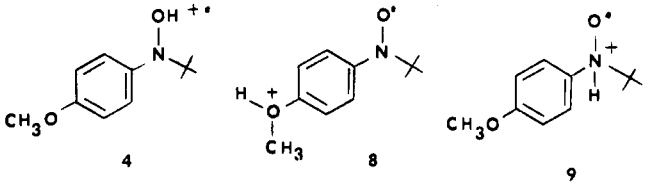
then diluted 1:10 with CH_3COOD after 2 and 18 h, the ESR spectrum of 1 was regenerated in both cases (Table I); there was no evidence of deuterium incorporated into 1. Thus, none of the phenomena observed in CCl_2FCOOH and CF_3COOH is associated with electrophilic aromatic substitution.

Clearly the original species in CF_3COOH must be one of the three radical cations (**4**, **8**, or **10**) formed by pro-



tonation of one of the three heteroatoms belonging to **1**. Unfortunately, it is not possible with the present data to distinguish these possibilities unambiguously. The main point, however, is that the benzene ring of 1 is not protonated in CF_3COOH or the weaker carboxylic acids.[20]

Experimental Section

Spectroscopy. ^1H NMR spectra were recorded on a Varian T-60 spectrometer and IR spectra on a Perkin-Elmer 257 spectrometer.

Electron spin resonance spectra were recorded on a Varian 112 ESR spectrometer using 3-mm quartz tubes. The samples were degassed either by bubbling Ar or N_2 through the solution or by the freeze–pump–thaw technique.

Nitroxide samples were most often prepared by addition of a small amount (10–50 μL) of a concentrated solution in benzene to the solvent (ca. 2–3 mL) being used. Experiments demonstrated that traces of benzene made no difference in the ESR spectra.

***N*-(*p*-Methoxyphenyl)-*N*-*tert*-butylnitroxide (1).** *N*-(4-Methoxyphenyl)-*N*-*tert*-butylhydroylamine was prepared from (4-methoxyphenyl)magnesium bromide and 2-methyl-2-nitrosopropane[21] according to the procedure of Torssell and co-workers.[9b] The nitroxide was prepared by Ag_2O oxidation of the hydroxylamine in benzene.[9b]

Trifluoroacetic Acid-*d*. Trifluoroacetic anhydride was prepared by cooling trifluoroacetic acid (50 mL) to 0 °C with stirring and adding P_2O_5 (50 g). The mixture was allowed to warm to room temperature, and the anhydride was removed by distillation through a short Vigreux column; bp 38–39 °C.

Trifluoroacetic acid-*d* was prepared in a flask equipped with a reflux condenser by cooling the anhydride (14.9 g, 0.07 mol) to 0 °C and adding (carefully!) D_2O (1.4 g, 0.07 mol). **Caution**: this reaction is violent at room temperature. The mixture was allowed to warm to room temperature and then refluxed for 30 min. After the mixture cooled, the flask was equipped for distillation, and the acid was distilled through a short Vigreux column; bp 69.5–70 °C.

Dichloroacetic Acid-*d*. Dichloroacetic acid-*d* was prepared by the method of Greene and co-workers[22] (bp 97.5–98 °C/18 min). ^1H NMR showed 89% deuterium at the acid site.

Acknowledgment. We thank Dr. James Q. Chambers for allowing us to use his ESR spectrometer. R.J.S. thanks the Gulf Oil Co. for fellowship support.

Registry No. 1, 3229-43-4; CH_3CO_2H, 64-19-7; CH_3CO_2D, 35223-87-1; $CHCl_2CO_2H$, 79-43-6; $CHCl_2CO_2D$, 82093-18-3; CF_3CO_2H, 76-05-1; CF_3CO_2D, 599-00-8; CCl_2FCO_2H, 354-19-8; CF_3SO_3H, 1493-13-6; *p*-methoxynitrosobenzene, 1516-21-8; *p*-nitrosophenol, 104-91-6.

(20) *p*-Methoxynitrosobenzene, a model for nitroxide 1, and *p*-nitrosophenol are not deuterated in CF_3COOD at room temperature.
(21) Smith, R. J.; Pagni, R. M. *J. Org. Chem.* **1981**, *46*, 4307.
(22) Greene, F. G.; Ocampo, S. R.; Kaminski, L. A. *J. Am. Chem. Soc.* **1957**, *79*, 5957.

On the Lewis Acid Catalyzed Cyclocondensation of Silyloxy Dienes with α,β-Unsaturated Aldehydes

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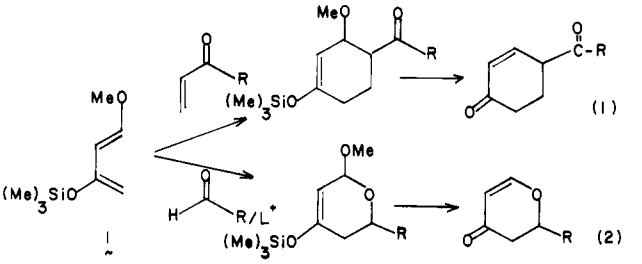
Received December 29, 1981

For some years we have investigated the thermal (i.e., noncatalyzed) Diels–Alder reactions of α,β-unsaturated carbonyl systems with siloxy dienes such as **1**.[1] Included among the dienophiles were α,β-unsaturated aldehydes (see eq 1).

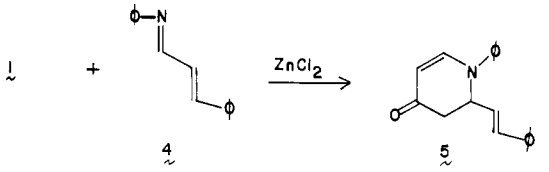


More recently we have discovered that a wide variety of aldehydes undergo "cyclocondensation" of the carbonyl linkage with diene 1 under very mild conditions under the influence of Lewis acid catalysis (L^+). Of the Lewis acid catalysts, the most extensively studied have been zinc chloride and boron trifluoride etherate (see eq 2).[2]

It was of interest to ascertain the effects of such catalysis on the reaction of diene 1 with α,β-unsaturated aldehydes. In particular we wanted to establish whether Lewis acid catalysis of "conventional" Diels–Alder reactions would now render the processes implied in eq 1 and 2 competitive.

A number of α,β-unsaturated aldehydes were subjected to Lewis Acid catalyzed reaction with diene 1 at -78 °C. The results are summarized in Scheme I. In no case could we discern product derived from addition to the carbon–carbon double bond (i.e., a classical Diels–Alder product).[3]

We have also extended the Lewis acid catalyzed cyclocondensation reaction of silyloxy diene 1 to include α,β-unsaturated imines.[5] Thus, reaction of imine **4** with diene 1 in the presence of zinc chloride gave adduct **5** in 41% yield. A new route to 2-vinyl-2,3-dihydro-4-pyridinones is thus opened. Further work in this area is continuing.



(1) Danishefsky, S.; Yan, C. F.; Singh, R. K.; Gammill, R. B.; McCurry, P. M., Jr.; Fritsch, N.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7001.
(2) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, *104*, 358. Danishefsky, S.; Kato, N.; Askin, D.; Kerwin, J. F., Jr. *Ibid.* **1982**, *104*, 360.
(3) Minor products from these reactions have been identified. They bear on the mechanism of the cyclocondensation reaction and will be discussed separately (Larson, Eric, unpublished results).
(4) A mixture of diasteromers in a 1:2 ratio (trans/cis) which was separated by HPLC on a Waters μ-Porasil column (7.8 mm i.d. × 30 cm) by using 5% ethyl acetate in hexane as elutant.
(5) We have also demonstrated the feasibility of this reaction with simple imines (Kerwin, J. F., Jr., unpublished results).

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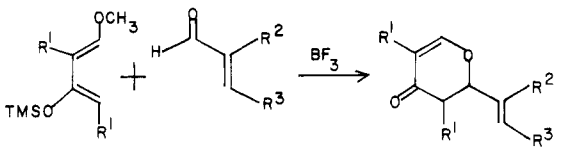
Scheme I



entry	R^1	R^2	R^3	%
a	H	H	H	50
b	H	CH_3	H	62
c	H	H	CH_3	70
d	H	H		75
e	H	H	$CH=CHCH_3$	61
f[4]	CH_3	H	CH_3	68

Experimental Section[6]

General Procedure. To a 0.1 M solution of α,β-unsaturated aldehyde in anhydrous diethyl ether under an inert atmosphere at -78 °C is added 1.1–1.2 equiv of diene followed by 1.0 equiv of boron trifluoride etherate. The reaction is continued until the aldehyde or diene has been consumed. A solution of saturated aqueous bicarbonate is added, and the ethereal layer is separated. The aqueous layer is extracted with diethyl ether. The ether solutions are combined and dried over magnesium sulfate. Filtration, evaporation of the volatiles, and chromatography[7] of the residue provides adduct **3**.

Adduct 3a: IR $\bar{\nu}$ 1685, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.37 (d, 1 H, J = 6 Hz), 5.95 (ddd, 1 H, J = 14, 10.5, 6 Hz), 5.33 (m, 2 H), 5.22 (m, 1 H), 4.9 (m, 1 H), 2.55 (m, 2 H); ^{13}C NMR δ 191.5, 162.8, 134.5, 118.2, 107.2, 79.4, 41.5; mass spectrum, m/e 124 (M^+).

Adduct 3b: IR $\bar{\nu}$ 1680, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.4 (d, 1 H, J = 6 Hz), 5.38 (d, 1 H, J = 6 Hz), 5.08 (br s, 1 H), 5.02 (br s, 1 H), 4.8 (dd, 1 H, J = 12, 5 Hz), 2.55 (m, 2 Hz), 1.8 (s, 3 H); ^{13}C NMR δ 192.2, 163.2, 141.5, 114.3, 107.1, 82.2, 40.7, 18.3; mass spectrum, m/e 138 (M^+), 123, 109, 97.

Adduct 3c: IR $\bar{\nu}$ 1690, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.37 (d, 1 H, J = 6 Hz), 5.45–6.05 (m, 2 H), 5.3 (d, 1 H, J = 6 Hz), 4.8 (m, 1 H), 2.5 (m, 2 H), 1.7 (d, 3 H, J = 6 Hz); ^{13}C NMR δ 192.3, 163.2 131.4, 127.9, 107.3, 80.1, 42.3, 18.0; mass spectrum, m/e 138 (M^+), 123, 109.

Adduct 3d: IR $\bar{\nu}$ 1680, 1600, 1500, 1450 cm^{-1}; ^1H NMR δ ($CDCl_3$, 90 MHz) 7.4 (br s, 6 H), 6.78 (d, 1 H, J = 16 Hz), 6.3 (dd, 1 H, J = 6, 16 Hz), 5.45 (d, 1 H, J = 6 Hz), 5.02 (m, 1 H), 2.55 (m, 2 H); ^{13}C NMR δ 191.9, 163.1, 135.8, 133,8, 128.9, 128.7, 127, 125.4, 107.4, 79.8, 42.1; mass spectrum, m/e 200 (M^+); mp 39–40 °C.

Adduct 3e: IR $\bar{\nu}$ 1680, 1595 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.35 (d, 1 H, J = 6 Hz), 5.4–6.8 (m, 4 H), 5.35 (d, 1 H, J = 6 Hz), 4.9 (m, 1 Hz), 2.5 (m, 2 H), 1.8 (d, 3 H, J = 6 Hz); ^{13}C NMR 192.1, 163.2, 134.5, 132.9, 130.4, 126.0, 107.4, 79.9, 42.2, 18.4; mass spectrum, m/e 164 (M^+), 149, 145, 135, 121.

Adduct 3f. Trans isomer: IR $\bar{\nu}$ 1705, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.2 (br s, 1 H), 5.35–6.10 (m, 2 H), 4.33 (dd, 1 H, J = 7, 12 Hz), 2.2–2.6 (m, 1 H), 1.8 (d, 3 H, J = 6 Hz), 1.65 (s, 3 H), 1.05 (d, 3 H, J = 7 Hz); ^{13}C NMR δ 195.2, 158.7, 132.5, 128.2, 113.0, 85.5, 43.9, 17.9, 10.9; mass spectrum, m/e 166 (M^+), 151, 137, 123.

Cis isomer: IR $\bar{\nu}$ 1705, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.20 (br s, 1 H), 5.4–6.05 (m, 2 H), 4.75 (dd, 1 H, J = 3, 6 Hz), 2.45 (dd, 1 H, J = 3, 7 Hz), 1.75 (d, 3 H, J = 6 Hz), 1.67 (s, 3 H), 1.03 (d, 3 H, J = 7 Hz); ^{13}C NMR δ 196.9, 158.5, 131.1, 125.4, 112.2, 82.7, 44.2, 17.9, 10.6, 9.9; mass spectrum, m/e 166 (M^+), 151, 137, 123.

Adduct 5: IR $\bar{\nu}$ 1640, 1580, 1490 cm^{-1}; ^1H NMR δ ($CDCl_3$, 90 MHz) 7.0–7.6 (m, 11 H), 6.57 (d, 1 H, J = 15 Hz), 6.32 (dd, 1 H, J = 5, 15 Hz), 5.3 (d, 1 H, J = 7 Hz), 4.85 (m, 1 H), 3.18 (dd, 1 H, J = 6, 15 Hz), 2.55 (dd, 1 H, J = 3, 15 Hz); ^{13}C NMR δ 190.9, 147.6, 145.0, 136.2, 132.8, 130.0, 128.4, 126.9, 125.1, 124.8, 119.1, 102.8, 60.6, 45.0; mass spectrum m/e 275 (M^+), 247, 172, 117; mp 137.5–38.5 °C.

Acknowledgment. This research was supported by PHS Grant HL48136-02. NMR spectra were obtained through the auspices of the Northeast Regional NSF/NMR Facility at Yale University which was supported by the NSF Chemistry Division Grant CHE-7916210.

Registry No. **1a**, 59414-23-2; **1f**, 82093-19-4; **2a**, 107-02-8; **2b**, 78-85-3; **2c**, 4170-30-3; **2d**, 104-55-2; **2e**, 80466-34-8; **3a**, 82093-20-7; **3b**, 82093-21-8; **3c**, 82093-22-9; **3d**, 82093-23-0; **3e**, 82093-24-1; *cis*-**3f**, 82093-25-2; *trans*-**3f**, 82093-26-3; **4**, 953-21-9; **5**, 82093-27-4; zinc chloride, 7646-85-7; boron trifluoride etherate, 109-63-7.

(6) ^1H NMR were recorded on a Varian EM-390 90-MHz spectrometer and ^{13}C NMR on a Joel FX-900 in $CDCl_3$ solution. IR spectra were measured as films on a Perkin-Elmer 710B infrared spectrometer using sodium chloride plates. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

(7) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

3a,6,7,7a-Tetrahydro-1*H*-indene-4-carboxylic Acid

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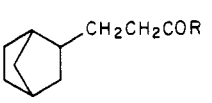
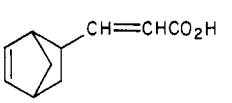
Received February 4, 1982

In an extention of an ω-modified prostaglandin project,[1] we required the optically active [[[2-(bicyclo[2.2.1]heptan-2-yl)ethyl]carbonyl]methylene]triphenylphosphorane (**1**). This phosphorane would be prepared readily from



1, R = $CH=PPh_3$
2, R = OH



3

2 by the imidazolide procedure.[2] The bicycloheptane-2-propionic acid **2** might be prepared by an optical resolution followed by hydrogenation of 5-norbornene-2-acrylic acid (**3**).

Commercial[3] "99% pure" **3** was treated with 1 equiv of (+)-α-methylbenzylamine in ether. The crystalline precipitates were recrystallized from acetone until the optical rotation reached a constant value. The (+)-amine salt was then treated with aqueous hydrochloric acid to liberate a crystalline (-)-acid which was presumed to be the levorotatory[4] 5-norbornene-2-acrylic acid (**3**). The ^1H NMR spectrum of this acid was, to our surprise, totally incompatible with the presumed structure (**3**). The (+)-acid, prepared in a similar manner by resolving the commercial **3** with (-)-methylbenzylamine, exhibited a ^1H NMR spectrum ($CDCl_3$) identical with that of the (-)-acid.

The elemental analysis demonstrated that these optically active acids were $C_{10}H_{12}O_2$, that is, isomeric to **3**. The UV (MeOH) absorption of 215 nm (ϵ 8600) as well as the IR ($CHCl_3$) bands at 1693 and 1645 cm^{-1} suggested the

(1) Dajani, E. Z.; Rozek, L. F.; Sanner, J. H.; Miyano, M. *J. Med. Chem.* **1976**, *19*, 1007.

(2) Miyano, M.; Stealey, M. A. *J. Org. Chem.* **1975**, *40*, 2840.

(3) Three U.S. manufacturers used to supply this substance: "Chemical Sources-U.S.A."; Directories Publishing Co., Inc.: Ormond Beach, FL, 1977; p 610; 1978; p 401. The purchase was made from two of them.

(4) The optically active 5-norbornene-2-acrylic acids were not found in the literature.

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