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Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carbonyls. 2. Reaction of $Fe(CO)_5$ with 7-Phenyl- and 7-*o*-Anisylnorbornadiene

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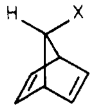
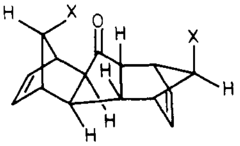
The thermal reaction of 7-phenylnorbornadiene (3) with iron pentacarbonyl in refluxing di-*n*-butyl ether under nitrogen for 24 h affords a single product, the anti-exo-trans-exo-anti dimer ketone 5, in 20% yield. Lithium aluminum hydride reduction of 5 affords a single alcohol 7 in 85% yield. The corresponding thermal reaction of 7-*o*-anisylnorbornadiene with iron pentacarbonyl similarly affords only the corresponding anti-exo-trans-exo-anti dimer ketone (8, 26% yield). Hydrogenation of 8 over palladized charcoal affords the corresponding saturated dimer ketone 9 whose structure has been determined via single-crystal X-ray structural analysis.

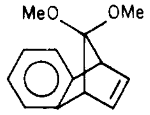
We recently reported[1] our observation that 7-*tert*-butoxynorbornadiene (1) reacts with $Fe(CO)_5$ to afford the syn-exo-trans-endo-syn (SXTNS) dimer ketone (2) along with at least four other products. This result was interpreted as providing evidence for the direct mechanistic involvement of the 7-Lewis base substituent in the iron carbonyl promoted coupling of 1 with carbon monoxide. In order to further delineate the role of syn-7-Lewis base substituents in directing the stereochemical outcome of this reaction we have undertaken a corresponding study of the thermal reactions of 7-phenylnorbornadiene (3) and of 7-*o*-anisylnorbornadiene (4) with $Fe(CO)_5$.



1, X = O-*t*-Bu
3, X = Ph
4, X = *o*-C_6H_4OMe



2, SXTNS



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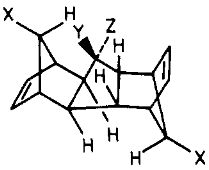
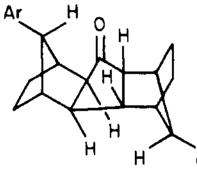
Our rationale for choosing 3 and 4 as substrates in this study was as follows: unlike lone pair substituents (such a O-*t*-Bu), a phenyl group lacks sufficient Lewis basicity to coordinate with Fe(0).[2] Hence, the 7-phenyl group should function only to block the exo face of the double bond syn to that substituent in 3. Coupling of 3 with carbon monoxide, accordingly, should occur through the corresponding anti double bond. Prior experience with the results of the thermal reaction of norbornadiene itself with $Fe(CO)_5$ suggests that coupling through the anti double bond in 3 should occur via the exo face, thereby affording the anti-exo-trans-exo-anti (AXTXA) dimer ketone (5).[3]

The situation conceivably could be different for the corresponding thermal reaction of 4 with $Fe(CO)_5$. Here, the *o*-methoxy group potentially can enter into complexation with Fe(0) and thereby direct coupling through the double bond syn to the 7-*o*-anisyl substituent. Indeed, such direct involvement of the syn-7-Lewis base substituent was suggested previously to account for the observed SXTNS stereochemistry of the dimer ketone formed via $Fe(CO)_5$-promoted coupling of 1[1] and of 6[4] to carbon monoxide. Thus, it was hoped that the present study might provide further evidence for the mechanistic involvement of a Lewis base substituent in additional $Fe(CO)_5$-promoted coupling reactions of this type.[5]

The reaction of 3 with iron pentacarbonyl in refluxing di-*n*-butyl ether under nitrogen for 24 h afforded a single dimer ketone (20% yield). This product was identified as possessing structure 5 on the basis of spectral evidence (see Experimental Section), thereby confirming the expectations noted above. In addition, lithium aluminum hydride reduction of 5 afforded a single alcohol, 7, in high yield (85%); the fact that a single product was obtained in this reaction suggests that 5 has the trans configuration (AXTXA) rather than the cis configuration (AXCXA).[6]



5, X = Ph; Y, Z = O; AXTXA
7, X = Ph; Y = OH; Z = H; AXTXA
8, X = *o*-C_6H_4OMe; Y, Z = O; AXTXA



9, Ar = *o*-C_6H_4OMe; AXTXA

The corresponding thermal reaction of 4 with $Fe(CO)_5$ similarly afforded a single dimer ketone (8, 26% yield). This material was saturated by reaction with hydrogen gas over palladized charcoal; the structure of the resulting saturated dimer ketone (9) was established as being the AXTXA isomer via single-crystal X-ray structural analysis (vide infra).[7]

The bond distances for non-hydrogen atoms in 9 calculated on the basis of the final position parameters are shown in Figure 1. Disregarding the cyclopentanone ring, the molecule has a pseudocenter of symmetry. Both

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[1] Marchand, A. P.; Hayes, B. R. *Tetrahedron Lett.* **1977**, 1027.

[2] (a) King, R. B. "Transition Metal Organic Chemistry"; Academic Press: New York, 1969; pp 143-144. (b) Pettit, R.; Emerson, G. F. *Adv. Organometal. Chem.* **1964**, *1*, 1.

[3] (a) Green, M.; Lucken, E. A. C. *Helv. Chim. Acta* **1962**, *45*, 1870. (b) Cookson, R. C.; Henstock, J.; Hudec, J. *J. Am. Chem. Soc.* **1966**, *88*, 1059.

[4] Speert, A.; Gelan, J.; Anteunis, M.; Marchand, A. P.; Laszlo, P. *Tetrahedron Lett.* **1973**, 2271.

[5] Cf. Weissberger, E.; Laszlo, P. *Acc. Chem. Res.* **1976**, *9*, 209.

[6] Mantzaris, J.; Weissberger, E. *J. Am. Chem. Soc.* **1974**, *96* 1873, 1880.

[7] We chose to perform single-crystal X-ray analysis on 8 rather than on 7 for reasons of expediency; it proved to be considerably easier to obtain a good quality single crystal of 8 than of 7 for this purpose.

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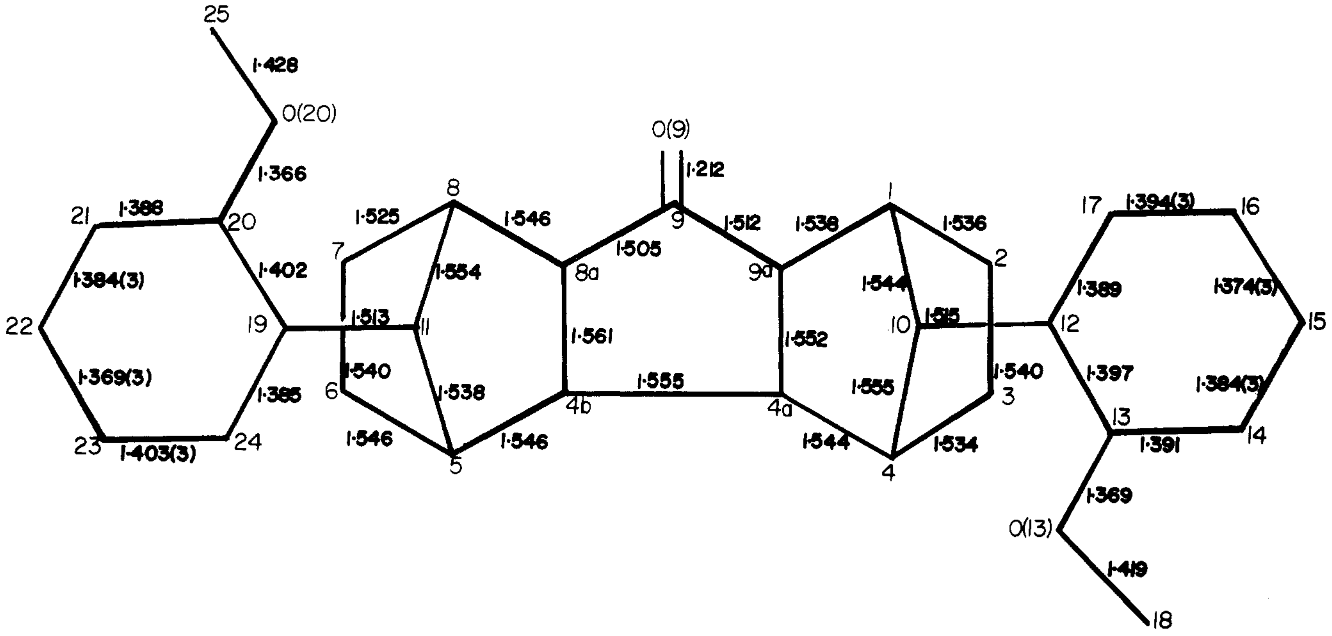

Figure 1. Atom numbering and bond distances for non-hydrogen atoms in **9**. Standard deviations for all bond lengths except those shown in parentheses are 0.002 Å.

Table I

length of C–C bonds directly attached to cyclopentanone ring	av	molecule	ring type
1.538, 1.544, 1.546, 1.546	1.544	present structure	norbornane
1.548, 1.539, 1.525, 1.535	1.534	trimer ketone	norbornane
1.569, 1.563, 1.563, 1.560	1.564	trimer diketone	norbornene
1.566, 1.567, 1.562, 1.564	1.565	dimer ketone	norbornene

phenyl rings are nearly perpendicular to the central five-membered ring; the interplanar angles between the phenyl rings and the five-membered ring are 77° and 79°, respectively.

The cyclopentanone ring in **9** displays a high degree of planarity, probably due to constraints imposed by the presence of the norbornyl moieties. A similar situation exists for the corresponding central cyclopentanone ring in **2**[8] and in a structurally related trimer diketone.[9] The positions of the two methoxyl oxygens [O(13) and O(20)] and of the methoxyl methyl carbon atoms [C(18) and C(25)] deviate only very slightly from the plane of the phenyl ring to which each methoxyl group is attached, respectively.

The bond angles in the norbornyl moieties in **9** deviate significantly from the normal tetrahedral angle, thus indicating the presence of considerable strain in the molecule. However, **9** does not show any unusual lengthening of the carbon–carbon bonds directly attached to the cyclopentanone ring; both dimer ketone **2**[8] and a structurally related trimer diketone[9] showed this lengthening effect. The relevant carbon–carbon bond lengths in these three molecules are compared in Table I. It may be concluded from these data that the presence of a double bond in the norbornyl moieties of a dimer ketone or related trimer diketone introduces additional strain into the system which results in lengthening of the carbon–carbon bonds directly attached to the cyclopentanone ring. The carbon–hydrogen bond distances in **9** range between 0.97 (1) Å and 1.04 (1) Å.

The observations that **9** and its precursor (**8**) possess the AXTXA configuration is noteworthy, as **4** is the first example of a norbornadiene bearing a 7-Lewis base substituent which does *not* couple through the double bond syn to that substituent. This observation may have significant bearing upon the mechanism of the coupling reaction. An important step in the Fe(0)-promoted olefin–CO coupling reaction mechanism suggested by Mantzaris and Weissberger[6] involves the reversible reaction of an (olefin)Fe$(CO)_3$ complex with a molecule of noncomplexed olefin to afford an $(olefin)_2Fe(CO)_3$ complex. There is considerable evidence which suggests that norbornenes and norbornadienes bearing 7-oxygen-containing substituents undergo complexation with Fe(0) in syn,exo fashion.[5,10] However, the distance between the *o*-anisyl oxygen atom and the syn double bond in **4** appears to be too small to permit incorporation of an Fe(0) moiety between these two groups; accordingly, coupling through the exo face of the syn double bond in **4** is unlikely on steric grounds.

In contrast to this result, inspection of molecular models suggests that there is ample room for the unshared electrons on the *o*-anisyl oxygen atom to interact with the exo π-lobes of the syn double bond in *noncomplexed* **4**. This interaction should result in bishomoconjugative, *antiaromatic* electronic activation of the syn double bond by the *o*-anisyl oxygen atom. The net result of this interaction should be to raise the energy of the HOMO of the syn double bond relative to that of the anti double bond in **4**.[11,12] This electronic interaction in the noncomplexed olefin might explain the occurrence of coupling in, e.g., **1** and **6**, through the endo face of one of the two norbornenyl moieties which results in the formation of an exo-trans-endo dimer ketone in the respective thermal reactions of these substrates with $Fe(CO)_5$. However, an option which

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[8] Ealick, S. E.; van der Helm, D. *Cryst. Struct. Commun.* **1975**, *4*, 369.

[9] Ealick, S. E.; van der Helm, D.; Hayes, B. R.; Marchand, A. P. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3219.

[10] Laszlo, P.; Stockis, A. *J. Organometal. Chem.* **1976**, *117*, C41.

[11] (a) Astin, K. B.; Mackenzie, K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1004. (b) Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *92*, 6482. (c) Dougherty, D. A. California Institute of Technology, personal communication.

[12] Marchand, A. P. "Abstracts of Papers", 38th Southwest and 6th Rocky Mountain Regional Meeting of the American Chemical Society, El Paso, TX, December 1-3, 1982; American Chemical Society: Washington, D.C., 1982, Abstr. 235.

is open to the methoxyl group in 4 which is *not* available to any other 7-Lewis base substituent in a norbornene or norbornadiene thus far studied is its ability to avoid the (unfavorable) antiaromatic bishomoconjugated orbital interaction discussed above simply by rotating about the C(7)–aryl bond. Once this occurs, the methoxyl oxygen atom is removed from the reaction site, and the 7-*o*-anisyl group in 4 becomes operationally indistinguishable from 7-phenyl in the coupling reaction with $Fe(CO)_5$. For this reason, 4 reacts with $Fe(CO)_5$ in the same manner as does 3, both substrates affording only the corresponding AXTXA dimer ketones (5 and 8, respectively).[12]

Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra were obtained with Varian Model T-60 and Model XL-100-15 NMR spectrometers; signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with Perkin-Elmer Model IR-8 and Model 710B infrared spectrophotometers. Mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-7E mass spectrometer (70 eV). Elemental microanalyses were performed by Chemalytics, Inc., Tempe, AZ. All reagents and solvents utilized in this study were reagent grade unless otherwise specified. Additional purification of solvents was performed as follows: acetone was distilled from potassium permanganate; ethyl ether, di-*n*-butyl ether, and tetrahydrofuran each were purified by distillation from lithium aluminum hydride. 7-*tert*-Butoxynorbornadiene (1) was used as obtained from Frinton Laboratories, Vineland, NJ. 7-Phenylnorbornadiene (3), also obtained from Frinton Laboratories, was vacuum distilled prior to use.

7-*o*-Anisylnorbornadiene (4). Compound 4 was prepared via the reaction of 7-*tert*-butoxynorbornadiene with (*o*-methoxyphenyl)magnesium bromide using the procedure described by Story and Fahrenholtz.[13] The crude product was purified by column chromatography on silica gel (pentane eluent). The eluate was concentrated in vacuo, and the residue was recrystallized from pentane to afford pure 4 as a colorless waxy solid (8.56 g, 86.5%): mp 51.5–53.0 °C; ^1H NMR ($CDCl_3$) δ 3.8 (s, 3 H, OCH_3), 3.9 (m, 3 H, benzylic and bridgehead protons), 6.6–6.9 (complex m, 8 H, vinyl and aryl protons); IR spectrum (CCl_4 solution) 3075 (w), 3000 (s), 2840 (w), 1600 (m), 1580 (m), 1540 (w), 1480 (s), 1460 (s), 1430 (m), 1335 (w), 1295 (m), 1280 (m), 1240 (s), 1210 (m), 1120 (w), 1100 (m), 1045 (m), 1020 (m), 920 (w), 860 (w), 825 (w), 700 (m), 645 (m), 620 cm^{-1} (m).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.73; H, 7.21.

Reaction of 3 with Iron Pentacarbonyl. To a solution of freshly distilled 3 (5.0 g, 30 mmol) in dry di-*n*-butyl ether (30 mL) was added iron pentacarbonyl (12 g, 61 mmol) under nitrogen. The resulting mixture was refluxed 24 h under nitrogen and then allowed to cool to room temperature. To the cooled reaction mixture was added a solution of ferric chloride hexahydrate (26 g, excess) in acetone (100 mL), and the resulting mixture was stirred at room temperature for one week to decompose any unreacted iron pentacarbonyl and Fe(0) complexes which might be present.[14] The reaction mixture was then diluted with water (300 mL) and extracted several times with ether (5 × 100 mL portions). The combined extracts were washed with water, dried (anhydrous sodium sulfate), filtered, and the filtrate was concentrated in vacuo to afford 5 as an off-white microcrystalline solid (1.05 g, 20%). An analytical sample of 5 was obtained via recrystallization from diethyl ether as a colorless microcrystalline solid: mp 197.5–198.5 °C; ^1H NMR ($CDCl_3$) AB pattern (J_{AB} = 7 Hz) δ_A 2.13 (2 H), δ_B 2.76 (2 H), δ 3.2 (m, 4 H), 3.5 (m, 2 H), 6.1 (m, 4 H), 7.17 (s, 10 H); IR (film) 3070 (w), 3020 (m), 2980 (w), 2940 (w), 2900 (w), 1720 (s), 1600 (w), 1500 (m), 1450 (w), 1325 (m), 1180 (m), 1080 (w), 1020 (w), 960 (w), 880 (m), 810 (w), 710 (m), 690 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) 364 (M^+, 2.4), 222 (7), 195 (2), 179 (3), 166 (16), 152 (7), 142 (100), 131 (33), 115 (25), 105 (10), 91 (49), 77 (15), 65 (10).

Compound 5 was assigned the AXTXA configuration on the basis of its ^1H NMR spectrum. The fact that the cyclopentanone ring protons in 5 appear as a simple AB pattern rather than as a more complicated A_2B_2 pattern suggests that 5 possesses the trans (rather than cis) configuration about the C(4a)–C(4b) bond (Figure 2 in supplementary material). Importantly, the ^1H NMR spectrum of 5 is virtually identical in overall appearance with that of 8; the AXTXA stereochemistry of 7 was established unequivocally via single-crystal X-ray structural analysis of its hydrogenation product 9 (vide infra).

Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88,.76; H, 6.76.

Reaction of 5 with Lithium Aluminum Hydride. To a refluxing solution of lithium aluminum hydride (0.700 g, 18.7 mmol) in dry THF (50 mL) was added dropwise a solution of 5 (0.5055 g, 1.39 mmol) in dry THF (50 mL). Refluxing was continued for 4 h after the addition had been completed. The reaction mixture was then allowed to cool to room temperature, and excess lithium aluminum hydride was destroyed by careful, dropwise addition of excess 5% aqueous sodium hydroxide solution. The resulting mixture was then suction filtered, and the residue was washed with $CHCl_3$. The filtrate was dried (anhydrous sodium sulfate), filtered to remove drying agent, and the resulting filtrate was concentrated in vacuo to afford the corresponding alcohol (7, 0.432 g, 85%). An analytical sample of 7 was obtained via recrystallization from carbon tetrachloride as a colorless microcrystalline solid: mp 162.5–163.5 °C; ^1H NMR ($CDCl_3$) δ 1.6–2.3 (complex m, 7 H), 3.05 (m, 2 H), 4.2 (dd, J = 3.0 Hz, J' = 6.4 Hz, 2 H), 5.9 (m, 4 H), 7.18 (s, 10 H); IR (KBr) 3550 (s), 3450 (m), 3030 (m), 2920 (s), 1680 (w), 1600 (m), 1500 (s), 1450 (m), 1330 (s), 1200 (w), 1090 (m), 1050 (s), 1020 (w), 900 (w), 720 cm^{-1} (s).

Anal. Calcd for $C_{27}H_{26}O$: C, 88.46; H, 7.17. Found: C, 88.24; H, 7.08.

Reaction of 4 with Iron Pentacarbonyl. To a solution of 4 (4.0 g, 20 mmol) in dry di-*n*-butyl ether (30 mL) was added iron pentacarbonyl (9.8 g, 50 mmol) under nitrogen. The resulting mixture was refluxed under nitrogen for 24 h. Workup of the reaction mixture was performed in the manner described above for the reaction of 3 with iron pentacarbonyl. The reaction product was purified via fractional column chromatography on silica gel H (TLC grade, 10–15% ethyl acetate–hexane gradient elution). The fractions containing the major reaction product (as indicated by TLC) were combined and concentrated in vacuo, and the combined residues were recrystallized from chloroform–ether mixed solvent, affording 8 as a colorless microcrystalline solid (1.10 g, 26%): mp 214–215 °C; ^1H NMR ($CDCl_3$) AB pattern (J_{AB} = 7 Hz), δ_A 2.12 (2 H), δ_B 2.56 (2 H), δ 3.0 (m, 4 H), 3.2 (m, 2 H), 3.50 (s, 6 H), 5.65 (m, 4 H), 6.4 (m, 8 H); IR (KBr) 3050 (w), 2925 (m), 2840 (w), 1725 (s), 1600 (m), 1590 (m), 1500 (s), 1460 (s), 1440 (m), 1360 (w), 1330 (w), 1300 (m), 1245 (s), 1190 (s), 1120 (s), 1050 (m), 1030 (m), 890 (w), 800 (m), 750 (s), 720 cm^{-1} (m).

Anal. Calcd for $C_{29}H_{28}O_3$: C, 82.02; H, 6.66. Found: C, 82.11; H, 6.71.

Compound 8 was hydrogenated over palladized charcoal on a Parr shaker apparatus at 40 psig. The hydrogenation product, 9, was obtained in essentially quantiative yield as a colorless microcrystalline solid. Suitable crystals of this material, mp 193–194 °C, were grown via careful recrystallization from ethyl acetate.

Single-Crystal X-ray Structural Analysis of 9. A crystal of dimensions 0.78 × 0.24 × 0.14 mm was chosen for single-crystal X-ray diffraction studies. Preliminary investigation showed the crystal to be monoclinic. The space group was determined as $P2_1/c$ from systematic extinctions ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ absent). Relevant crystal data of the compound are as follows: $C_{29}H_{32}O_3$; M_r 428.28; monoclinic; a = 9.466 (1) Å, b = 19.413 (2) Å, c = 13.095 (1) Å, β = 106.82 (1)°, V = 2303.4; space group $P2_1/c$, $z = 4$; D = 1.235 g cm^{-3}, D_m = 1.238 g cm^{-3}; μ (Cu Kα) = 6.25 cm^{-1}.

The cell parameters were determined by a least-squares fit to the observed $+2\Theta$ and -2Θ values of 40 reflections distributed throughout all quadrants of the reciprocal lattice. All measurements were made on a Nonius CAD-4 automatic diffractometer which employed Ni-filtered Cu $K\bar{\alpha}_1$ radiation (λ = 1.5405 Å) at room temperature. The density was determined by the method

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(13) Story, P. R.; Fahrenholtz, S. R. *J. Org. Chem.* **1963**, *28*, 1716.

(14) See Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336.

of flotation; an aqueous potassium iodide solution was employed for this purpose.

The intensity data of all 4346 reflections with $2\Theta \leq 140°$ were collected on the CAD-4 automatic diffractometer; Ni-filtered Cu K$\bar{\alpha}$ radiation (λ = 1.5418 Å) was employed at 22 °C. The data were obtained by $\Theta - 2\Theta$ scan techniques using variable scan width of $(1.0 + 0.1 \tan \Theta)°$. The receiving aperture had a variable width of $(4.0 + 0.86 \tan \Theta)$ mm, a height of 6 mm, and was at a distance of 173 mm from the crystal. A reflection was scanned for a maximum time of 50 s; two-thirds of this time was used to measure the peak intensity, and one-sixth of this time was spent on scanning each of the left and right background. A monitor reflection intensity was checked after every 25 measurements. Three orientation control reflections were centered after every 100 reflections. In the event that a change occurred in the orientation of more than 0.1° for any angle, a new orientation matrix was automatically obtained. Of the total reflections, 893 were considered indistinguishable from background, having $I < 2\sigma(I)$, where $I = P - 2(\mathrm{RB} + \mathrm{LB})$ peak count, RB being the right background and LB being the left background. Lorentz and polarization corrections were applied to the intensity data, but no absorption corrections were made.

The program MULTAN[15] was used to solve the structure by direct methods. All non-hydrogen atoms were located from the E map calculated with 250 reflections with largest E values ($E \leq 1.5$). The structure was refined using a block-diagonal least-squares program[16] employing isotropic thermal parameters, to an R index of 0.160 ($R = \sum (|kF_0| - |F_c|)/\sum |kF_0|$). In the next stage, all the atoms were given anisotropic thermal parameters, and the structure was further refined to an R value of 0.100. A difference Fourier map calculated at this stage revealed all the hydrogen atom positions. The hydrogen atoms were assigned isotropic temperature factors and refined. The refinement was terminated when the maximum parameter shift was less than two-thirds of the corresponding standard deviation.

In all least-squares cycles, the quantity $\sum w_F(|kF_0| - |F_c|)^2$ was minimized, where $w_F = 1/\sigma_F 2$, and σ_F was obtained from the intensity statistics.[17] The scattering factors for carbon and oxygen atoms were taken from the International Tables for X-ray Crystallography,[18] and those for the hydrogen atoms were taken from the paper by Stewart and co-workers.[19] The final R index for all 4346 reflections was 0.056. The final difference Fourier map was featureless with maximum peak height of 0.11 e Å^{-3}.

Acknowledgment. Financial support of our study by The Air Force Office of Scientific Research (Grant No. AFOSR-84-0085), The Robert A. Welch Foundation (Grant B-963), The North Texas State University Faculty Research Committee, and the Faculty Research Fund, University of Oklahoma Research Council is gratefully acknowledged. The X-ray crystallographic structure determination of **9** was supported in part by a grant from the DHHS, National Cancer Institute, CA17562 (to D. van der Helm); we also thank the University of Oklahoma Computing Center for providing computing facilities and service in this connection.

Registry No. **3**, 40156-12-5; **4**, 90991-04-1; **5**, 90991-05-2; **7**, 90991-06-3; **8**, 90991-07-4; **9**, 90991-08-5; Fe(CO)$_5$, 13463-40-6.

Supplementary Material Available: Stereoviews of the single molecule of **9** and of the molecular packing of **9**, a listing of atomic parameters, bond angles, and observed and calculated structure factors for **9** (24 pages). Ordering information is given on any current masthead page.

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[15] Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

[16] Ahmed, F. R. SFLS Program, NRC-10, National Research Council, Ottawa, Ontario, Canada, 1966.

[17] van der Helm, D.; Ealick, S. E.; Burks, J. E. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1013.

[18] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[19] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Mechanism of Hydrolysis and Alcoholysis of 2-Ethoxy-*N*-vinylpyrrolidiniminium Tetrafluoroborate[1]

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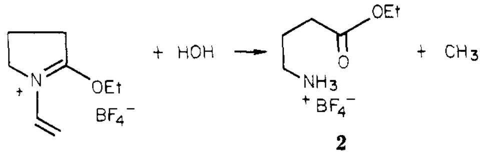
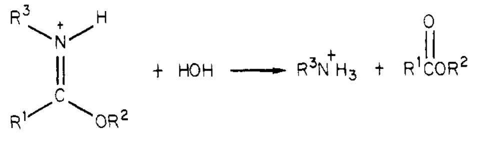
N-Vinyl-2-ethoxypyrrolidiniminium tetrafluoroborate, **1**, undergoes rapid hydrolysis to give acetaldehyde and ethyl 2-aminobutyrate, **2**. Imidate **1** reacts with methanol or ethanol, however, to give the *N*-(1-alkoxyethyl)-2-alkoxypyrrolidiniminium tetrafluoroborate **7** or **9**, respectively. Both hydrolysis and alcoholysis appear to be pseudo first order and the mechanism of each can be explained by initial formation of an "enamine-like" intermediate. The mechanism of both reactions is presented.

We have recently reported the preparation of a new imidate, *N*-vinyl-2-ethoxypyrrolidiniminium tetrafluoroborate, **1**, which undergoes remarkably facile hydrolysis under neutral conditions to give ethyl 4-aminobutyrate, **2**, and acetaldehyde, as shown in reaction 1.[2] This is similar to the behavior of the related acyclic imidates **3** which undergo hydrolysis to give an amine and the corresponding ester. Such hydrolysis is normally slow except under acidic conditions[3] and stands in contrast to the



(1)

1 **2**



(2)

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[1] (a) Presented, in part, at the 13th Northeast Regional Meeting of the American Chemical Society, Hartford, CT, June 29, 1983; ORGN 181 [Smith, M. B.; Shroff, H. N.].

[2] Smith, M. B.; Shroff, H. N. *Tetrahedron Lett.* **1983**, *24*, 2091.

[3] (a) Patai, S., Ed. "The Chemistry of Amidines and Imidates"; Wiley: London, 1975. (b) Schmir, G. L.; Cunningham, B. A. *J. Am. Chem. Soc.* **1965**, *87*, 5692. (c) Chaturvedi, R. K.; Schmir, G. L. *Ibid.* **1968**, *90*, 4413. (d) Pletcher, T. C.; Koehler, S.; Cordes, E. H. *Ibid.* **1968**, *90*, 7072. (e) DeWolfe, R. H. *J. Org. Chem.* **1971**, *36*, 162. (f) Okuyama, T.; Sahn, D. J.; Schmir, G. L. *J. Am. Chem. Soc.* **1973**, *95*, 2345. (g) Okuyama, T.; Pletcher, T. C.; Sahn, D. J.; Schmir, G. L. *Ibid.* **1973**, *95*, 1253.

0022-3263/84/1949-2900$01.50/0