Non-Volatile *a*-Branched Chain Fatty Acid Derivatives: IV. Addition of Aryl Esters to Long Chain Olefins

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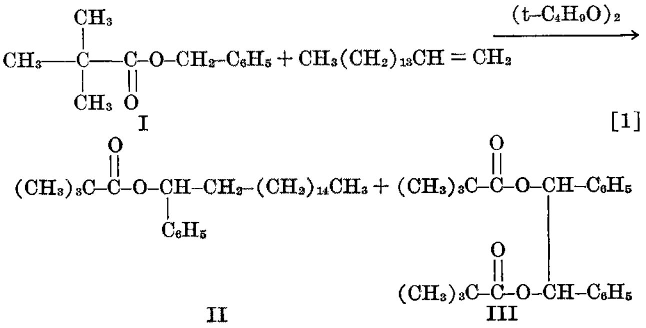
Abstract

The di-tertiary butyl peroxide initiated free radical addition of methyl phenylacetate, methyl *p*-tolylacetate and methyl *p*-methoxyphenylacetate to 1-decene gives two types of products. In addition to the expected α-branched esters, dehydrodimer (both *meso* and *dl*) esters were also obtained. The highest yield of α-branched ester was obtained from methyl phenylacetate. Higher yields of the dehydrodimer esters were obtained from the substituted phenyl esters. Attempts to add methyl *p*-nitrophenylacetate to 1-decene were not successful and no evidence for the formation of a dehydrodimer product was observed.

Introduction

The production of α-branched chain fatty esters resulting from the free radical promoted addition of a variety of fatty acid derivatives to terminal olefins has been the subject of a number of recent contributions from this laboratory (1–7). Generally, the branched compounds were obtained when a free radical, generated as a result of hydrogen abstraction from the fatty derivative, added to the olefin forming 1:1 addition products. The site of hydrogen removal was that giving rise to the most stable free radical, namely, the carbon located adjacent to carbonyl group in the acyl portion of the molecule. An exception to this rule was found in the attempted addition of benzyl 2,2-dimethylpropionate (1) to an olefin (1-hexadecene). As expected, this ester, which contains no α-hydrogen in the acyl portion, reacted by loss of a benzylic hydrogen atom in the alkyl section, as in the following equation:



$$\underset{\text{I}}{(CH_3)_3C\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}CH_2\text{–}C_6H_5} + CH_3(CH_2)_{13}CH = CH_2 \xrightarrow{(t\text{–}C_4H_9O)_2} \underset{\text{II}}{(CH_3)_3C\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}\underset{C_6H_5}{\underset{|}{CH}}\text{–}CH_2\text{–}(CH_2)_{14}CH_3} + \underset{\text{III}}{\begin{matrix}(CH_3)_3C\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}CH\text{–}C_6H_5\\ |\\ (CH_3)_3C\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}CH\text{–}C_6H_5\end{matrix}} \quad [1]$$

However, the anticipated product, 1-phenylhexadecyl pivalate (II), was accompanied by a second product, hydrobenzoin bis-2,2-dimethylpropionate (III), hydrobenzoin bis-pivalate. The latter compound, which can be considered the dehydrodimer of benzyl pivalate, was clearly formed by the coupling of two radicals. Paschke et al. (8) have reported the formation in low yields of similar type dimers derived from methyl oleate and from methyl stearate by α,α′-coupling.

Previous experience, then, suggests that fatty esters having α-phenyl groups should be capable of undergoing two types of reactions under the same reaction conditions which lead to α-branched products when applied to straight chain fatty esters. These reactions are addition to olefins and dimer formation. The present work was undertaken to test the degree to which the direction of the reaction can be controlled by means of substituents on the benzene ring. The model system chosen for these studies was the *t*-butyl peroxide initiated addition of some methyl arylacetates to 1-decene according to a modification of a procedure first described by Petrov (9–12).

Experimental Procedures

Materials

Initiators. Di-tertiary butyl peroxide was purchased from Monomer-Polymer Laboratories Division of the Borden Chemical Co. and was used without further treatment.

1-Decene. This olefin, obtained from the Gulf Oil Corporation, was redistilled, and the fraction boiling at 170 C was used. It was estimated to be 99% pure when examined by gas liquid chromatography (GLC).

Esters. Methyl phenylacetate, 99% grade, was purchased from Aldrich Chemical Co. and was used as received. Methyl *p*-tolylacetate, methyl *p*-methoxyphenylacetate and methyl *p*-nitrophenylacetate were prepared by refluxing the appropriate acid with excess absolute methanol using *p*-toluenesulfonic acid as catalyst. After the usual purification procedures were applied, the esters were shown to be 97+% pure by GLC examination.

Addition of Methyl Phenylacetate to 1-Decene. In a three-necked flask equipped with stirrer, addition funnel and thermometer, were placed 33.6 g (⅔ of 0.337 mole) of methyl phenylacetate. The mixture in the addition funnel was composed of 17.0 g of methyl phenylacetate (⅓ of 0.337 mole), 4.63 g (0.033 mole) of 1-decene and 1.20 g (0.0082 mole) of di-tertiary butyl peroxide. The contents of the reaction flask were heated and maintained at 160 C, while the mixture in the funnel was added, with stirring, over a period of 5 hr. After the addition was completed, the reaction mixture was heated and stirred for an additional hour. On cooling a small amount of solid separated out (0.6 g) and was subsequently removed and reserved. The total weight of the flask contents was 56.3 g. Fifty-four grams of the mixture were subjected to vacuum distillation (60–61 C at 0.3 mm) and yielded a distillate (46.0 g) consisting essentially of excess methyl phenylacetate plus a small amount of *t*-butyl alcohol and unreacted olefin. The trap contents (5.0 g) consisted of 1-decene, *t*-butanol and perhaps acetone. The distillation residue (3.1 g) was dissolved in hexane (30:1) and allowed to crystallize at −30 C. The precipitate (1.1 g) plus the 0.6 g of solid recovered earlier was recrystallized five times from methylene chloride (30:1) at −30 C to obtain dimethyl *meso*-α,α′-(bisphenyl)succinate (0.5 g, mp 219 C). Literature (10): mp 218.5–219.5 C. The combined methylene chloride filtrates were evaporated to a solid residue (0.8 g). This material, recrystallized from acetone (100:1) at −30 C, gave semi-pure product (0.2 g). Further purification by preparatory TLC (developed with 70:30, benzene-Skellysolve B) yielded pure dimethyl *dl*-α,α'-(bis-phenyl)-succinate, mp 174–175 C. The hexane filtrate, from which the dimers had been crystallized initially, was evaporated, and the residue (2.0 g) was chromatographed on Florisil (1:35). Elution with mixtures of Skellysolve B and benzene gave methyl 2-phenyldodecanoate (0.88 g). The results of elemental analyses of all products are listed in Table I.

Addition of Methyl p-Tolylacetate to 1-Decene. The addition of methyl *p*-tolylacetate (16.5 g, 0.10 mole) to 1-decene (1.4 g, 0.01 mole) employing di-tertiary butyl peroxide (0.37 g, 0.0025 mole) was carried out in the manner described for the addition of methyl phenylacetate. A portion of the reaction mixture, after cooling, was spotted on a TLC preparatory plate, the plate developed with a 70% benzene-30% Skellysolve B mixture, and the separated products scraped, eluted and weighed. Extrapolation of weights from the spotted portion to the reaction mixture gave the following results: methyl 2-(p-tolyl)-dodecanoate, 0.24 g; dimethyl *meso*-α,α'-(bis-p-tolyl)succinate, 0.19 g; di-methyl *dl*-α,α'-(bis-*p*-tolyl)succinate, 0.14 g.

Analytically pure samples of the three compounds described above were prepared by distillation in vacuo (45–50 C at 0.3 mm Hg) of the crude reaction mixture to remove unreacted starting materials and *t*-butanol, followed by repeated TLC separations monitored by analytical TLC. All TLC preparatory plates were developed with benzene-Skellysolve B (70:30) and analytical plates were developed with benzene-chloroform (70:30). Physical constants and elemental analyses of the products are shown in Table I.

Addition of Methyl p-Methoxyphenylacetate to 1-Decene. Methyl *p*-methoxyphenylacetate (23.4 g, 0.13 mole), 1-decene (1.82 g, 0.013 mole) and di-tertiary butyl peroxide (0.48 g, 0.0033 mole) were combined by the method described for methyl phenylacetate, above. A portion of the cooled reaction mixture was analyzed by preparatory TLC as described for the methyl *p*-tolylacetate products. Extrapolation gave the following results: methyl 2-(*p*-methoxyphenyl)dodecanoate 0.375 g; dimethyl *meso*-α,α'-(bis-*p*-methoxyphenyl)succinate and dimethyl *dl*-α,α'-(bis-*p*-methoxyphenyl)succinate combined, 0.408 g. Because of the similarity of the retention values of the dimeric products, these could not be separated quantitatively. Analytically pure samples of the three *p*-methoxyphenyl derivatives were prepared by the methods described in the *p*-tolyl experiment above. Preparatory TLC plates were developed with benzene-hexane, 60:40 and analytical plates with benzene-chloroform, 60:40. Physical constants and elemental analyses of the products are shown in Table I.

Addition of Methyl p-Nitrophenylacetate to 1-Decene. The addition of methyl *p*-nitrophenylacetate (36.2 g, 0.20 mole) to 1-decene (2.8 g, 0.02 mole) in the presence of di-tertiary butyl peroxide (0.74 g, 0.005 mole) was carried out in the conventional manner, with one exception. Since the mixture in the addition funnel consisted of two phases, the lower ester phase was added rapidly, and the upper olefin phase was added in the usual drop by drop fashion. TLC and GLC analysis of the crude product obtained in the usual manner indicated absence of the expected α-branched and dimeric products. This absence was confirmed by comparison with standards, i.e., nitro α-branched ester and nitro dimer esters, prepared by nitrating the respective products obtained from the methyl phenylacetate addition experiments.

In a second experiment benzene was added to the addition funnel mixture to form a homogeneous solution. The apparatus was modified to include a steam jacketed tube, which permitted the benzene, vaporized as it contacted the heated reaction mixture, to leave the reaction flask. This second experiment also yielded none of the expected products.

Results and Discussion

The yields of the α-aryldodecanoate esters shown in Table I are based on olefin and are calculated from TLC preparatory plate data on samples withdrawn from the reaction mixture after completion of the experiment. The yields of the dehydrodimers, also calculated from TLC preparatory plate data, are the combined yields of both isomeric by-products, and are based on the amount of initiator employed, since

TABLE I

Addition of Esters to 1-Decene Catalyzed by Di-*t*-Butyl Peroxide

Ester added[a]	Products	Yield[b] %	Mp °C	n^{60}_{d}	Analysis C % Calc.	Analysis C % Found	Analysis H % Calc.	Analysis H % Found
Methyl phenylacetate	Methyl 2-phenyldodecanoate	22.0[c]	Liquid at RT	1.4681	78.57	78.33	10.41	10.56
	Methyl *meso*-α,α'-(bis-phenyl) succinate	29.9[d]	219	....	72.47	72.70	6.08	6.14
	Methyl *dl*-α,α'-(bis-phenyl) succinate		174–5	....	72.47	72.60	6.08	6.10
Methyl *p*-tolylacetate	Methyl 2-*p*-tolyldodecanoate	7.9[c]	Liquid at RT	1.4708	78.89	79.30	10.60	10.76
	(M) Methyl α,α'-(bis-*p*-tolyl) succinate	40.6[d]	208.5–209	....	73.60	73.44	6.79	6.89
	(D) Methyl α,α'-(bis-*p*-tolyl) succinate		134.8	....	73.60	73.62	6.79	6.84
Methyl *p*-methoxyphenylacetate	Methyl 2-*p*-methoxyphenyl-dodecanoate	8.9[c]	Liquid at RT	1.4755	74.95	75.04	10.07	9.89
	(M) Methyl α,α'-(bis-*p*-methoxyphenyl) succinate	34.5[d]	188–9	....	67.02	66.78	6.19	6.34
	(D) Methyl α,α'-(bis-*p*-methoxyphenyl) succinate		109–10	....	67.02	66.72	6.19	6.99

[a] Molar ratio-ester: 1-decene-peroxide, 40:4:1.
[b] Calculated from TLC results.
[c] Based on 1-decene.
[d] Combined yield of isomeric dehydrodimer byproduct; based on peroxide.

these compounds undoubtedly result from the combination of a pair of free radicals produced by benzylic hydrogen abstraction. The elemental analyses, NMR spectra and mass spectra of the isolated and purified aryldodecanoates and diaryl succinates were consistent with the assigned structures.

The letters (M) and (D) in Table I preceding the names of two pairs of dehydrodimers are used to label what are presumed to be the *meso* and *dl* isomers respectively. This assumption is based upon comparison of the properties of these compounds (melting point and R_f value) with those of the known *meso* and *dl* isomers of methyl α,α'-(bisphenyl)succinate. That the higher melting compound is the *meso* derivative is consistent with a similar assignment by Huang et al. (14,15) in the case of the dimers from ethyl *p*-methoxyphenylacetate as well as dimers of the radicals from β-phenylpropionitrile. The *meso* isomer has the higher R_f value and is produced in greater amount than the *dl*. The preferential formation of this stereoisomer has been explained on theoretical grounds in terms of the differences in their free energies by Eliel (16).

In the present series of experiments, TLC examination of the reaction mixtures revealed that the order of increasing R_f values was: *dl*-dehydrodimer, *meso*-dehydrodimer, unreacted arylacetate and α-aryldodecanoate. For purposes of comparison the developing solvent was 35% benzene and 65% chloroform. Figure 1 shows the TLC comparisons.

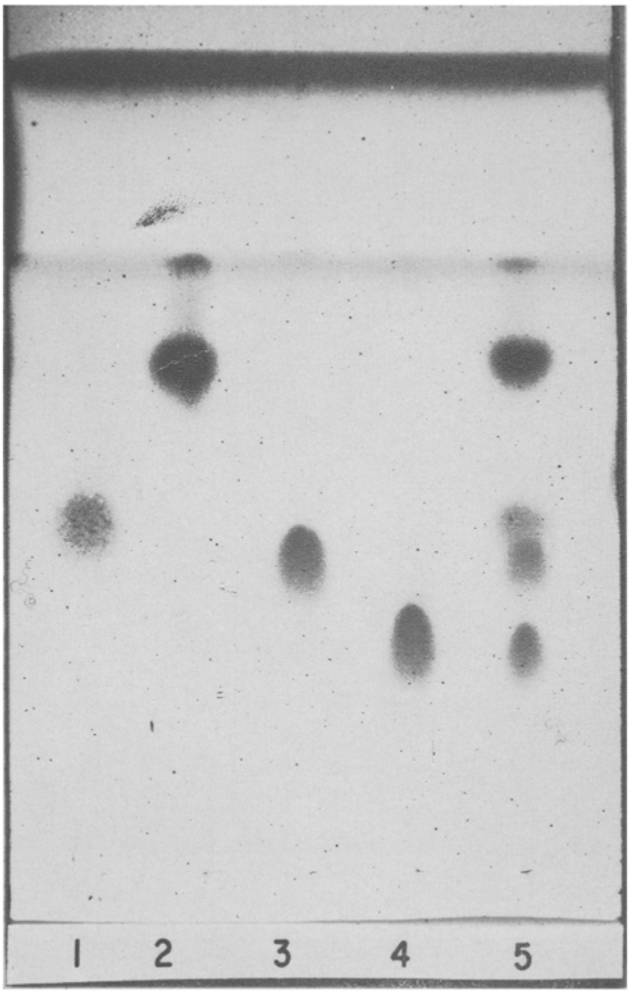


FIG. 1. 1, Methyl phenylacetate; 2, Methyl 2-phenyldodecanoate; 3, Dimethyl *meso*-α,α'(bis-phenyl)succinate; 4, Dimethyl *dl*-α,α'(bis-phenyl)succinate; 5, Mixture of 1–4. System 35% benzene–65% chloroform. (Plate prewashed with developing mixture.)

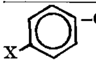
No evidence for the formation of methyl 2-(*p*-nitrophenyl)dodecanoate or methyl α,α'-(bis-*p*-nitrophenyl)succinate was observed by either TLC or GLC examination of the reaction products. Lack of success was first attributed to the lack of homogeneity of the addition phase. In a subsequent experiment benzene was added to the separatory funnel to give a homogeneous solution of the materials to be added, but again the desired products were not formed. In order to assure that the proper *p*-nitrophenyl substituted products were detected if present, standards were prepared by nitration of the corresponding phenyl substituted compounds. Comparison of the gas liquid and thin layer chromatograms clearly demonstrated that methyl *p*-nitrophenylacetate did not add to 1-decene and did not form the dehydrodimer.

The methyl arylacetates exhibit considerably lower tendency to form addition products with terminal olefins than do the long chain fatty esters. Under essentially the same conditions which cause methyl stearate to add to 1-decene in 66% yield based on olefin (3), methyl phenylacetate gives a 22% yield of product. The arylacetates, as well as the benzyl esters mentioned above, give rise to substituted benzyl radicals which are stabilized by electron delocalization. It would appear that the greater stability of the benzyl radicals, and their great reluctance to add to olefins as compared with their aliphatic counterparts, allow their concentration to build up to a point where dimerization becomes an important side reaction. On this basis it would be expected that para-substituted benzyl radicals such as *p*-methyl- and *p*-methoxybenzyl would have a greater degree of stabilization than their unsubstituted counterparts and therefore would give rise to a relatively greater amount of dehydrodimer. This expectation is realized in the experimental results (Table II). While the data seem to indicate a slightly larger relative amount of dimer for *p*-tolylacetate than for *p*-methoxyphenylacetate, this difference is within the limits of the experimental accuracy. Overall yields of radical-generated products are lower for the phenyl derivatives, since the coupling reaction leading to dimer formation is a termination step, while olefin addition is a chain propagation sequence.

Failure of methyl *p*-nitrophenylacetate to yield either olefin adduct or dehydrodimer may be due to the inability of *t*-butoxy radical to abstract hydrogen from this compound. Pryor (17) has demonstrated a correlation between the Hammett σ^+ constants and the relative rates of hydrogen abstraction from substituted toluenes by such electrophilic radicals as Cl· and $(CH_3)_3C–O·$. This Hammett plot indicates that all electron-withdrawing substituents of toluene retard hydrogen abstraction by Cl· and that the p–NO_2 group, having the highest positive value of

TABLE II

Relative Amounts of α-Branched Ester and Dehydrodimer Formed by Arylacetates[a]

 X –$CH_2CO_2CH_3$ X–	α-Branched ester (A) moles × 10^3	Dehydrodimer (B) moles × 10^3	Ratio A:B
H–	22.0	7.47	2.95
CH_3–	7.9	10.3	0.77
CH_3O–	8.9	8.63	1.03
NO_2–	None	None	......

[a] Calculated using the following quantities of reactants: 1 mole of arylacetate; 0.1 mole 1-decene; 0.025 mole ditertiary butyl peroxide.

σ^+, is the most effective in this respect. Consequently it would be expected that the hydrogens of methyl *p*-nitrophenylacetate, which has two electron-withdrawing substituents attached to the methylene group in question, will resist abstraction by the *t*-butoxy radical.

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