

Pyrolysis of Alkyl Acetates. A Radical Pathway for the Formation of Minor Products

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Decyl acetate and decene pyrolysis under the same reaction conditions show that the formation of the minor products during the pyrolysis of esters occurs by a parallel, and not a secondary, reaction. The radioactivity observed in the CO₂ and CO produced during the pyrolysis of 1-hexyl acetate-1-¹⁴C and the radioactivity in the methane from the pyrolysis of 1-hexyl acetate-2-¹⁴C strongly suggested a radical reaction pathway for the formation of the minor products. Considering the above results together with the radioactivity data of gas samples from the pyrolysis of 1-decyl-1-¹⁴C acetate, 1-hexyl-1-¹⁴C acetate, and 1-heptadecyl-1-¹⁴C acetate leads to the conclusion that the mechanism of pyrolysis of esters may be viewed as a cyclo-DE₂NA₂N mechanism for the formation of the major alkene product and a radical mechanism for the formation of minor products. A useful synthetic procedure for the preparation of high carbon number alkenes (>10) also results from this study.

Introduction

The pyrolysis of esters is a useful method for the preparation of alkenes and has been studied extensively.¹ On the basis of the stereochemistry of the reaction, a cyclic, concerted mechanism was suggested;² this was later conformed on the basis of the cis-stereospecificity.^{3,4} The studies on the pyrolysis of (-)-menthyl benzoate⁵ and the pyrolysis of deuterium-labeled *sec*-butyl acetate⁶ proved that the reaction is both homogeneous and unimolecular. It seems clear that the mechanism of the pyrolysis of an ester is by the cyclo-DE₂NA₂N mechanism in the IUPAC system.⁷

Most studies have focused on the formation of the major product(s); less attention was given to the minor products. The question of whether the minor products come from a minor primary reaction pathway or from secondary reactions of the alkene is not clear. In order to understand the mechanism of pyrolysis of ester fully, it is necessary to learn how the minor products are formed.

We have utilized the pyrolysis of acetates to synthesize isotopically labeled alkenes. The pyrolysis of carbon-14 labeled acetates enable us to obtain additional data to address the above mechanistic considerations.

Results

Carbon-14 labeled alkenes were synthesized by the procedure in Scheme 1.

The location of the ¹⁴C in the alkene was determined by the oxidation of labeled alkene using aqueous KMnO₄. In

the case of 2-O, greater than 95% of the total radioactivity was found in formic acid which was produced by the oxidation. In the case of 3-O, the radioactivity of formic acid was greater than 98% of the total radioactivity. These experiments show, considering the experimental errors associated with the olefin oxidation procedure, that the ¹⁴C is located in the 1-position of the 1-alkenes synthesized using the procedure outlined in Scheme 1.

The labeled hexyl acetate esters [*n*-C₆H₁₃O¹⁴COCH₃ (4) and *n*-C₆H₁₃OCO¹⁴CH₃ (5)] were prepared by the reaction of the appropriate radioactive sodium acetate with bromohexane.

Before the pyrolysis was conducted to synthesize a ¹⁴C-labeled alkene, the pyrolysis of the corresponding unlabeled ester was studied using different temperatures and flow rates to obtain the best reaction conditions. These experimental data permit a calculation of the first-order rate constants and a study of the mechanisms for the pyrolysis of alkyl acetates.

It is necessary to know the contact time to calculate first-order rate constants. Assuming 1 mol of reactant leads to 2 mol of products, the average contact time, *t*, can be calculated using eq 1

$$t = (LA(3.6)(273))/[m(22.4)T(1 + a)] \quad (1)$$

where *L* = length of reactor in cm, *A* = cross-sectional area of reactor in cm², *m* = input of ester in g-mol/h, *T* = temperature of reactor in K, and *a* = conversion. The first-order rate constant can then be calculated using eq 2.

$$k = 1/t \ln 1/(1 - a) \quad (2)$$

For the pyrolysis of 1-decyl acetate, the data are given in Table 1. The plot of ln *k* vs 1/*T* (Figure 1) shows a reasonably good linear relationship. Deviations from a first-order reaction may be due to the calculation of the contact time assuming that 1 mol of reactant produces 2 mol of products which may be true for the formation of the major products but is not valid for the formation of minor products. Because about 10–20% of the minor

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(3) (a) Barton, D. H. R.; Rosenfelder, W. J. *J. Chem. Soc.* 1949, 2459.
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(b) Arnold, R. T.; Smith, G. G.; Dodson, R. M. *J. Org. Chem.* 1950, 15, 1256.
(5) Barton, D. H. R.; Head, A. J.; Williams, R. J. *J. Chem. Soc.* 1952, 453.
(6) Dabbagh, H. A.; Davis, B. H. *J. Org. Chem.* 1990, 55, 2011.
(7) IUPAC rules for representation of reaction mechanisms: *Pure. Appl. Chem.* 1989, 61, 23. Other material related to this may be found in the following: Guthrie, R. D.; Jencks, W. P. *Acc. Chem. Res.* 1989, 22, 343. Guthrie, R. D. *Stud. Org. Chem.* 1986, 31, 321.

Scheme 1

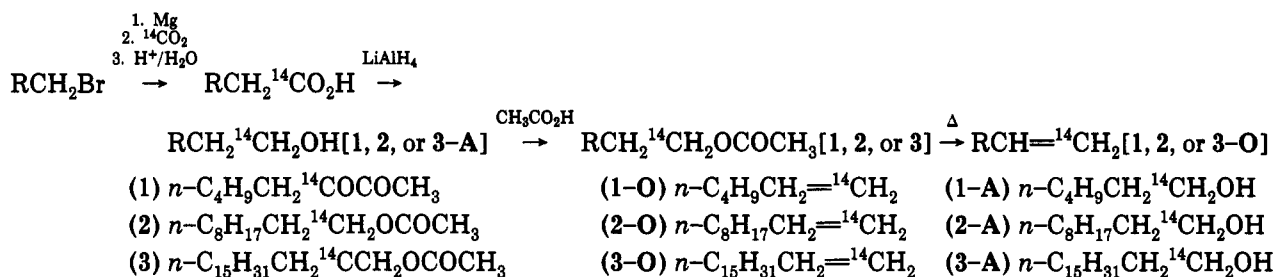


Table 1. Rate Constants for the Pyrolysis of Decyl Acetate

temp, °C	350	375	395	405	445	495
flow rate, mL of ester per h	3.4	0.2	3.4	0.57	5.1	5.1
conversn of ester, %	1.33	36.7	7.39	99.96	37.6	94.1
contact time, t, s	92.7	1060	81.6	2940	39.5	26.2
k, s ⁻¹	0.000 144	0.000 430	0.000 941	0.00 267	0.01 20	0.108
log k + 4	0.158	0.633	0.974	1.43	2.08	3.03

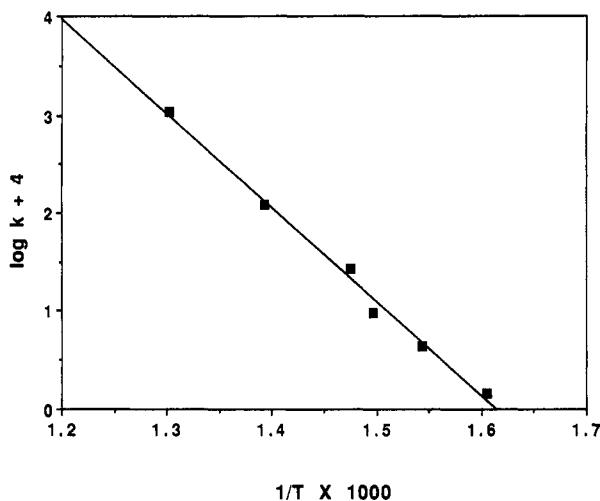


Figure 1. Arrhenius plot for the pyrolysis of decyl acetate at 1 atm.

Table 2. Relative Amount of Minor Products and Decene in the Pyrolysis Products from Decyl Acetate

temp, °C	conversn, %	minor products, wt %	decene, wt %
350	1.33	13.2	86.8
375	36.7	13.1	86.9
395	7.39	10.5	89.5
405	~100	15.9	84.1
445	37.6	12.6	87.4
445	98.8	13.9	86.1
495	94.1	13.7	86.3
500	99.0	15.3	84.7
500	93.3	15.4	84.6

products may be produced (as shown in Table 2), and since most of these products are low molecular weight compounds (Table 3), this assumption will create an error in calculating the contact time t and the rate constant k for runs at high conversion. Assuming that the conversion of 1 mol of reactant generates n mol of minor products, the conversion (a) in eq 1 should be corrected using eq 3:

$$a = \text{conversion X major \%} + \frac{\text{conversion X minor \% X } n}{3} \quad (3)$$

On the basis of calculations using the above equations, a value of 43.9 kcal/mol for the activation energy for the pyrolysis of decyl acetate was obtained. This value is comparable to values reported for other esters.¹

Data for the composition of the liquid fraction of the products from the conversion of 1-decyl acetate and 1-decene are summarized in Table 3. In addition to the major product, 1-decene, the identity of the compounds corresponding to more than 50–70% of the minor products was obtained from GC/MS data. A variety of alkenes, dienes, and cycloalkanes, ranging from C₅ to C₁₃, were produced. As shown in Table 2, the amount of minor products relative to 1-decene increased little, if at all, as the temperature was increased.

The pyrolysis of 1-decene, under the same reaction conditions as used for pyrolysis of the acetate, was performed to learn whether the minor products are due to secondary reactions of 1-decene. The data in Table 4 show that about 2–7% of the 1-decene was converted to minor products under the most severe conditions used for acetate pyrolysis. The amount of secondary conversion of 1-decene indicates at least 5–10% of the decyl acetate is converted in a minor pathway (see Figure 2).

In the preparation of carbon-14 labeled alkenes, five alkyl acetates were pyrolyzed. Gas samples were collected and analyzed by GC/MS, and the compound identity was confirmed with authentic compounds. The C₂–C₆ components produced in these runs are summarized in Table 5. The same compounds were present in the gas samples obtained from different esters; however, the relative amounts of these compounds depend upon the ester. Gaseous alkenes and dienes were formed as the dominant minor products in the gas sample.

For the pyrolysis of 5 at 400 °C over glass beads, the gas flow was measured to be 4.3 mL/h. On the basis of the gas sample only, about 2–3% of the hexyl acetate was converted to minor products. For the pyrolysis of 1-decyl acetate, about 1% of ester was converted to gases (C₁–C₅).

The relative radioactivities of compounds in the gas sample are given in Table 6. In the case of 4 and 5, no radioactivity was observed in the C₂–C₆ compounds in the gas fraction, and this is expected. In the case of 1, the radioactivity per carbon of C₃ is larger than that of C₂ and C₄ and is about the same as that of C₆. The radioactivity per carbon of C₅ is less than that of C₄. In the case of 2, the radioactivity per carbon of the C₂ increases from C₂ to the C₅ products; the radioactivity per carbon of C₅ is about the same as that of C₁₀. The radioactivity per carbon for the C₂ to C₄ products from the pyrolysis of 3 increases

Table 3. Product Distribution^a in the Pyrolysis Products from Decyl Acetate and 1-Decene

temp, °C conversn, % compds	decyl acetate				decene
	375	405	445	495	495
conversn, %	36.7	~100	37.6	94.1	8.0
compds					
cyclopentene	0.201	0.607	0.054	0.45	0.546
1-hexene	1.84	2.05	0.093	1.03	1.01
4-methylcyclopentene	0.102	0.576	0.005	0.162	0.15
1,4-hexadiene		0.686	0.001	0.277	0.168
1,2-dimethylcyclopentane	0.098	4.31	0.103	1.91	1.31
2-methyl-1,4-hexadiene		0.419		0.015	
toluene		0.404		0.077	
4-methyl-1,4-hexadiene		0.432	0.007	0.045	
1-butyl-2-methylcyclopropane	0.246	2.12	0.233	1.20	0.463
exo-2-methylbicyclohexane		0.190		0.050	
ethylcyclohexene	0.126	0.140	0.011	0.052	
1-methyl-2-pentylcyclopropane	0.235	1.60	0.045	0.497	0.017
1-decene	31.9	84.1	32.9	81.3	92.0
1-undecene		0.305	0.041	0.108	
1-dodecene	0.509	0.138	0.047	0.036	
tetradecene		0.008			
others	1.47	1.91	4.10	6.94	4.31
1-decyl acetate	63.3	0.043	62.4	5.91	

^a Product distribution (wt %) was determined by using GC; only the compounds that were identified are shown in this table; the unidentified compounds are grouped as "others".

Table 4. Relative Amount (wt %) of Minor Products from the Pyrolysis of 1-Decene and from the Pyrolysis of Decyl Acetate in Toluene (35 mol %)

temp, °C conversn, % minor products, wt % 1-decene, wt %	1-decene				decyl acetate in toluene
	350	395	445	495	495
conversn, %					84.14
minor products, wt %	0.50	1.55	3.76	7.52	7.98
1-decene, wt %	99.50	98.45	96.24	92.48	92.02

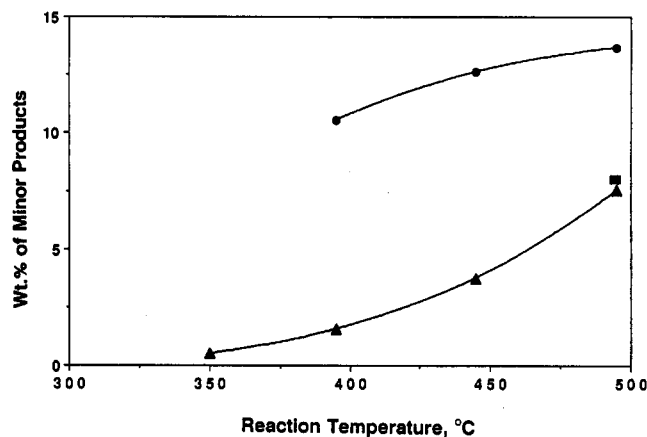


Figure 2. The weight percent of the minor products from the conversion of decyl acetate (●), decyl acetate with toluene (■), and 1-decene (▲) as a function of temperature.

as the carbon number increases. These results are presented in Figure 3.

The relative radioactivities of the C₁ products are given in Table 7. In the case of 1-3, all of the radioactivity is present in methane. For the C₁ products from the pyrolysis of 4 over different silicas, about 80% of the radioactivity is in the CO₂ and the other 20% is in the CO. This was the case whether the reaction tube was filled with glass beads or a low (about 1 m²/g) or medium (about 50 m²/g) surface area silica. Furthermore, the ratio [percent activity/percent compound] for CO and CO₂ was essentially the same (about 1.5; Table 7) for the three forms of silica used to fill the tube. Thus, the distribution of the

Table 5. Product Distribution of Gas Fraction^a in the Pyrolysis of Alkyl Acetates

ester	1 ^b	2 ^c	3 ^c	4 ^d	4 ^e
temp, °C	390	400	400	400	400
compds ^f					
ethane	43.4	14.6	23.4	18.7	20.7
ethylene	5.10	36.1	52.6	39.9	29.0
propane	2.40	3.47	1.80	0.01	4.27
propylene	15.4	38.1	20.6	22.8	21.4
1-butene	4.20	5.41	1.03	6.66	6.40
t-2-butene	2.10	0.20	0.01	0.50	0.25
c-2-butene	1.60	0.13	0.01	0.27	0.21
1,3-butadiene	5.50	1.05	0.41	4.74	2.34
pentenes	3.20	0.89	0.14	1.68	3.41
hexenes	17.1	0.13	0.01	4.91	12.1

^a Only C-2 to C-6 hydrocarbon products are included in this table; the product distribution is based on GC analysis in mol %. ^b This compound was run over SiO₂ (OX-50, 50 g/m²). ^c These compounds were run over glass beads (3 mm). ^d This compound is hexyl acetate-2-¹⁴C and was run over glass beads. ^e This compound is hexyl acetate-2-¹⁴C and was run over OX-50 silica. ^f Compounds were identified by GC/MS and confirmed by authentic compounds based on GC retention time.

Table 6. Relative Radioactivity per Carbon of the C₇-C₈ Compounds^a in the Pyrolysis Products from Alkyl-1-¹⁴C Acetates

ester	1	2
temp, °C	390	400
compd class		
C-2	0.782	0.452
C-3	0.973	0.633
C-4	0.374	0.946
C-5	0.115	0.945
C-6	1.00	0.591
C-7		0.012 ^b
C-8		0.011 ^b
C-9		0.016 ^b
C-10		1.00

^a Radioactivity of gas sample was determined from GC and proportional counter peak areas; in the case of decyl-1-¹⁴C acetate, HPLC was used to separate C-7-C-10 compounds, and the radioactivity of eluent was measured by a liquid scintillation counter. ^b These values were obtained from HPLC/liquid scintillation analysis.

CO, CO₂, and CH₄ and the activity of the CO and CO₂ do not depend upon the form of silica used to fill the reactor.

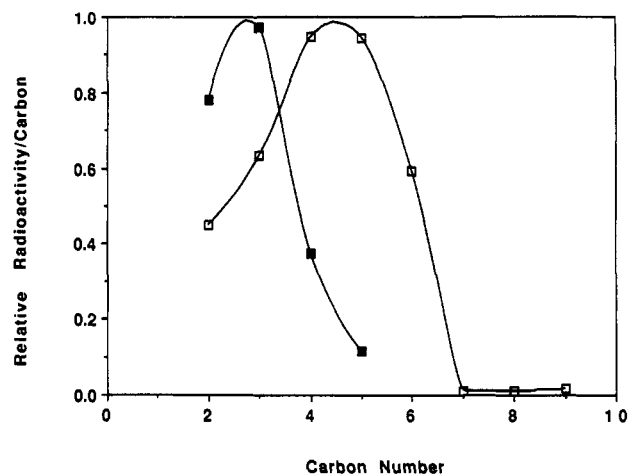


Figure 3. Relative radioactivity/carbon $[(\text{DPM}/\text{mol}/N)_i/(\text{DPM}/\text{mol}/C_R)]$, where i is the carbon number of the minor product and C_R is the carbon number of the primary alkene product] versus carbon number for the pyrolysis of hexyl-1- ^{14}C acetate (■) and decyl-1- ^{14}C acetate (□).

Table 7. Relative mol % and Radioactivity Distribution in the C_1 Products from the Pyrolysis of Alkyl Acetates

ester	CO		CO ₂		CH ₄	
	mol %	activity, %	mol %	activity, %	mol %	activity, %
1 ^a	2.2	0	1.4	0	96.4	100
2 ^a	3.3	0	13.3	0	83.3	100
3 ^a	25.0	0	29.0	0	46.0	100
4 ^a	13.0	23.0	51.0	77.0	36.0	0
4 ^b	13.0	20.0	53.0	80.0	34.0	0
4 ^c	13.0	16.5	57.0	83.5	30.0	0

^a These runs were over glass beads at 400 °C. ^b This run was over OX-50 silica (about 50 m²/g) at 400 °C. ^c This run was over silica at (about 1 m²/g) 390 °C.

Table 8. Product Distribution in the Pyrolysis Products from Heptadecyl Acetate in Toluene

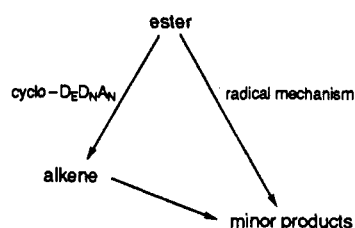
temp, °C	490 ^a	495 ^a	400 ^b
conversion, wt %	89.6	96.19	98.12
1-heptadecene, wt %	91.1	91.2	93.73
minor products, wt %	8.89	8.85	6.27
comps ^c			
benzene	0.112	0.135	1.056
toluene	81.9	81.3	79.8
ethylbenzene	0.006	0.007	0.021
(<i>p,m</i>)-xylene	0.019	0.023	0.022
<i>o</i> -xylene	0.040	0.056	0.059
1-ethyl-2-methylbenzene	2.26	2.45	0.107
1-ethenyl-2-methylbenzene	0.046	0.056	0.023
1-undecene	0.065	0.085	0.086
(1-methyl-2-cyclopropen-1-yl)benzene	0.040	0.050	0.012
1-tetradecene	0.074	0.002	0.203
1-heptadecene	13.2	14.5	17.4
others	0.554	0.669	0.824
1-heptadecyl acetate	1.69	0.648	0.357

^a These runs were conducted in a small (24.13 cm × 0.8024 cm²) reactor. ^b This run was carried out in a large (48.26 cm × 4.56 cm²) reactor. ^c Compounds were identified by GC/MS and confirmed by authentic compounds based on GC retention time.

This indicates that these products arising from the reaction of the acetate species are the result of a gas-phase reaction.

To facilitate pumping solid heptadecyl acetate, the ester was dissolved in toluene. A number of substituted benzenes were produced during the pyrolysis as minor products (Table 8). Calculation of the conversions shown in Table 8 is based on the assumption that all of the alkyltoluenes comes from the reaction of toluene with some

Scheme 2. Reaction Pathway for the Pyrolysis of Esters



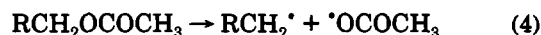
fragment derived from heptadecyl acetate. Thus, only the alkyl group of the alkyltoluenes are considered to be products derived from heptadecyl acetate. If only the C₅–C₁₉ alkene, diene, and cycloalkane minor products and the contribution to the alkyl group of the alkyltoluenes are considered, the relative amount of minor products is smaller for the pyrolysis of heptadecyl acetate in toluene than that of the pyrolysis of decyl acetate in the absence of toluene. When about 35% of toluene was added to the 1-decyl acetate, the amount of minor products formed during the pyrolysis also decreased (Table 4, Figure 2). Toluene therefore inhibits the production of minor products during acetate pyrolysis.

Discussion

In an early study of the mechanism of pyrolysis of esters and acetals, a radical mechanism was proposed for the pyrolysis of esters.⁸ Because the pyrolysis of esters is unaffected by addition of radical inhibitors such as propylene or nitric oxide, in some cases even in large amounts,⁵ a radical or radical-chain mechanism was rejected. Most evidence suggests that the formation of alkene is through a cyclo-DEDNA mechanism in the pyrolysis of certain carboxylic esters even though evidence for a radical mechanism is also presented.⁹

However, it is very difficult to use the cyclo-DEDNA mechanism to explain the formation of the minor products. The results of the present study show that the formation of a portion of the minor products may occur by secondary reactions of the primary alkene; however, for the pyrolysis of decyl acetate the cracking of decene contributes 30% or less of these minor products. For the 10–15% of the ester that is converted to minor products, at least 60% of the minor products are formed by a reaction that parallels the alkene formation as shown in Scheme 2.

The formation of a variety of alkenes, dienes, and cycloalkanes, as shown in Table 2 for the pyrolysis of 1-decyl acetate, can be explained by the radical mechanism shown in eq 4:

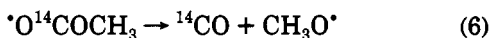
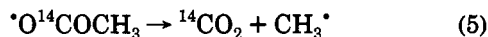


The first step of this reaction is the generation of alkyl and acetoxy radicals. The low carbon number alkenes occur by decomposition of the alkyl radical, presumably by the well-founded β -scission mechanism. Cyclization of a radical provides a pathway to produce cycloalkanes and cycloalkenes. Dimerization and/or rearrangement of the free radicals can also produce alkenes, alkanes, and even higher carbon number olefins. The radical mechanism can also explain the formation of the compounds present in the gas samples (Table 6).

(8) Bilger, E. M.; Hibbert, H. *J. Am. Chem. Soc.* 1936, 58, 823.

(9) Louw, K. *Recl. Trav. Chim. Pays-Bas.* 1965, 84, 1511.

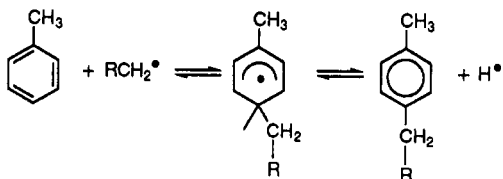
The radioactivity data shown in Table 8 support the radical mechanism for the formation of minor products. The radioactivity observed in CO₂ and CO in the case of 4 can be explained by eqs 5 and 6:



Evidence for the occurrence of the reaction in eq 6 is provided by the formation of methanol. In all runs, methanol was found in the liquid products. Because of the difficulties in accurately measuring the amount of methanol, it has not been included in Table 3. In the case of alkyl-1-¹⁴C acetate, the radioactivity in CH₄ can be explained by the cleavage of the alkyl radical. Thus, the acetate portion of the reactant, in addition to leading to the acetic acid product, provides a source of radicals to initiate the secondary reactions.

The data presented in Table 6 and Figure 3 suggest that the dominant intermediate in the formation of the minor products from the alkyl group arises by a mechanism where the radical is located in terminal position that is labeled with the ¹⁴C. Thus, for hexyl acetate (1) the C₃ products have essentially the same activity/carbon as the hexene product. The C₄ and C₅ products have considerably lower, but still significant, activity compared to hexene; thus, there appears to be some hydrogen atom migration to locate the free radical at secondary carbons prior to β scission. For hexyl acetate (1) pyrolysis the C₂ fraction has a lower activity/carbon than the 1-hexene. This implies that C₂ is also formed by the combination of two unlabeled methyl radicals derived from the decomposition of the acetyl radical. The data for the pyrolysis of 2 fits the same pattern as for 1 except now C₅ is expected to have a similar activity/carbon as the 1-decene products, and it does. It appears in this case that a higher fraction of C₂, and a considerable fraction of C₃, is formed from the unlabeled methyl radicals derived from the acetyl radical.

Toluene is well-known as a strong radical inhibitor.⁵ When toluene was added to the decyl acetate or the heptadecyl acetate, the relative amount of minor products produced during the pyrolysis was decreased. Also, the formation of substituted benzenes can be explained by the participation of toluene in a radical process such as shown in eq 7:



In summary, pyrolysis of esters is an important synthetic method for producing alkenes. The detailed mechanism for this reaction is important, therefore, not only from a theoretical consideration but also from a synthetic point of view. For the formation of major alkenes the cyclo-DE_NAN mechanism operates, but for the formation of minor products a radical mechanism seems valid. On the basis of this study, the amount of minor products can be reduced by adding an inhibitor such as toluene. For synthesizing higher carbon number alkenes (>10), pyrolysis of the ester in the presence of toluene seems to provide a valuable alternative route to the pyrolysis of a mixture

of the alcohol and aldehyde.¹⁰ The addition of toluene is also convenient for synthesis of alkenes; by passing the reaction mixture through a silica gel column, toluene and any unreacted ester can be easily separated from the alkene product.

Experimental Section

Materials. Decyl acetate was obtained from Lancaster and used as received. Decene was obtained from Aldrich and was purified by fractional distillation to give 98% purity (GC). The glass beads (3 mm) and all starting materials were purchased from Aldrich Chemical Co.

Compounds 4 and 5 were prepared by a reaction of radioactive sodium acetate (16.41 g, 0.2 mol) with bromohexane (33.01 g, 0.2 mol) in 120 mL of *N,N*-dimethylformamide (DMF). The reaction mixture was stirred at 67 °C for 72 h. After the reaction mixture was cooled to room temperature, 500 mL of dichloromethane was added. The organic layer was separated and washed with water until DMF was not detected. After the solvent was removed, distillation at 100 °C/100 mmHg yielded 23.7 g of hexyl acetate. GC analysis indicated that this ester is 98% pure.

1-Decyl-1-¹⁴C acetate (2) was prepared by the following procedure: 1-Decanoic-1-¹⁴C acid was prepared by the reaction of the Grignard reagent of 1-bromononane in ethyl ether with ¹⁴CO₂ which was produced in a vacuum system from the reaction of ¹⁴C-labeled barium carbonate with concentrated sulfuric acid. The reduction of decanoic-1-¹⁴C acid with lithium aluminum hydride in anhydrous ether gave 1-decanol-1-¹⁴C. A mixture of 1-decanol-1-¹⁴C (22.7 g, 0.144 mol), sodium acetate (5.3 g, 0.064 mol), and acetic anhydride (16.2 g, 0.159 mol) in 32 mL of benzene was stirred for 2 h and then refluxed for 4 h. After the reaction mixture was cooled to room temperature, 80 mL of water was added. Sodium carbonate, 50 mL of 50% solution, was added to the separated benzene layer, and then the mixture was stirred for 2 h to remove residual acetic anhydride. The benzene layer was separated, washed with water, and then dried over magnesium sulfate. After the solvent was removed, 29.0 g of 1-decyl-1-¹⁴C acetate was obtained. GC analysis indicated that the purity of this ester was 97%. 1-Hexyl-1-¹⁴C acetate (1) and 1-heptadecyl-1-¹⁴C acetate (3) were prepared using the same procedure.

Pyrolysis Procedure. A glass plug flow reactor (small, *L* = 24.13 cm, *A* = 0.8024 cm²; or large, *L* = 48.26 cm, *A* = 4.56 cm²) was filled with glass beads (3 mm) or silica (Degussa OX-50). The esters were added at the top of the reactor at a constant rate using a syringe pump. Products were collected at room temperature. A typical example of the synthesis of an alkene is shown by the preparation of 3 as follows:

A solution of 27 g of 1-heptadecyl-1-¹⁴C acetate in 75 mL of toluene was introduced at 3.4 cc²/h into the large glass plug flow reactor at 400 °C. The liquid fraction was collected and washed with 10% sodium carbonate and then water. After the low molecular weight impurity was dried and evaporated by a rotovapor evaporator, the liquid was passed through a column filled with 85 g of silica gel; hexane was used to elute the products from the column. After the hexane was removed, 15.3 g of 1-heptadecene-1-¹⁴C was obtained (yield, 74.3%).

Product Analysis. Total conversion and the product composition were determined by GC using DB-5 column (60-m × 0.32-mm fused silica column). The determination of minor products was performed using a GC/MS; the gas chromatograph was interfaced with an HP5971A mass selective detector that was operated under the control of a Vectra 05/165 computer using HPG1034B software. Gas compositions were determined by GC using a Poropak Q column; this gas chromatograph was interfaced in series with a Radiomatic detector so that the chemical composition and the radioactivity of each gas component could be determined for the same sample. In the case of 1-decyl-1-¹⁴C acetate, HPLC separation of the liquid fraction was performed using a C-17 column. The radioactivity in each HPLC fraction that was collected was determined using a 1500 Tri-Carb liquid scintillation analyzer.

(10) Aubrey, D. W.; Barnatt, A.; Gerrard, W. *Chem. Ind. (London)* 1965, 681.