and photolysis with an unfiltered medium-pressure mercury arc ("reversed" 2537 Å line) also yields **4**.

(9) Thermal isomerization of the syn and anti dimers of cyclobutadiene itself is discussed by H. M. Frey, H. D. Martin, and M. Hekman, *J. Chem. Soc., Chem. Commun.*, 204 (1975); R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Slegeir, *J. Am. Chem. Soc.*, **96**, 7581 (1974).

(10) For other examples of this phenomenon see, e.g., D. R. Arnold, N. C. Baird, J. R. Bolton, J. C. D. Brand, P. W. M. Jacobs, P. deMayo, and W. R. Ware, "Photochemistry", Academic Press, New York, N.Y., 1974, Chapter 6.

(11) Direct photolysis of cyclic anhydrides is described by A. Zweig, K. R. Huffman, J. B. Gallivan, M. K. Orloff, and F. Halverson, *J. Am. Chem. Soc.*, **96**, 1449 (1974). For mercury-sensitized decomposition, see I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 4349 (1969).

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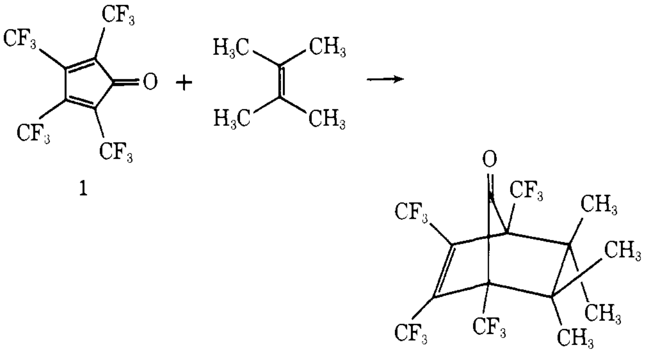
Received April 21, 1975

Perfluorotetramethylcyclopentadienone as a Diels–Alder Diene

Sir:

Largely ignored since its discovery and characterization by Wilkinson's group in the early 1960's,[1,2] perfluorotetramethylcyclopentadienone (**1**) is nonetheless a remarkable compound. This highly volatile yellow solid is stable as a monomer, apparently by virtue of the bulk of its trifluoromethyl substituents.[3] Its resistance to dimerization disguises the fact that **1** is an extremely reactive molecule, one aspect of whose multifaceted chemistry provides the substance of this report.

When petroleum ether solutions of the dienone and tetramethylethylene are combined, a deep burgundy color attributable to π-complexation[4] develops immediately but fades upon standing at room temperature. Removal of the solvent gives the Diels-Alder adduct **2** in excellent yield.



1

2

The structure of **2** is established by its microanalysis, ^{19}F and ^{1}H NMR spectra (Table I), high-frequency carbonyl stretching absorption (1825 cm^{-1}, CCl$_4$),[5] and an ultraviolet maximum at 235 nm (ε 903, cyclohexane) attributable to the homoconjugated enone chromophore. Diels-Alder addition of **1** to ethylene is much faster, presumably for steric reasons (k = 0.3 l. mol^{-1} sec^{-1} in dioxane, 28°). This rate is virtually identical with that of the reaction between ethylene and dimethyl *sym*-tetrazinedicarboxylate, a super "diene" in the "Diels-Alder reaction with inverse electron demand".[6]

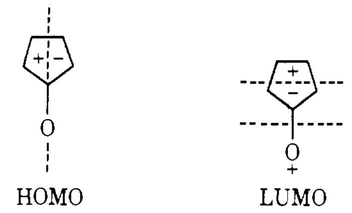
More vigorous conditions are required for reaction of **1** with conventional dienophiles, but dimethyl maleate and fumarate, for example, add readily and stereospecifically at 120°. The reactions yield a single cis and the trans diester, respectively.[7] Table I also contains adducts obtained from several other olefins.[8]

Acetylene adds to **1** rapidly even below room temperature, yielding, after spontaneous extrusion of carbon monoxide, perfluoro-1,2,3,4-tetramethylbenzene. Again, the reaction is general for acetylenes; e.g., dimethyl acetylenedicarboxylate gives the expected phthalate in excellent yield at 120°.

Attack of dienone **1** on conjugated dienes was explored in order to learn which component would assume the diene role in the Diels-Alder addition. In very facile reactions with 1,3-cyclohexadiene, furan, and cyclopentadiene, the dienone played that part in every case (see Table I).

When naphthalene and **1** are combined, the green charge transfer complex[2] slowly disappears even at 80° with the formation, in high yield, of a mixture of 1:2 adducts. Not surprisingly, attempts to obtain adducts with benzene, which gives an orange charge-transfer complex,[2] have failed.[9]

Cyclopentadienones owe their great reactivity principally to a low-lying LUMO and the consequently narrow gap between frontier molecular orbitals.[10] The four powerfully electron-withdrawing trifluoromethyl groups of dienone **1** should increase the effective Coulomb integral at the attached ring carbons, thus dropping both HOMO and LUMO energies below those of the parent molecule. The gap between them should widen somewhat since the HOMO encompasses only these carbons while the LUMO has substantial coefficients at all six skeletal atoms. Indeed, the long-wavelength uv maximum of **1** (340 nm, CCl$_4$[2]) is consistent with this surmise (cf. that of 3-*tert*-butylcyclopentadienone: 380 nm, isooctane[10]). More important for explaining the special properties of **1** is the fact that the LUMO, which is "bonding" even in the parent dienone (HMO approximation[11]), must lie extraordinarily low. Hence, the perfluorodienone's enthusiasm for charge-transfer complex formation and cycloaddition with donor π-systems is easily understood.



The regiochemistry of the reactions of **1** with dienes runs counter to the clear prediction from simple molecular orbital theory that the dienone should function as the dienophile.[10,12] Theory gains credence from the finding that cyclopentadienone itself behaves as expected toward cyclopentadiene.[13] Examination of models suggests that the aberrant behavior of **1**, which is shared by other highly substituted cyclopentadienones,[3] is determined by steric interactions in the Diels-Alder transition states.

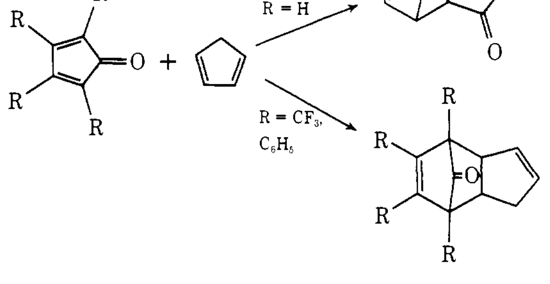
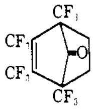
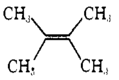
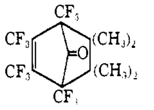
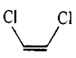
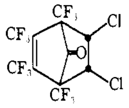
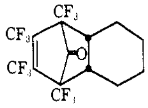
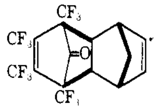
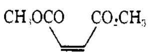
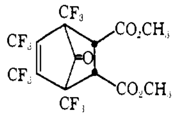
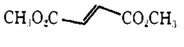
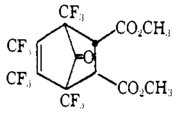
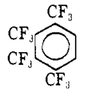
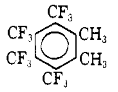
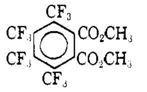
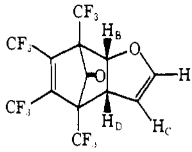
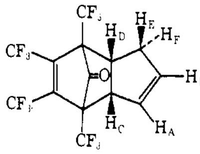


Table I. Diels–Alder Products from Perfluorotetramethylcyclopentadienone[a, b]

Addend	Product	Mp, °C	^{19}F NMR spectrum[c]		^1H NMR spectrum[d]
			Bridgehead	Vinyl	
$H_2C{=}CH_2$		27–28	11.74	20.57	1.74–2.83, nearly symmetrical pattern
		128	18.12	21.70	1.17 (s, 6 H, endo), 1.26 (q, J = 2.4 Hz, 6 H, exo)
		79–80	12.27	20.39	5.03 (s)
		123–124	13.33	20.89	0.88–1.98 (m, 8 H), 2.65–3.03 (m, 2 H)
	[e]	98	13.40	20.12	1.36, 1.79 (AB d, J = 11 Hz, 2 H), 2.80 (s, 2 H), 3.17 (subsplit s, 2 H), 6.34 (subsplit s, 2 H)
		118	13.55	21.77	3.71 (s, 6 H), 4.00 (s, 2 H)
		75	13.26 (q, J = 12 Hz) 15.30 (q, J = 12 Hz)	20.85	3.24, 4.18 (AB d's, J = 5 Hz, 2 H), 3.78 (s, 3 H), 3.82 (s, 3 H)
$HC{\equiv}CH$		21 (bp 176)	14.97	18.57	8.13 (subsplit s)
$CH_3C{\equiv}CCH_3$		98	23.37	27.02	2.49 (q, J = 2.8 Hz)
$CH_3O_2CC{\equiv}CCO_2CH_3$		109.5	24.08	25.96	3.93 (s)
		68.5–68.8	9.66	15.51	4.18 (subsplit d, H_D), 5.07 (t, H_C), 5.58 (d, H_B), 6.45 (d of d, H_A), $J_{AC} \cong 2.5$; $J_{AD} \cong 1.5$, $J_{BD} \cong 9.5$, $J_{CD} \cong 2.5$ Hz
		79–80	13.00 (q, J = 11 Hz) 13.25 (q, J = 11 Hz)	21.42	2.06–3.04 (subsplit AB q, H_F, H_E), 3.28–3.64 (t of d, H_D), 3.93–4.23 (m, H_C), 5.47–5.72 (m, H_B), 5.94–6.14 (septet, H_A)

[a] All products gave satisfactory elemental analyses. [b] All reactions proceeded readily at room temperature or below except those with dienophiles bearing methoxycarbonyl groups or chlorines. [c] Spectra were run in $CDCl_3$ and chemical shifts are reported in ppm downfield from external trifluoroacetic acid. Except where indicated, each signal is a multiplet, symmetrical or nearly so. Some of the ^{19}F chemical shifts were found to be rather concentration dependent. [d] Spectra were run in $CDCl_3$ and chemical shifts are reported in ppm downfield from internal tetramethylsilane. [e] The narrowness of the ^1H NMR signal at δ 2.80 indicates that the fluorinated moiety is joined in exo fashion to the norbornene skeleton.

Perfluorotetramethylcyclopentadienone decomposes only slowly at 300° ($t_{1/2} > 1$ hr), and it is photostable in the absence of oxygen even when irradiated with an unfiltered mercury arc in the gas phase. The dienone's combination of thermal and photostability with power and versatility as a Diels-Alder diene is, to our knowledge, unique. These characteristics suggest a variety of uses for **1**, including in particular the trapping of labile intermediates in both thermal and photochemical transformations.[14]

Other aspects of the chemistry of **1** are currently under investigation in our laboratory.

Acknowledgments. We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

References and Notes

(1) J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962); R. S. Dickson and G. Wilkinson, *Chem. Ind. (London)*, 1432 (1963).

(2) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).

(3) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

(4) The notable ability of **1** as charge-transfer acceptor was studied by Dickson and Wilkinson (ref 2).

(5) This carbonyl band has satellites at 1808 and 1851 cm^{-1}, and several of the other adducts have a single close-lying satellite band. In all of the bridge carbonyl-containing products in the table, however, the major band in this region appears at or very close to 1825 cm^{-1}.

(6) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

(7) Another electron-deficient diene, hexachlorocyclopentadiene, violates not only the Alder endo rule but the cis rule as well in many of its Diels-Alder reactions. V. Mark, *J. Org. Chem.*, **39**, 3179, 3181 (1974).

(8) While the cis rule is consistently upheld, the question of endo vs. exo addition has not yet been answered. The usefulness of NMR shift reagents in this connection is sharply limited by the fact that the electron-deficient bridge carbonyl shows no tendency to complex with, for example, $Eu(fod)_3$. See Z. W. Wolkowski, C. Beauté, and R. Jantzen, *J. Chem. Soc., Chem. Commun.*, 619 (1972).

(9) Methyl-substituted benzenes form highly colored complexes[2] and then react further with dienone **1** at elevated temperatures in a manner to be described elsewhere. This reaction is not, however, Diels-Alder addition.

(10) E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **91**, 6785 (1969); **88**, 3433, 3434 (1966).

(11) Using the Hückel parameters $\alpha_O = \alpha + \beta$ and $\beta_{C=O} = \beta_{C=C}$, one finds the LUMO at $\alpha + 0.19\beta$ and the HOMO at $\alpha + 0.62\beta$ for cyclopentadienone itself.

(12) This orientational preference emerges from a full HMO treatment of transition state interactions, but it is traceable principally to lower LUMO coefficients at the diene termini in the dienone than in the diene. See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Mill, New York, N.Y., 1969, Chapter 6.

(13) C. H. De Puy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964).

(14) Owing to its great volatility, the dienone is also valuable as a trapping reagent in gas phase experiments. As an example, tetrafluorocyclobutadiene has been intercepted in the vapor phase with this compound. M. J. Gerace, unpublished results; see also M. J. Gerace, D. M. Lemal, and H. Ertl, *J. Am. Chem. Soc.*, preceding paper in this issue.

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Competitive Intramolecular Displacement of the Neutral Amide Group. Rearrangement and Dehydration Reactions of Asparagine and Glutamine

Sir:

The rearrangement and dehydration of N-blocked asparagine and, to a lesser extent, glutamine derivatives have been reported to give either nitriles or imides.[1] We now report the first observation of both products from a single derivative in a reaction which apparently involves competitive O and N displacement by an amide under neutral conditions.

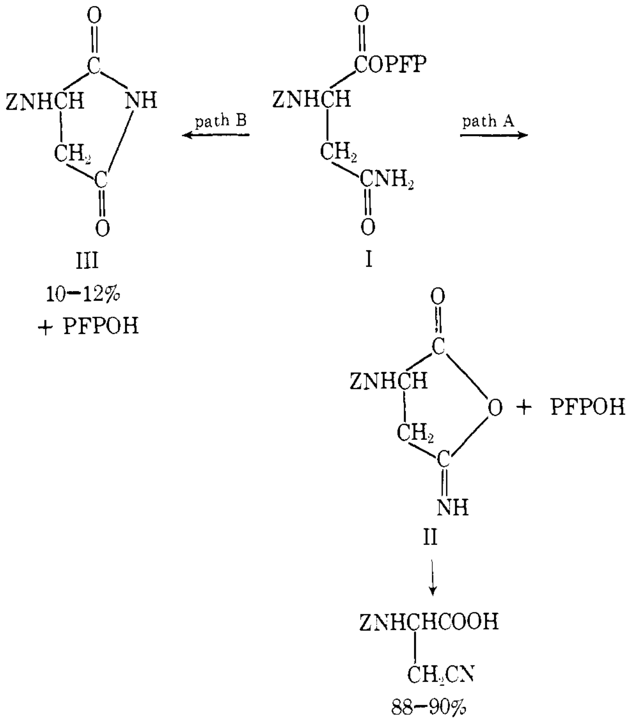
We recently described the decomposition of the pentafluorophenyl ester of *N*-benzyloxycarbonyl-L-asparagine (I) (Z-Asn-OPFP).[2] A kinetic study of this reaction and the reaction of related active esters was undertaken, and products have been identified. Rate constants were obtained for the rearrangement of the esters (Table I) as 0.1 *M* solutions in DMF (treated with Amberlyst-15) by spectrophotometric determination of the liberated phenols.

Isolation of the products of Z-Asn-OPFP by silica gel column chromatography, using the solvent system of ref 3, revealed that two simultaneous reactions were contributing to the overall first-order reaction observed; the first being nucleophilic attack by oxygen (path A, Scheme I) giving eventually the optically active β-cyanoalanine derivative, II,[3] and the second involving attack by nitrogen (path B) to yield the optically active succinimide derivative III.[4] As the specific rotations of all products and starting materials were known, the reaction could also be monitored by polarimetry and gave results in agreement with those of Scheme I. In the case of other active esters of Z-Asn, indicated in Table I, roughly the same ratio of these products could be detected on elevated temperature.

Table I. The Rearrangement of Z-Asn and Z-Gln Active Esters in DMF at 25°

Compound	k, sec^{-1}	$t/2$
Z-Asn-OPFP	9.9×10^{-5}	117 min
Z-Asn-OPCP	5.2×10^{-5}	222 min
Z-Asn-ONP	8.9×10^{-6}	1296 min
Z-Gln-OPFP		100 hr

Scheme I. The competitive intramolecular displacement by the amide group of Z-Asn-OPFP in DMF at 25°



Several conclusions may be drawn from this observed reaction. (1) The rearrangement does not compete with acylations during peptide synthesis since the half-life of the coupling reaction of I with proline-*tert*-butyl ester is about 2 min under these conditions. (2) The rearrangement is strongly temperature dependent; the ester I can be prepared in pure form only at 0°, a temperature at which kinetic studies showed the rearrangement to be slow. (3) The reaction also shows strong solvent dependence: no reaction was observed in dioxane or ethyl acetate. In the case of Gln active esters generally the imide formation is favored, accelerated by protic solvents. Thus Z-Gln-OPFP is stable in DMF, but the addition of 10% water produces the corresponding glutarimide derivative in 41% yield. In another example, recrystallization of crude Z-Gln-OSu from ethyl acetate produces pure active ester with good yield, while recrystallization from isopropyl alcohol causes the formation of the imide.[1h] Similarly, isopropyl alcohol favors the imide formation of Z-Asn-OSu. In pyridine, the nitrile is formed exclusively.

These observations are in agreement with those of Mey-