fields at constant accelerating voltage with the B/E ratio constant to obtain the daughters of parents or by scanning the accelerating voltage at constant B and E for determination of parents of daughters. Samples were introduced by using a direct probe. The normal ionizing voltage was 70 eV with a source temperature of 250 °C.

Isolation of Eremone (1). The dried plant *Eremocarpus setigerus* (collected in California) was ground in a Wiley mill and stored at −10 °C prior to extraction. The ground material was extracted with petroleum ether in a Lloyd extractor for 72 h. The dried petroleum ether extract residue was separated into acetone-soluble and -insoluble fractions. The acetone-insoluble fraction was further separated into acetonitrile-soluble and -insoluble fractions. The combined acetone- and acetonitrile-soluble fraction, after removal of the solvent, was treated with a small amount of petroleum ether, cooled, and filtered. Evaporation of the solvent from the filtrate yielded an oily residue which was placed on the top of an EM SiO_2-60 column and eluted with hexane followed by ether and methanol. The fraction eluted with ether was subjected to EM SiO_2-60 column chromatography, eluting the column with hexane with an increasing concentration of ether. Fractions eluted with hexane/ether (40:60), hexane/ether (20:80), and ether (100%) were combined and rechromatographed on an EM SiO_2-60 column, eluting the column with various concentrations of hexane/ether as before. Fractions eluted with hexane/ether (1:1) yielded a residue which when subjected to further chromatography (EM SiO_2-60) gave a fraction from which eremone was crystallized out when treated with isopropyl ether: mp 106–107 °C; $[\alpha]^{25}_D$ −93.1° (in pyridine); ^{1}H NMR (pyridine-d_5) δ 7.36 (H-15, 1 H, t, J = 1.7 Hz), 7.22 (H-16, 1 H, m), 6.25 (H-14, 1 H, dd, J = 1.6, 0.8 Hz), 5.82 (H-3, 1 H, q, J = 1.3 Hz), 2.72 (H-8, 1 H, q, J = 6.6 Hz), 2.45–2.63 (H-1α, H1β, H-10, 3 H, m), 2.51 (H-6, 2 H, s), 2.37 (H-12, 2 H, t, J = 8.5 Hz), 1.90 (H-17, 3 H, d, J = 1.3 Hz), 1.74, 1.56 (H-11, 2H, ddd, J = 17.2, 10.5, 6.6 Hz), 1.12 (H-18, 3 H, s), 1.00 (H-19, 3 H, d, J = 6.6 Hz), 0.82 (H-20, 3 H, s); ^{13}C NMR, Table I; mass spectrum, m/z (relative intensity) 314 ($M^{+\cdot}$, 22.6), 299 (4), 286 (2), 243 (12.4), 232 (6.8), 220 (25.4), 219 (69.8), 205 (6.3), 201 (5.4), 191 (4.8), 189 (4.7), 187 (5.8), 178 (10.8), 177 (12.2), 175 (7.3), 173 (10.6), 163 (7.8), 161 (6.3), 149 (26.7), 137 (11.6), 136 (25.6), 135 (48.7), 123 (24.5), 122 (34.1), 121 (25.8), 109 (33.5), 107 (17.1), 105 (8.4), 95 (86.8), 83 (51.7), 81 (100), 79 (28), 77 (15.6), 69 (22.3), 67 (20), 65 (10.5), 55 (22.6), 53 (30.3), 44 (12.8), 43 (16.2), 41 (50.6). The IR, ^{1}H NMR, ^{13}C NMR, and mass spectra were in accord with structure 1.

Anal. Calcd for $C_{20}H_{26}O_3 \cdot 0.5H_2O$: C, 74.35; H, 8.35. Found: C, 74.97; H, 8.32.

Crystallographic Study of Eremone (1). A 0.4 × 0.6 × 0.8 mm crystal was mounted on a Syntex $P2_1$ diffractometer with a graphite monochromator (Mo Kα, λ 0.71069 Å). The cell lengths determined by least-squares treatment of 15 reflections were a = 6.890 (1) Å, b = 12.954 (3) Å, c = 9.984 (2) Å, and β = 102.44 (1)°; the space group was $P2_1$ with Z = 2. The θ–2θ scan technique was used with a 0.8° scan range and a background to scan time ratio of 0.5; 1754 reflections with $2\theta < 50°$ were measured, and 969 with $I > 3\sigma_I$ were considered observed. All nonhydrogen atoms were located on the first E map from MULTAN.[12] Isotropic refinement reduced R to 0.147; anisotropically, it dropped to 0.098. Hydrogen positions were calculated, and when they were included in further nonhydrogen refinements with the isotropic temperature factors of the attached atoms, R dropped to its final value of 0.070.

Isolation of Hautriwaic Acid (2b). The dried plant (collected in Oregon) was milled and extracted with petroleum ether in the same way as for eremone. The dried petroleum ether extract was separated into ether-soluble and -insoluble fractions. The ether-soluble fraction was vacuum dried and subjected to three-funnel partition between 20% aqueous MeOH and petroleum ether. The lower phase was dried under vacuum and separated into ether-soluble and -insoluble fractions. Chromatography of the ether-soluble residue on EM silica gel-60 and elution with hexane/ether (75:25) gave a fraction which on concentration deposited crystals of crude hautriwaic acid (**2b**) which were separated by filtration, washed with ether, and recrystallized from ether/acetone as colorless lustrous rectangular prisms: mp 191–192 °C; $[\alpha]^{25}_D$ −133.5° (in pyridine; lit.[3,4] mp 183–184 °C; $[\alpha]^{25}_D$ −105°). The IR, ^{1}H NMR, and mass spectra were in accord with literature values.[5-7]

Acetylation of Hautriwaic Acid. Acetylation of **2b** with Ac_2O–pyridine at room temperature for 24 h yielded a mixture of **2c** and **2d** whose separation was effected by preparative TLC [EM SiO_2-60 PF-254; methylene chloride/methanol (60:1)] and isolated as TLC-pure samples. No attempt was made to crystallize these samples: mass spectrum, m/z (relative intensity) 374 ($M^{+\cdot}$, 1.5), 357 (2.6), 356 (10.3), 314 (14.8), 301 (12.2), 283 (26), 279 (26.9), 261 (31.1), 255 (7), 220 (22.6), 219 (89.5), 207 (11.2), 203 (10.4), 201 (21.8), 189 (22.5), 173 (20.8), 163 (30.4), 161 (13.7), 159 (11), 151 (22), 149 (39.6), 147 (11.6), 145 (19), 137 (17.3), 135 (16.3), 133 (15), 131 (12.7), 125 (14.3), 123 (12), 121 (17), 119 (16.7), 117 (12.3), 109 (17.6), 107 (21), 105 (29.2), 97 (10.2), 96 (47.6), 95 (82.2), 94 (16.7), 93 (24.7), 91 (43.7), 83 (15.1), 82 (48.2), 81 (100), 79 (30), 77 (26.5), 69 (17.6), 67 (25.3), 65 (14), 60 (15), 55 (30.7), 53 (29.6). The IR and mass spectra of **2c** were in accord with the proposed structure.

The IR, ^{1}H NMR, and mass spectra of **2d** were in accord with literature values.[5-7]

Acknowledgment. This investigation was supported by Grants No. 5-R01-Ca22336-02 and 1-R01-Ca29626-01, awarded by the National Cancer Institute, Department of Health, Education, and Welfare, Bethesda, MD 20014.

Registry No. 1, 80594-75-8; **2b**, 18411-75-1; **2c**, 35060-24-3; **2d**, 18411-74-0.

Supplementary Material Available: Mass spectral fragmentation patterns of 1 and **2b** (Schemes I and II) and bond lengths, bond angles, stereoview of a unit cell, fractional coordinates, and temperature factors for 1 (6 pages). Ordering information is given on any current masthead.

(12) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B.* **1970**, *B26*, 274.

Proton Nuclear Magnetic Resonance Analysis for Meso and *dl* Isomers of Succinic-d_2 Acid

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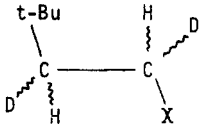
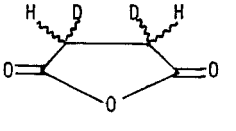
Received September 9, 1981

The ability to quantitatively analyze vicinal dideuteriated systems for erythro/threo[2,3] (e.g., **1**) and meso/*dl*[4,5] (e.g., **2**) ratios have been useful in many



1



2

mechanistic investigations. The analysis of representative examples of compound **1** is relatively straightforward since J_{H_1,H_2} differs substantially and is directly measurable for erythro and threo isomers. Symmetry prevents a simple

(1) Dyson Perrins Laboratory, South Parks Rd., Oxford, England OX1 3QY.

(2) Whitesides, A. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529.

(3) Labinge, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

(4) Childs, C. R., Jr.; Bloch, K. *J. Org. Chem.* **1961**, *26*, 1630.

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Table I. Chemical Shift Difference and Coupling Constants (Hz)

compd	$\Delta\delta$ [b]	$J_{H,H\,(cis)}$	$J_{H,H\,(trans)}$	$J_{H,H\,(gem)}$
succinic anhydride[a]		10.72 ± 0.01	5.21 ± 0.01	−18.05 ± 0.8
3[a]	0.22 ± 0.01	9.95 ± 0.06	4.44 ± 0.03	−18.15 ± 0.02
4	0.22		4.4	
5	0.22			

[a] By complete spectral analysis.[7] [b] Chemical shift difference (in parts per million) between proton sites; acetone-d_6 solution at 25 °C.

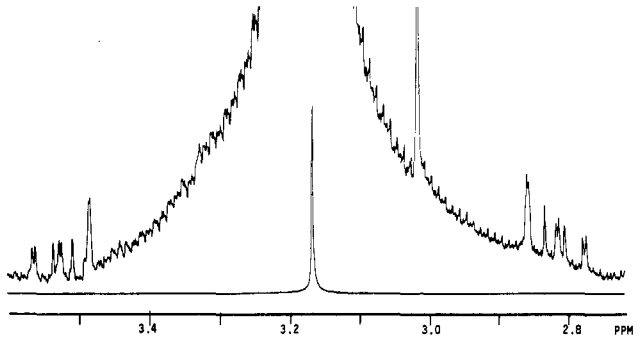

Figure 1. ^{1}H NMR spectrum of the ^{13}C satellite peaks in perprotiosuccinic anhydride.

NMR solution to this analysis for **2** and most of its derivatives, and previous workers have employed IR[4] and Raman[5] methods. We have found IR to be difficult to apply quantitatively and Raman to be subject to fluorescent impurity problems and present here a novel method of analysis using high-resolution ^{1}H NMR spectroscopy.

In principle, the proton–proton couplings of *meso*- and *dl*-**2** should be quite different, and examination of the satellite peaks resulting from ^{13}C–proton coupling allows proton–proton couplings in the molecule to be ascertained.[6] Figure 1 shows the 200-MHz ^{1}H NMR spectrum of the ^{13}C satellite peaks of perprotiosuccinic anhydride. Through the use of standard computer simulations and iterative calculations,[7] the proton–proton and ^{13}C–proton couplings can be obtained; these indicate that $J_{H,H(cis)}$ is 10.7 Hz and $J_{H,H(trans)}$ is 5.2 Hz.[6] The cis and trans vicinal coupling constants are sufficiently different to allow the meso and *dl* dideuterio derivatives of **2** to be distinguished by directly observing the ^{13}C satellites in their ^{1}H spectra with deuterium decoupled. However, the inherently low signal strengths make this approach impractical for the quantitative assay of small amounts of mixtures of succinic-d_2 anhydrides.

We report here an alternative means of magnetically distinguishing the proton sites in the succinic anhydride skeleton via the readily accessible *N*-(*o*-biphenyl)succinimide derivative **3**. Rotation about the aryl–N bond is slow on the NMR time scale ($k \approx 1$ s^{-1} at 25 °C), and this effectively locks the conformation of the molecule such that an aromatic ring is above one face of the succinimide ring. The NMR spectrum clearly differentiates the two pairs of cis protons as an AA′BB′ spin system (Figure 2a, Table I).

With deuterium decoupled, the aliphatic region of the NMR spectrum of *meso*-*N*-(*o*-biphenyl)succinimide-d_2 (**4**) exhibits only two singlets, separated by 0.22 ppm, whereas *dl*-*N*-(*o*-biphenyl)succinimide-d_2 (**5**) exhibits two doublets (J = 4.4 Hz), also separated by 0.22 ppm (Figure 2b,c). Typically, the spectra of mixtures of **4** and **5** are not sufficiently resolved to permit accurate integration of the components, but simple curve addition of computer-simulated spectra allows estimation of the mixture compositions routinely within ±5%.

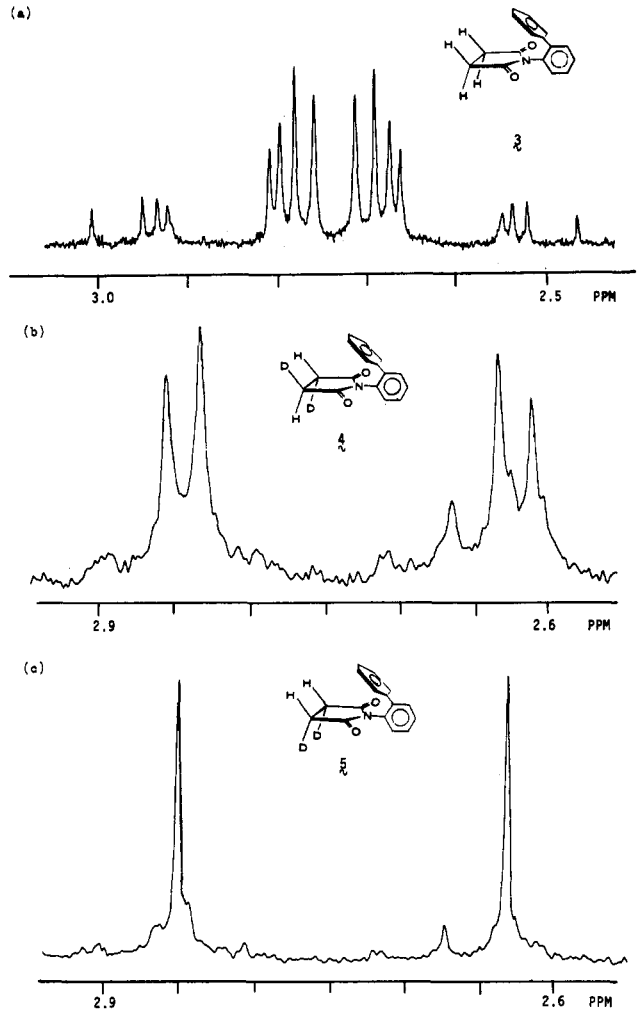

Figure 2. (a) ^{1}H NMR spectrum of perprotio-*N*-biphenylsuccinimide; (b) ^{1}H NMR of *dl*-*N*-biphenylsuccinimide-d_2; (c) ^{1}H NMR of *meso*-*N*-biphenylsuccinimide-d_2.

Experimental Section

General Methods. NMR spectra were recorded at either 100 or 200 MHz (Varian XL-100 or XL-200 spectrometers) with deuterium decoupling. Spectral simulation and iterative calculation were carried out by using a modified version of the computer program UEA8;[7] simulation of dynamic NMR behavior was performed through the use of the program DNMR3.[8] Spectra were run in acetone-d_6.

***dl*- and *meso*-Succinic-d_2 Anhydrides.** *dl*- and *meso*-succinic-d_2 acids were prepared by the catalytic reduction of fumaric and maleic acids, respectively, with deuterium gas over 10% palladium on charcoal catalyst (75 °C, 1 atm, ethyl acetate). When the uptake of deuterium had ceased, the mixture was cooled,

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(8) DNMR3: Kleier, D. A.; Bensch, G. Program 165, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, 1970.

and the solid products were filtered and recrystallized from ethyl acetate. *dl*- and *meso*-succinic-d_2 acids were cyclized to the corresponding anhydrides by gentle warming with acetyl chloride.[9]

***N*-Biphenyl Succinimides.** To 0.10 g (0.001 mol) of succinic anhydride in 2 mL of anhydrous ether was added 0.169 g (0.001 mol) of 2-aminobiphenyl (Aldrich) dissolved in 1 mL of anhydrous ether. The reaction mixture was refluxed with stirring for 2 h, and then the solid amide–acid produced was filtered off.

To 0.1 g of the above solid were added 0.14 g of acetic anhydride and 0.02 g of sodium acetate, and the mixture was warmed and stirred for about 1 h until no solid was evident. The reaction mixture was cooled slowly to room temperature and then poured onto ice to yield a precipitate. This was recrystallized from a small amount of methanol to give a 60% overall yield of product, mp 135–137 °C (uncor).

Acknowledgment. Financial support from NSF Grant CHE 80 12233 is gratefully acknowledged.

Registry No. *dl*-**2**, 80655-73-8; *meso*-**2**, 80655-74-9; **3**, 80584-50-5; **4**, 80584-51-6; **5**, 80584-52-7; *dl*-succinic-d_2 acid, 21156-52-5; *meso*-succinic-d_2 acid, 21156-53-6; 2-aminobiphenyl, 90-41-5.

(9) Blatt, A. M., Ed. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 560.

A Novel, Nonoxidative Method for the Conversion of Aldehydes to Esters

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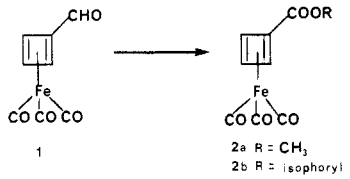
Received August 21, 1981

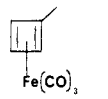
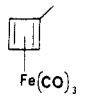
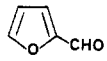
In connection with an attempted application of (cyclobutadiene)iron tricarbonyl chemistry to terpene synthesis,[2] we required a method for the conversion of the readily available[3] **1** to its esters **2a** and **2b** (eq 1). The direct



(1) (1)

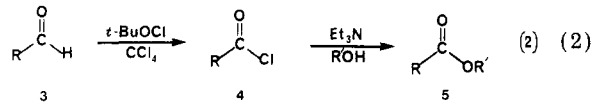
oxidation of aldehyde **1** to the corresponding acid with Ag_2O proceeds in only 1% yield.[6,7] Oxidation at the metal center is an obvious problem. We report herein a unique solution to the problem that is fairly general and represents a "nonoxidative" aldehyde oxidation.

Table I. Conversion of Aldehydes 3 to Esters 5 (eq 2)

entry	R	R′	% yield	time[d]
1		CH_3	90	3 min
2		isophoryl	39	3 min
3	Ph	CH_3	76[a]	2 h
4	PhCH=CH	CH_3	80[b]	4 h
5	*m*-OCH_3Ph	CH_3	98[c]	4 h
6		CH_3	60	4 h

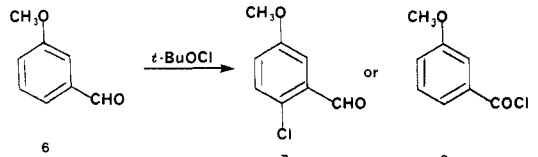
[a] Ginsburg obtained benzoic acid in 96% yield.[8a] [b] The reaction of *tert*-butyl hypochlorite with cinnamaldehyde[17] *in methanol* was reported in 1941 in a paper describing the chlorination of double bonds with the reagent. 2-Chloro-3-methoxy-3-phenylpropanal was obtained in 30% yield, another example of the solvent effect. [c] Ginsburg obtained compound **7** with acetic acid as the solvent. [d] 25 °C.

The approach takes advantage of the almost forgotten[8] selective conversion of aldehydes to acid chlorides with *tert*-butyl hypochlorite (eq 2). This reaction of aldehydes



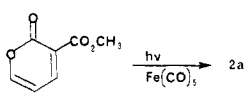
(2) (2)

was first discussed in detail in a 1951 paper by Ginsburg.[8,9] The reaction probably involves *tert*-butoxy radical abstraction of the aldehydic hydrogen. Competition between free-radical H abstraction and electrophilic chlorination results in a marked solvent effect. For example, *m*-methoxybenzaldehyde (**6**) reacts with *tert*-butyl hypochlorite in acetic acid to yield **7**, whereas we have found that in CCl_4 (see Table I) the only product is **8**. Examination of other entries in the table[10] reveals that the reaction works well for the tricarbonyliron complexes with no attack at the metal. Oxidation of aromatic aldehydes and heterocycles are not a problem.



Three limitations were uncovered.[11] Attempted reaction of **9** gave an ester with chlorination in the aromatic ring. Compound **10**, substituted with electron-withdrawing groups, did not react. And finally, attempts were made to convert benzaldehyde to methyl benzoate in the presence of the thioketal **11**. Unfortunately, the aldehyde was unscathed and destruction of **11** was the only observed reaction.[12]

(1) Department of Chemistry, Indiana University, Bloomington, IN.
(2) Wilson, S. R.; Phillips, L. R.; Pelister, Y.; Huffman, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 7373–7379.
(3) Compound **1** was prepared in 64% yield as reported[4] by Vilsmeier formylation of commercially available[5] (cyclobutadiene)iron tricarbonyl.
(4) Fitzpatrick, J. D.; Watts, L.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3254–3255.
(5) Strem Chemicals, Inc., Newburyport, MA.
(6) Fitzpatrick, J. Ph.D. Thesis, University of Texas, Austin, TX, 1966.
(7) The inaccessibility of (cyclobutadienecarboxylic acid)iron tricarbonyl lead to another approach, based on 3-(carbomethoxy)-2-pyrone, in 21% overall yield.



Agar, J.; Kaplan, F.; Roberts, B. W. *J. Org. Chem.* **1974**, *39*, 3451–3452.

(8) (a) Ginsburg, D. *J. Am. Chem. Soc.* **1951**, *73*, 702–704. (b) Anbar, M.; Ginsburg, D. *Chem. Rev.* **1954**, *54*, 925–958.
(9) Ansell, M. F. In "The Chemistry of Acyl Halides"; Patai, S. Ed.; Interscience: New York, 1972, p 35 ff.
(10) Complete spectral data for compounds **2a** and **2b** are available as supplementary material (see supplementary material available paragraph).
(11) Although the conversion of an aliphatic aldehyde to the acid bromide with NBS has been reported[16], the reaction of heptaldehyde with *tert*-butyl hypochlorite gave extensive chlorination of the alkyl chain. The reaction with citral gave a complex mixture of products.

0022-3263/82/1947-1360$01.25/0