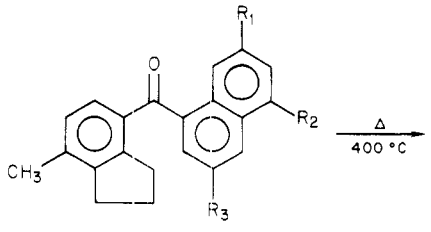
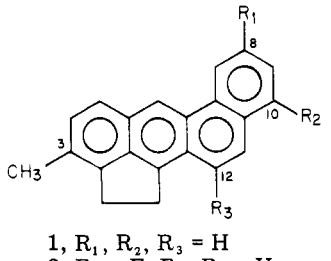
preparing fluorinated and hydroxylated methylcholanthrenes for use by researchers interested in learning if the bay region theory of carcinogenesis[4] is applicable to 1. In this paper we report the synthesis of 8-fluoro-3-methylcholanthrene, 3, and 10-fluoro-3-methylcholanthrene, 4, by the Elbs reaction but the failure of attempts to prepare 10-methoxy-3-methylcholanthrene and 12-fluoro-3-methylcholanthrene. The successful syntheses of 3 and 4 show that fluorinated methylcholanthrenes containing fluorine in the angular benzene ring can be readily prepared. However, the failures to produce 11-fluoro-3-methylcholanthrene[5] and 12-fluoro-3-methylcholanthrene (this paper) show that alternate synthetic schemes to the Elbs route must be developed. The failure to prepare the 10-methoxy compound parallels the failure to produce the 11-methoxy compound previously reported,[6] whereas both 8-methoxy-[6] and 9-methoxy-3-methylcholanthrenes[7] have been prepared.

The substituted 7-methyl-4-(substituted naphthoyl)-hydrindenes, 5–8, were prepared by reaction of the appropriate naphthyl Grignard reagents with 4-cyano-7-methylhydrindene[8] followed by hydrolysis of the imines.



2, R_1, R_2, R_3 = H
5, R_1 = F; R_2, R_3 = H
6, R_2 = F; R_1, R_3 = H
7, R_3 = F; R_1, R_3 = H
8, R_2 = OCH_3; R_1, R_3 = H



1, R_1, R_2, R_3 = H
3, R_1 = F; R_2, R_3 = H
4, R_2 = F; R_1, R_3 = H

Experimental Section[9]

4-(7-Fluoro-1-naphthoyl)-7-methylhydrindene*, 5. The Grignard reagent prepared from 12.5 g of 1-bromo-7-fluoronaphthalene,[10] 9.4 g of ethylene dibromide, and 2.7 g of sublimed magnesium in 200 mL of ether (dried by distillation from Grignard reagent) was treated with a solution of 7.85 g of 4-cyano-7-methylhydrindene[8] in 150 mL of benzene. After being held at reflux for 24 h, the mixture was treated with ammonium chloride solution and concentrated HCl. The pale yellow solid was collected after the usual workup and heated with 200 mL of water for 2.5 h. After the usual workup the product was crystallized from hexene to yield 12.5 g (82%) of 5, mp 104–105 °C.

4-(5-Fluoro-1-naphthoyl)-7-methylhydrindene*, 6. Reaction of 4-cyano-7-methylhydrindene with the Grignard reagent from 1-bromo-5-fluoronaphthalene[11] as above yielded 6, mp 110–111 °C, in 67% yield.

4-(3-Fluoro-1-naphthoyl)-7-methylhydrindene*, 7. In a similar way 1-bromo-3-fluoronaphthalene[12] afforded 7, mp 86–87 °C, in 69% yield. In the preparation of the bromofluoronaphthalene, the reduction of 1-bromo-3-nitronaphthalene to the amino compound, mp 70–71 °C, was effected in 95% yield by heating with iron powder and 65% alcohol with a small amount of concentrated HCl essentially as described for a different nitro compound.[13]

4-(5-Methoxy-1-naphthoyl)-7-methylhydrindene*, 8. 1-Amino-5-bromonaphthalene was prepared as described[11] and converted into 1-bromo-5-methoxynaphthalene[14] which, via the Grignard reagent, was used to prepare 8, mp 108–109 °C, in 60% yield.

8-Fluoro-3-methylcholanthrene*, 3. After 6.0 g of 5 was heated at 405–410 °C for 30 min by means of a sodium nitrate–potassium nitrite salt bath,[12] the product was chromatographed on neutral alumina, using benzene–petroleum ether (1:3), to yield 1.2 g (21%) of pale yellow prisms of 3, mp 182–183 °C.

10-Fluoro-3-methylcholanthrene*, 4. In a similar way 2.0 g of 6 afforded 0.9 g (47%) of 4 as pale yellow prisms, mp 208–209 °C.

Registry No. 3, 74924-89-3; 4, 74924-90-6; 5, 74924-91-7; 6, 74924-92-8; 7, 668-84-8; 8, 74924-93-9; 1-bromo-7-fluoronaphthalene, 13790-91-5; 4-cyano-7-methylhydrindene, 15085-20-8; 1-bromo-5-fluoronaphthalene, 315-56-0; 1-bromo-3-fluoronaphthalene, 343-53-3; 1-bromo-3-nitronaphthalene, 7499-65-2; 3-amino-1-bromonaphthalene, 74924-94-0; 1-amino-5-bromonaphthalene, 4766-33-0; 1-bromo-5-methoxynaphthalene, 74924-95-1.

(4) See ref 1 and 2 in Yagi, H.; Thakker, D. R.; Lehr, R. E.; Jerina, D. M. *J. Org. Chem.* **1979**, *44*, 3439.
(5) Unpublished work by Dr. Kannan in this laboratory.
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(8) Fieser, L. F.; Seligman, A. M. *J. Am. Chem. Soc.* **1936**, *58*, 2482.
(9) All melting points are uncorrected. All compounds marked with an asterisk gave analyses within ±0.3% of the theoretical and NMR spectra consistent with the proposed structures. The phase "worked up in the usual way" means that an ether–benzene solution of the products was washed with dilute Na_2CO_3 solution, dilute HCl, and saturated salt solution and dried by passing through dry $MgSO_4$.
(10) Newman, M. S.; Tuncay, A. *J. Org. Chem.* **1980**, *45*, 348.
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Pyrolysis of Alkyl 2- or 6-Alkoxynicotinates. An Unexpected Decarbalkoxylation Reaction[1]

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Received June 4, 1980

During our studies related to the thermal conversion of pyridinol to pyridinone macrocycles (1 → 2) via an O → N rearrangement,[3,4] we conducted preliminary studies on a series of alkyl 2- or 6-alkoxynicotinates in order to define the reaction parameters. When ethyl 2-ethoxynicotinate (3a, R = R′ = Et) was pyrolyzed at 240 °C for 30 h, 4a (30%) was isolated, along with unchanged starting material, whereas at 280 °C for 30 h the exclusive (>95%)

(1) Chemistry of Heterocyclic Compounds. Part 58. For the previous related paper in this series, see: Newkome, G. R.; Kawato, T.; Benton, W. H. *J. Org. Chem.* **1980**, *45*, 626.
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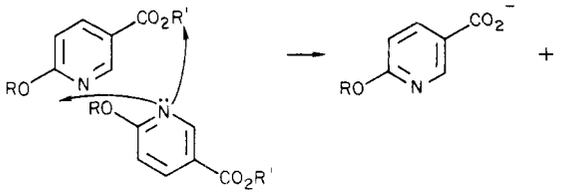
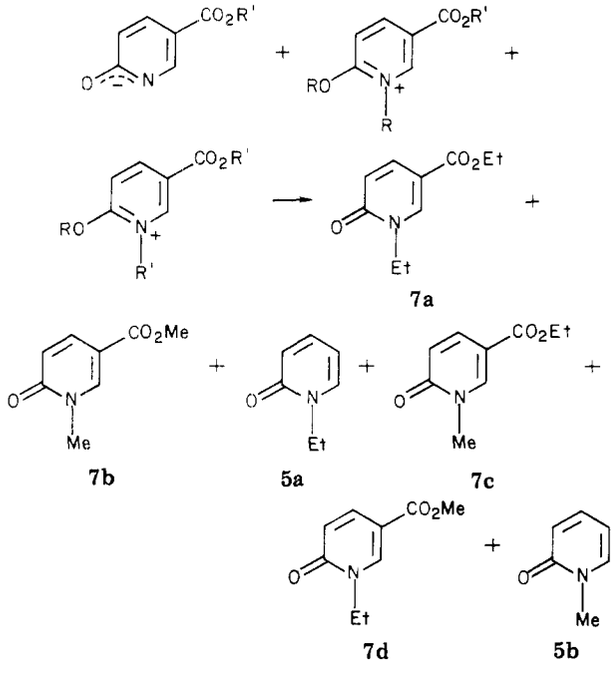
0022-3263/80/1945-4508$01.00/0

Scheme I

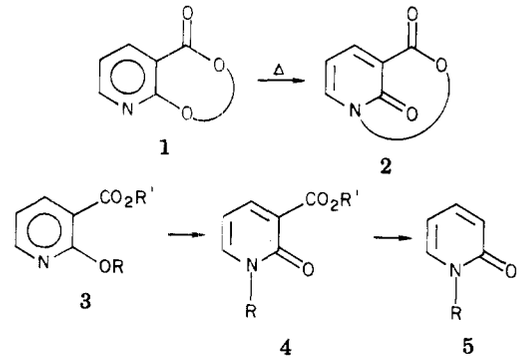


6c, R = Me; R′ = Et
d, R = Et; R′ = Me



7a 7b 5a 7c 7d 5b

product was **5a**, which was derived from decarbethoxylation of **4a**.

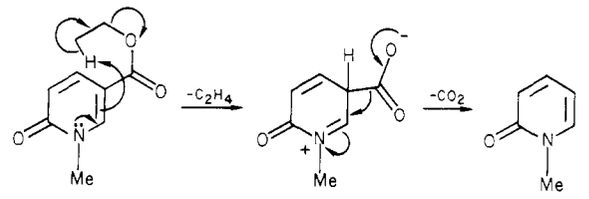


1 2 3 4 5

a, R = R′ = Et; b, R = R′ = Me

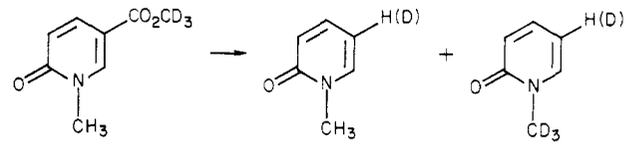
Such a complete loss of the carbethoxy group was unusual since the thermolysis of esters has been reported[5,6] to give predominantly alkylative decarboxylated products. A similar decarbalkoxylation was observed (100%) for **3b** upon thermolysis in vacuo at 280 °C for 20 h. Pyrolysis of **3a,b** or **6a** at temperatures less than 240 °C resulted in products derived predominantly from O → N migration *without* loss of the carbalkoxy moiety. At >240 °C, variable percentages of decarbalkoxylated products were obtained. The results are summarized in Table I.

Scheme II



7c 5b

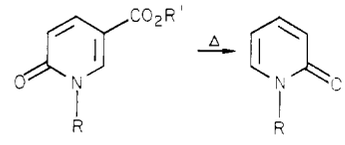
Scheme III



8

In the case of unsymmetrically substituted nicotinates (**6c** and **6d**), thermolysis leads to a mixture of products which originate from nucleophilic attack of the pyridine nitrogen at *both* the carbalkoxy group and *O*-alkyl groups (Scheme I). Attack of the imidate and carboxylate anions on the R and R′ groups of the pyridinium intermediates will then lead to some of the observed products.

In order to determine if the *N*-alkylnicotinates (**7**) are intermediates in the decarbalkoxylation step, we pyrolyzed **7a** at 280 °C to give *only* pyridinone **5a**. Thus, it is the *N*-alkylnicotinates and *not* the *O*-ethers that are the source of the decarboxylated products.



7a, R = R′ = Et 5a, R = Et
b, R = R′ = Me b, R = Me

In all of the thermolysis reactions conducted, none of the products isolated resulted from alkylative decarboxylation. This suggests that the loss of the ester group may occur via an intramolecular process (Scheme II) involving transfer of hydrogen at C-5 of the pyridinone ring followed by loss of the remainder of the ester group in a stepwise manner.

For a further understanding of the mechanism of this decarbalkoxylation, 8 was synthesized and then thermolyzed at 280 °C for 3 days in vacuo to give a clean mixture of *N*-methyl-2-pyridinones (Scheme III). The ^2H NMR in acetone of the reaction product showed two singlets at δ 6.42 and 6.20 as well as a singlet at δ 3.44 for an NCD_3 group. ^1H NMR further supported the presence of *N*-methyl-2-pyridinone and the proton-decoupled ^{13}C NMR spectrum exhibited two resonances at 105.40 and 105.75 ppm, indicative of partial deuterium incorporation at C-5. The deuterium resonance at δ 6.2 clearly indicates the incorporation of a deuteron on C-5, which is also consistent with the upfield shift of the C-5 resonance by deuterium substitution.[7] Formation of both *N*-methyl- and *N*-

(5) (a) For a recent review on the pyrolysis of esters, see: Taylor, R. In "The Chemistry of Acid Derivatives"; Patai, S., Ed.; Wiley: New York, 1979; Part 2, pp 874–908. (b) Wilczynski, J. J.; Johnson, H. W., Jr. *J. Org. Chem.* **1974**, *39*, 1909. (c) Lewis, E. S.; Herndon, W. C. *J. Am. Chem. Soc.* **1961**, *83*, 1955. (d) Wiberg, K. B.; Shryne, T. M. *J. Am. Chem. Soc.* **1955**, *77*, 2774. (e) Houssa, A. H. J.; Phillips, H. *J. Chem. Soc.* **1932**, 1232. (f) John, W. *Chem. Ber.* **1935**, *68*, 2283. (g) Stabb, H. A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 351. (h) Newman, M. S.; Mladenovic, S. *J. Am. Chem. Soc.* **1966**, *88*, 4529.

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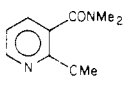
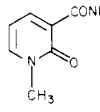
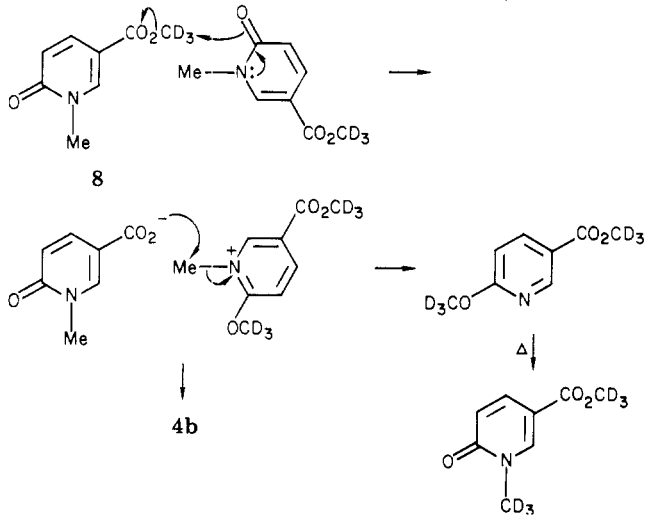
Table I. Reaction Conditions and Product Distribution of Decarbalkoxylations of Substituted Alkyl Nicotinates

starting material	conditions: temp, °C	conditions: time, h	products (% product distribution)[a]	isolated total yield, %
3a	260	30	4a (30), 3a (70)	80
	280	30	5a (100)	95
	300	10[b]	5a (80), 4a (20)	85
3b	200	48	4b (56), 3b (44)	80
	280	20	5b (100)	75
6a	260	30	7a (82), 5a (18)	90
	280	30	7a (78), 5a (22)	92
6c	280	30	7c (29), 7b (11), 5b (22), 7a (8), 7d (13), 5a (17)	75
7a	280	30	5a (100)	90
7c	280	24	5b (30), 7c (70)	87
7b	280	24	5b (22), 7b (78)	95
	280	24[b]	5b (46), 7b (54)	92
6d	280	30	7d (18), 7a (16), 5a (12), 7b (28), 7c (14), 5b (12)	95
	280	12	 (100)	100

[a] Actual isolated yields. [b] In vacuo ($<10^{-1}$ mmHg).

Scheme IV



methyl-d_3-2-pyridinone suggests that a transesterification occurred during the course of the reaction, which can arise by an alkyl oxygen to oxygen transfer followed by an alkyl nitrogen to oxygen transfer (Scheme IV).[8]

The thermal decarbalkoxylation of these (carbalkoxy)-pyridinones is an unexpected, high-yield reaction; however, the mechanistic course appears to be obscured due to the competing side reactions.

Experimental Section

General Comments. All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Unless otherwise noted, ^{1}H NMR spectra were taken in deuteriochloroform solutions with Me_4Si as internal standard (δ = 0 ppm) and were recorded on a Varian A-60A or Bruker WP 200. Mass spectral data were determined by Mr. D. Patterson on a Hewlett-Packard Model 5985 GC/mass spectrometer. The recorded R_f values were determined by a standardized thin-layer chromatography (TLC) procedure: 0.25-mm Brinkman silica gel 60 HF-254-366 plates, eluting with a stipulated mixture of ethyl acetate and cyclohexane. For preparative thick-layer chromatography (ThLC), 2-mm silica gel PF-254-366 plates were used, eluting with the given solvents. Elemental analyses were performed by Mr. R. Seab in these laboratories.

Ethyl 6-methoxynicotinate[9] **(6c), 1-methyl-5-(carbomethoxy)-2-pyridinone**[10] **(7b,** mp 138–139 °C), **1-methyl-5-(carbethoxy)pyridine**[9] **(7c,** mp 72–73 °C), **methyl 2-methoxynicotinate**[11] **(3b), ethyl 2-ethoxynicotinate**[11] **[3a,** bp 77 °C (2 mm)], and **ethyl 6-ethoxynicotinate**[9] **(6a)** were prepared according to known procedures.

5-(Carbomethoxy-d_3)-2(1*H*)-pyridinone. A mixture of 6-hydroxynicotinic acid (1.0 g, 7.2 mmol), methanol-d_4 (5 mL), and concentrated sulfuric acid (1 mL) was refluxed and worked up to give the labeled ester as colorless crystals: 610 mg (50%); mp 164–165 °C; NMR ($CDCl_3$) δ 6.60 (d, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, 1 H), 8.05 (dd, 4-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.23 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); IR (KBr) 3070–2900 (br, OH, NH), 1720, 1700 (CO_2CD_3), 1645 (CONH), 1610, 1430, 1322, 1130; mass spectrum, m/e (relative intensity) 156 (M^+, 92), 122 (100), 94 (34), 66 (11).

Anal. Calcd for $C_7H_4D_3NO_3$: C, 53.84; H, 4.51; N, 8.96. Found: C, 53.53; H, 4.43; N, 8.99.

Methyl 6-Ethoxynicotinate (6d). A mixture of 2-hydroxy-5-(carbomethoxy)pyridine[10] (1.1 g, 7.2 mmol), ethyl iodide (4.5 g, 29 mmol), and silver carbonate (2.62 g, 9.5 mmol) in anhydrous benzene (25 mL) was stirred at 25 °C in the dark for 4 days. After filtration, the residue was washed with benzene. The combined organic extract was washed with 10% sodium bicarbonate solution and then water, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give a light yellow oil, which was column chromatographed to give **6d** as a white crystalline solid: mp 51–52 °C; 1.1 g (85%); NMR ($CDCl_3$) δ 1.38 (t, OCH_2CH_3, J = 7.0 Hz, 3 H), 3.88 (s, $COOCH_3$, 3 H), 4.44 (q, OCH_2CH_3, J = 7.0 Hz, 2 H), 6.70 (d, 3-pyr-H, J = 8.5 Hz, 1 H), 8.07 (dd, 4-pyr-H, $J_{4,3}$ = 8.5 Hz, $J_{4,6}$ = 2.0 Hz, 1 H), 8.77 (d, 6-pyr-H, $J_{6,4}$ = 2.0 Hz, 1 H); mass spectrum, m/e (relative intensity) 181 (M^+, 20), 166 (100), 153 (37), 137 (53), 122 (70).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.65; H, 6.13; N, 7.73. Found: C, 59.40; H, 6.12; N, 7.67.

2-Methoxy-5-(carbomethoxy-d_3)pyridine and 1-Methyl-5-(carbomethoxy-d_3)-2(1*H*)-pyridinone. A mixture of 5-(carbomethoxy-d_3)-2(1*H*)-pyridinone (250 mg, 1.6 mmol), methyl iodide (1.02 g, 7 mmol), and silver carbonate (690 mg, 2.5 mmol) in benzene (10 mL) was stirred at room temperature in the dark for 48 h and then worked up as described above. Separation by column chromatography on silica gel, eluting with cyclohexane–ethyl acetate (1:1), gave 2-methoxy-5-(carbomethoxy-d_3)pyridine as colorless crystals: mp 40–41 °C; 70 mg (26%); NMR ($CDCl_3$)

(8) Beak, P.; Bonham, J.; Lee, J. T. *J. Am. Chem. Soc.* **1968**, *90*, 1569.

(9) Chung, N. M.; Tieckelman, H. *J. Org. Chem.* **1970**, *35*, 2517.
(10) Peterson, M. L. *J. Org. Chem.* **1960**, *25*, 565.
(11) Sliwa, H. *Bull. Soc. Chim. Fr.* **1970**, 631.

δ 4.0 (s, OCH_3, 3 H), 6.75 (d, 3-pyr-H, $J_{3,4}$ = 9.0 Hz, 1 H), 8.13 (dd, 4-pyr-H, $J_{4,3}$ = 9.0 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.81 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); IR (KBr) 1717 (CO_2CD_3), 1600, 1495, 1290 (vs), 1140, 1085, 1020 cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+, 73), 169 (M^+ – 1, 100), 140 (42), 136 (50).

Anal. Calcd for $C_8H_6D_3NO_3$: C, 56.46;, H, 5.32; N, 8.23. Found: C, 56.17; H, 5.58; N, 7.99.

A second component was eluted with chloroform–methanol (9:1) to give 1-methyl-5-(carbomethoxy-d_3)-2(1*H*)-pyridinone as colorless crystals: 20 mg (7.3%); mp 138–139 °C; NMR ($CDCl_3$) δ 3.60 (s, NCH_3, 3 H), 6.51 (d, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, 1 H), 7.83 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.18 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); IR (KBr) 1705 (CO_2CD_3), 1660 ($CONCH_3$), 1604, 1440, 1220, 1210, 1130, 1120, 1080 cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+, 80), 136 (100), 108 (69), 95 (12).

Anal. Calcd for $C_8H_6D_3NO_3$: C, 56.46; H, 5.32; N, 8.23. Found: C, 56.31; H, 5.28; N, 8.13.

General Pyrolysis Procedure. A weighed amount of pure sample (50–100 mg) was sealed in a glass tube either at atmospheric pressure or under vacuum (ca. 10^{-1} mmHg) and heated in a sand bath for 20–48 h at 200–300 °C, as stipulated in Table I. Analysis of the reaction mixture was conducted by TLC [silica gel, eluting with ethyl acetate or a mixture of ethyl acetate–cyclohexane (1:1)] and spectrally by NMR. Purification and separation of the pure components was conducted by either (1) preparative ThLC (silica gel), (2) column chromatography, or (3) recrystallization.

1-Methyl-2(1*H*)-pyridinone:[12] bp 63 °C (0.5 mm); NMR ($CDCl_3$) δ 3.58 (s, NCH_3, 3 H), 6.24 (t, 5-pyr-H, $J_{5,4} = J_{5,6}$ = 7.0 Hz, $J_{5,3}$ = 2.0 Hz, 1 H), 6.65 (dd, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{3,5}$ = 2.0 Hz, 1 H), 7.4 (m, 4,6-pyr-H, 2 H); mass spectrum, *m/e* (relative intensity) 109 (M^+, 100), 81 (78), 80 (75), 39 (10).

1-Ethyl-2(1*H*)-pyridinone:[13] bp 140 °C (0.5 mm); NMR ($CDCl_3$) δ 1.35 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 4.02 (q, NCH_2CH_3, *J* = 7.0 Hz, 2 H), 6.18 (dt, 5-pyr-H, $J_{5,4} = J_{5,6}$ = 6.5 Hz, $J_{5,3}$ = 1.5 Hz, 1 H), 6.57 (dd, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{3,5}$ = 1.5 Hz, 1 H), 7.3 (m, 4,6-pyr-H, 2 H); mass spectrum, *m/e* (relative intensity) 123 (M^+, 86), 95 (69), 80 (70), 67 (100).

1-Methyl-3-(carbomethoxy)-2(1*H*)-pyridinone: mp 71 °C (lit.[14] mp 70–71 °C; NMR ($CDCl_3$) δ 3.62 (s, NCH_3, 3 H), 3.92 (s, CO_2CH_3, 3 H), 6.25 (t, 5-pyr-H, *J* = 7.0 Hz, 1 H), 7.63 (dd, 4-pyr-H, $J_{4,5}$ = 7.0 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.18 (dd, 6-pyr-H, $J_{6,5}$ = 7.0 Hz, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, (relative intensity) 167 (M^+, 100), 136 (95), 108 (43).

1-Ethyl-3-carbethoxy-2(1*H*)-pyridinone: oil; NMR ($CDCl_3$) δ 1.30 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 1.41 (t, $CO_2CH_2CH_3$, *J* = 7.5 Hz, 3 H), 4.06 (q, NCH_2CH_3, *J* = 7.0 Hz, 2 H), 4.36 (q, $CO_2CH_2CH_3$, *J* = 7.5 Hz, 2 H), 6.22 (t, 5-pyr-H, *J* = 7.0 Hz, 1 H), 7.58 (dd, 4-pyr-H, $J_{4,5}$ = 7.0 Hz, $J_{4,6}$ = 2.0 Hz, 1 H), 8.05 (dd, 6-pyr-H, $J_{6,5}$ = 7.0 Hz, $J_{6,4}$ = 2.0 Hz, 1 H).

1-Methyl-5-(carbomethoxy)-2(1*H*)-pyridinone: mp 139–140 °C (lit.[15] mp 139 °C); NMR ($CDCl_3$) δ 3.62 (s, NCH_3, 3 H), 3.88 (s, CO_2CH_3, 3 H), 6.54 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.87 (dd, 4-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.23 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 167 (M^+, 76), 136 (100), 108 (57), 95 (12).

1-Methyl-5-(carbethoxy)-2(1*H*)-pyridinone: mp 72–73 °C (lit.[16] mp 72–73 °C); NMR ($CDCl_3$) δ 1.35 (t, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 3 H), 3.64 (s, NCH_3, 3 H), 4.33 (q, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 2 H), 6.53 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.85 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.27 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 181 (M^+, 42), 153 (25), 136 (100), 108 (43).

1-Ethyl-5-(carbomethoxy)-2(1*H*)-pyridinone: mp 93–94 °C; NMR ($CDCl_3$) δ 1.40 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 3.87 (s, CO_2CH_3, 3 H), 4.03 (q, NCH_2CH_3, *J* = 7 Hz, 2 H), 6.52 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.84 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.0 Hz, 1 H), 8.18 (d, 6-pyr-H, $J_{6,4}$ = 2.0 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 181 (M^+, 73), 153 (47), 150 (22), 122 (100).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.65; H, 6.13; N, 7.73. Found: C, 59.81; H, 6.09; N, 7.70.

1-Ethyl-5-(carbethoxy)-2(1*H*)-pyridinone:[9] bp 130 °C (0.7 mm); NMR ($CDCl_3$) δ 1.35 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 1.40 (t, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 3 H), 4.05 (q, NCH_2CH_3, *J* = 7.0 Hz, 2 H), 4.34 (q, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 2 H), 6.52 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.85 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.2 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 195 (M^+, 83), 150 (35), 139 (85), 122 (100).

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Registry No. 3a, 15441-51-7; **3b**, 67367-26-4; **4a**, 74925-36-3; **4b**, 67367-27-5; **5a**, 13337-79-6; **5b**, 694-85-9; **6a**, 24903-80-8; **6c**, 74925-37-4; **6d**, 74357-22-5; **7a**, 24903-82-0; **7b**, 6375-89-9; **7c**, 10561-91-8; **7d**, 74925-38-5; **8**, 74925-39-6; 6-hydroxynicotinic acid, 5006-66-6; 5-(carbomethoxy-d_3)-2(1*H*)-pyridinone, 74925-39-6; 2-hydroxy-5-(carbomethoxy)pyridine, 66171-50-4; ethyl iodide, 75-03-6; 2-methoxy-5-(carbomethoxy-d_3)pyridine, 74925-40-9; *N,N*-dimethyl-2-methoxynicotinamide, 74925-41-0; 5-(dimethylcarbamoyl)-1-methyl-2(1*H*)-pyridinone, 74925-42-1.

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Intramolecular Ene Reactions of 1,2-Diallylcyclohexanes

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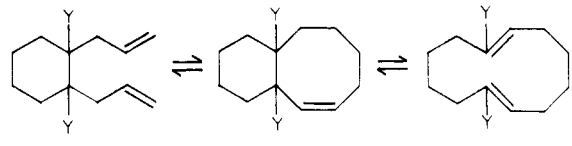
The ene reaction which interconverts 1,7-octadiene and cyclooctene is reversible and at temperatures above 300 °C the two components are in mobile equilibrium.[2] However, the reaction is limited to 1,7-dienes lacking terminal alkyl substituents.[3] There exists in this equilibrium the potential for a very interesting six-carbon ring expansion (eq 1), but so far as we can ascertain, no attempt



(1)

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to realize this possibility has been made. Before considering any experimental studies, we need to take note of some important thermodynamic considerations. From the group values of Benson,[4] one can get some rough approximations for $\Delta H°$ and $\Delta S°$ for the various equilibria of eq 1 (Y = H).[5] For 1 ⇌ 2 $\Delta H° \simeq -16$ kcal/mol and $\Delta S° \simeq -20$ eu; for 2 ⇌ for 3 $\Delta H° \simeq +14$ kcal/mol and $\Delta S° \simeq +25$ eu; for 1 ⇌ 3 $\Delta H° \simeq -2$ kcal/mol and $\Delta S° \simeq +5$ eu. Taken at face value, these values indicate that at 600 K

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