Acknowledgment. The support (to H.H.) of the Faculty Research Award Program, The City University of New York, Grant No. 11419, is gratefully acknowledged. We are indebted to Mr. S. Zolty of the Hoffman-La Roche Co., Inc. for carrying out the gas chromatographic analyses of the reduction products in the isobutyl alcohol and ethanol experiments.

Registry No. 1, 873-94-9; 4, 600-36-2; 5, 84752-55-6; $LiAlH_4$, 16853-85-3; CH_3OH, 67-56-1; CH_3CH_2OH, 64-17-5; $(CH_3)_2CHCH_2OH$, 78-83-1; $LiAl(OEt)_4$, 18460-81-6; 2-propanol, 67-63-0.

Palladium-Catalyzed Syntheses of Conjugated Polyenes

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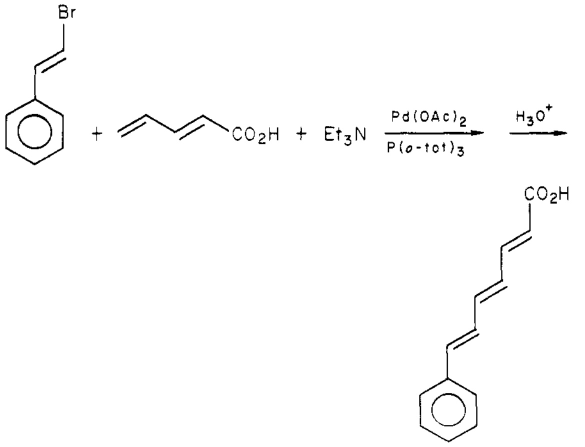
Conjugated trienes have been prepared by the palladium-catalyzed reaction of vinylic bromides with 2,4-pentadienoic acid and its 3-methyl derivative, in the presence of triethylamine. Methyl (*E*)-3-bromo-2-methylpropenoate also forms conjugated trienes and in some instances also tetraenes when it is reacted with 1,3-dienes under similar conditions. Some loss of stereochemistry in the starting vinylic bromide or, more often, in the diene may occur in the reactions presumably because equilibrating π-allylic intermediates are involved. 1,3,5-Hexatriene and 2 equiv of methyl (*E*)-3-bromo-3-methylpropenoate form orange-red dimethyl (*E,E,E,E,E*)-2,11-dimethyl-2,4,6,8,10-dodecapentaenedioate in modest yield.

Conjugated trienes often have been obtained as minor products in the palladium-catalyzed reactions of vinylic bromides with conjugated dienes and piperidine or morpholine.[1] In these reactions π-allylic palladium complexes were intermediates, and they underwent nucleophilic substitution with the secondary amine present more easily than they underwent elimination to form the conjugated trienes. The relative ease of elimination vs. substitution, however, depends significantly upon the substituents in the vinylic bromide and diene. We have reported the formation of a conjugated triene in reasonably good yield (57%) when a carboxyl group is conjugated with the diene group in the reaction employing triethylamine as the base.[2] (eq 1). The aromatic ring conjugated with the double bond in the vinylic bromide probably also assisted the reaction since it appears, not unexpectedly, that the π-allylic complexes in these reactions are relatively destabilized because decomposition by elimination gives highly conjugated systems. We have observed this effect frequently in reactions of vinylic halides with various alkenes.[3]



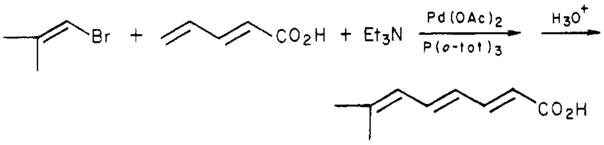
(1)

We now report further studies on the synthesis of conjugated polyenes by the reaction.

Results and Discussion

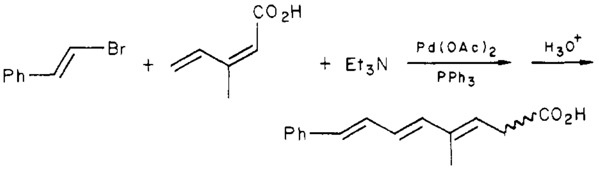
Conjugated Trienes. Several additional reactions of vinylic bromides with conjugated dienes have been studied to better define the scope of the reaction.

It is not necessary to have an aryl group in the vinylic bromide as well as the carboxyl group in the diene in order for the elimination to occur with triethylamine. 2-Methyl-1-bromo-1-propene reacts with (*E,E*)-2,4-pentadienoic acid with the usual $Pd(OAc)_2$–$P(o\text{-tol})_3$ catalyst and triethylamine to form (*E,E,E*)-7-methyl-2,4,6-octatrienoic acid in 50% yield (eq 2). The low yield is probably mainly due to instability of the product and reactants under the reaction conditions. We were unable to isolated a product from a similar reaction of (*E*)-1-bromo-1-propene with 2,4-pentadienoic acid.



(2)

The reaction of (*E*)-β-bromostyrene with (*Z*)-3-methyl-2,4-pentadienoic acid was carried out to determine the stereoselectivity of the reaction. If the reaction proceeds by way of a π-allylic palladium intermediate, equilibration of isomers would be expected, and the *E,E,E* product should be formed since syn-π-allylic complexes are favored. The reaction at 100 °C gave a 70:30 2*Z*,4*E*,6*E*/2*E*,4*E*,6*E* triene isomer mixture in 40% yield with 6% triphenyl phosphine and 2% $Pd(OAc)_2$ as a catalyst (eq 3). These conditions were the most favorable found for retention of the stereochemistry in reactions forming 2,4-



(3)

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(1) Patel, B. A.; Kao, L.; Cortese, N. A.; Minkiewicz, J. V.; Heck, R. F. *J. Org. Chem.* **1979**, *44*, 918.

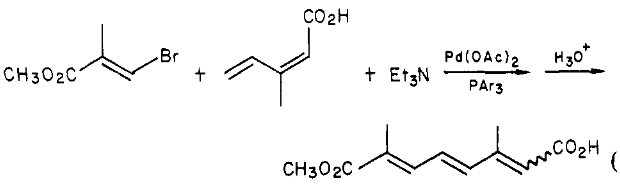
(2) Patel, B. A.; Dickerson, J. E.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 5018.

(3) Kim, J.-I.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1061.

0022-3263/83/1948-0948$01.50/0

dienoate esters.[3] It appears that the reaction is proceeding partly by way of the π-allylic intermediate since control experiments indicate starting materials and products are stable under the reaction conditions.

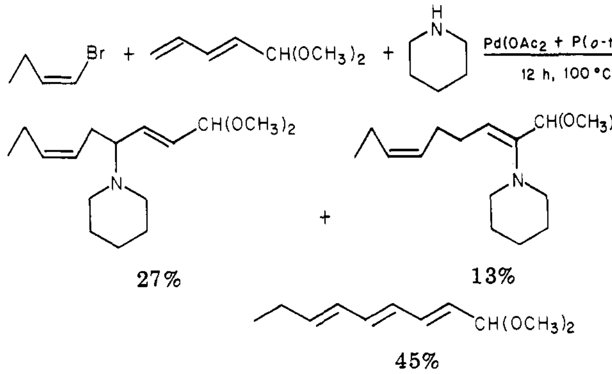
Similarly, the reaction of the (*Z*)-2,4-dienoic acid with (*E*)-methyl 3-bromo-2-methylpropenoate with either 2% or 6% triarylphosphine gave a 30:10 mixture of *Z,E,E*/*E,E,E* trienes (eq 4). The total yield with 2% P(*o*-tol)$_3$ was 55%, while 6% PPh$_3$ gave only 45%. Therefore, in this example it appears that the major part of the reaction occurs by way of the π-allylic palladium complex. The triarylphosphine concentration has no influence upon the amount of π-allylic complex formed, in contrast to the reactions of vinylic bromide with acrylate esters where π-hydridopalladium complexes are necessary intermediates on the way to the π-allylic complexes.[3] We believe in the last reaction that the π-hydridopalladium species are attacked by the PAr$_3$ and that the diene is liberated before π-allylic complexes are formed and equilibration takes place. The fact that in the triene synthesis π-hydridopalladium–triene complexes are not involved in the formation of the π-allylic complexes and isomerization is observed is consistent with that mechanism.



(4)

The presence of an acetal group next to the 1,3-diene system is not sufficient to cause facile elimination in reactions with vinylic halides. 2,4-Pentadienal acetals do not give significant yields of trienes when they are reacted with vinylic bromides and triethylamine. The use of piperidine as the base, however, gives some triene along with allylic amines resulting from nucleophilic attack of the amine on the π-allylic intermediates. We are not certain of the stereochemistry of the trienes that are formed but expect they are the most stable *E,E,E* isomers.

The examples in eq 5 and 6 illustrate the stepwise synthesis of trienes from monoenes with the palladium-catalyzed vinylic substitution reaction. The 2,4-pentadienal acetals used in the triene syntheses were prepared by the palladium-catalyzed reaction of vinyl bromide with acrolein acetal and piperidine followed by a Hofmann elimination of the allylic amine formed (eq 7). Another example of a step-wise triene synthesis begins with the palladium-catalyzed reaction of 2-bromopropene with styrene and piperidine (eq 8). The reaction produces 1-phenyl-3-methyl-1,3-butadiene in 67% yield along with only 2% of the possible allylic amines.[2] Reaction of the diene obtained with (*E*)-methyl 3-bromo-2-methylpropenoate (eq 9) forms the phenyl trienoate in 63% yield. The product is an 85:15 mixture of the *E,E,E* and *E,Z,E* isomers. The isomers do not equilibrate under the reaction conditions.



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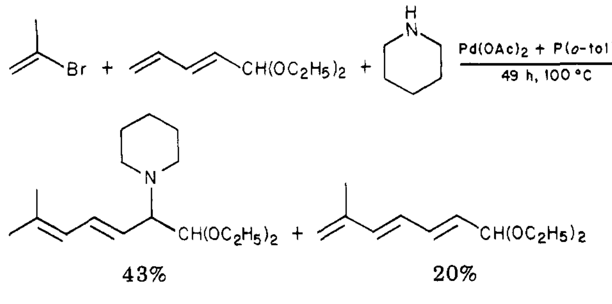

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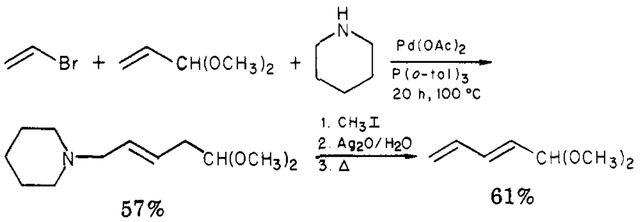

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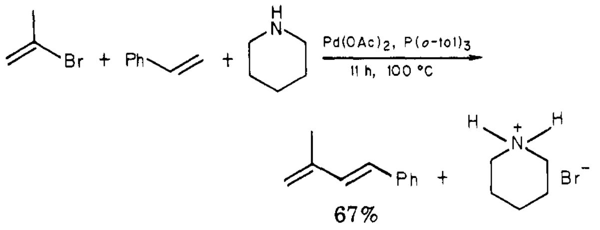

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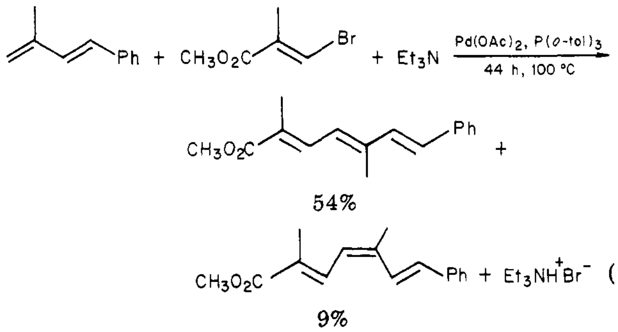
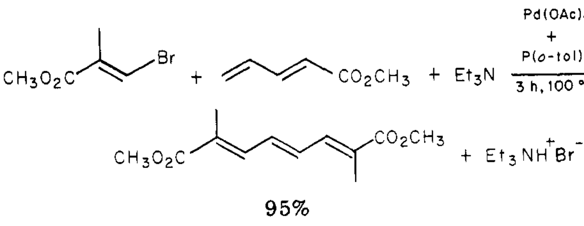


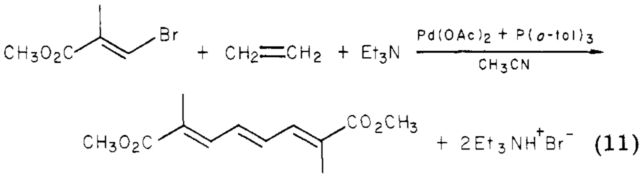
(9)

Unfortunately, 3-bromoacrylic acid or its esters cannot be used in the palladium-catalyzed reaction with alkenes or dienes and amines presumably because of facile dehydrobromination of the bromo acid or esters. The (*E*)-α-methyl derivative, as seen in examples above, reacts normally. It is, in fact, a very reactive vinylic bromide, and it always reacts with retention of its configuration. It is so reactive that it will often react twice with 0.5 equiv of a conjugated diene to form tetraenes (see below). With an excess of unsymmetrical dienes, however, trienes are usually formed predominantly. With (*E,E*)-methyl 2,4-pentadienoate, (*E*)-methyl 2-methyl-3-bromopropenoate forms the (*E,E,E*)-trienedioate in 95% yield, for example (eq 10).



(10)

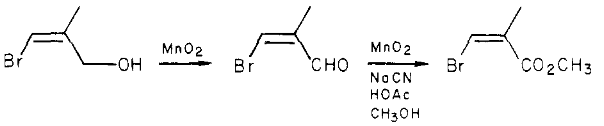
We looked briefly at the divinylation of ethylene with (*E*)-methyl 3-bromo-2methylpropenoate under 30 psi of ethylene (eq 11), and we found that the triene diester was formed readily but only in low yield (35% under a variety of reaction conditions).



(11)

We investigated the stereochemistry of the reaction of the (*E*)-bromo ester with *cis*- and *trans*-1,3-pentadiene, and, as expected from the results given above, both dienes gave the same mixture of trienoate isomers, a 90:10 mixture of *E,E,E* and *E,E,Z* isomers, presumably reflecting the relative stabilities of two isomeric π-allylic palladium intermediates. If the π-allylic intermediates involved are only those on carbons 5–7 of the chain, then the stereochemistry of the α,β double bond should be the same as in the reactant bromo ester. In order to check this point, we prepared (*Z*)-methyl 3-bromo-2-methylpropenoate and carried out its reaction with (*E*)-1,3-pentadiene.

The synthesis of the (*Z*)-bromo ester proved to be a problem. It was finally prepared by the oxidation of (*Z*)-3-bromo-2-methylprop-2-en-1-ol in two stages in 36% yield (eq 12). The (*Z*)-bromo ester was only half as reactive as the (*E*)-bromo ester toward (*E*)-1,3-pentadiene, and a mixture of trienes was obtained (eq 13). The product mixture consisted of 76% of the *Z,E,E* isomer and 24% of the *E,E,E* isomer with a total yield of 54%.



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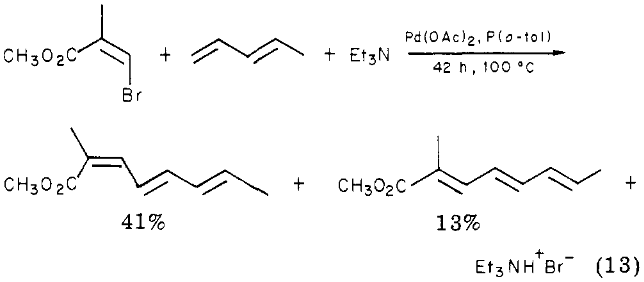
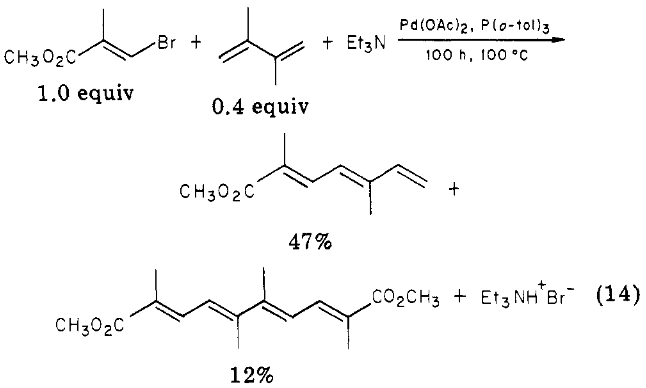


(13)

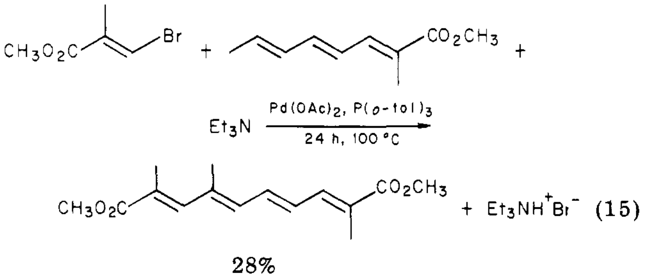
In view of the fact that (*Z*)-methyl 3-bromo-2-methylpropenoate reacts only slowly and in poor yield with acrylic acid to form the (*E,E*)-dienoate (15% yield) and that it does not give identifiable products with (*E*)-crotonic acid, it appears that a relatively unreactive chelated palladium derivative is the intermediate. Whether this derivative isomerizes before or after it adds to the diene is not clear. The (*Z*)-bromo ester itself, however, does not isomerize during the reaction as judged from analysis of the bromo ester remaining in partially reacted mixtures.

Four other conjugated dienes have been reacted with the (*E*)-bromo ester: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and (*E,Z*)-2,4-hexadiene. The yields of triene obtained were very dependent upon the structure of the diene. Butadiene and isoprene gave little or no trienoates presumably because the trienes were more reactive than the dienes with the bromo ester, and tetraenes (and polymers) were the main identifiable product under all conditions tried. The other two dienes gave the trienoate products in fair yields when the diene was present in excess or equivalent amounts. The trienoate ester from 2,3-dimethylbutadiene (47% yield) was a single, presumably *E,E,E* isomer while the (*E,Z*)-2,4-hexadiene gave a mixture of four isomeric trienes (eq 14). Conjugated tetraenes were formed in minor amounts along with the trienes when the bromo ester and the 2,4-hexadiene were reacted in a 1:1 molar ratio. We have not identified all of the triene esters produced in the reactions because of the difficulty of separating isomers. It appears that the more substituents present in the reactants, the more isomers of the trienes that are produced. In these cases, the reaction is more useful for preparing tetraene diesters because these, in general, are high-melting crystalline compounds and are easily purified. The reactions carried out with methyl 3-bromo-2-methylpropenoate are summarized in Table I.



(14)

Conjugated Tetraenedioates. Reaction of (*E,E,E*)-methyl 2-methyl-2,4,6-octatrienoate with (*E*)-methyl 3-bromo-2-methylpropenoate at 100 °C for 24 h with the usual catalyst and triethylamine gave a single tetraene in 28% yield (eq 15). We believe this to be the *E,E,E,E* isomer on the basis of comparisons of its UV and NMR specra with those of tetraenes of known structure, particularly with the spectra of the tetraenes from isoprene and (*E,Z*)-2,4-hexadiene (see below). Reaction of the (*Z,E,E*)-trienoate ester wth the (*E*)-bromo ester also produced only the same tetraenedioate ester but in lower (13%) yield. The low yields of tetraenes in this and other cases listed in Table I are due to competing polymerization reactions. Fortunately, in all cases studied the tetraenes are high-melting, nicely crystalline compounds which are very easily separated from polymeric side products.



(15)

The preparation of the tetraenedioates is achieved more conveniently in higher yield in a single step if 2 equiv of the bromo ester are reacted with 1 equiv of 1,3-diene. 1,3-Pentadiene gave 28% tetraene this way. The same procedure generates tetraenedioates from butadiene (52%), isoprene (15%), 2,3-dimethylbutadiene (37%), and (*E,Z*)-2,4-hexadiene (34%).

The reaction of the (*E*)-bromo ester with isoprene forms two isomeric tetraenes: the orange *E,E,E,E* isomer (15%)

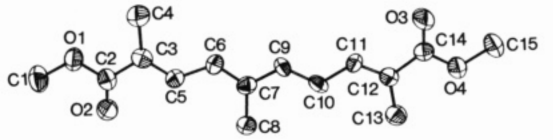


Figure 1. Structure of (*E,E,E,E*)-dimethyl 2,5,9-trimethyl-2,4,6,8-decatetraenedioate.

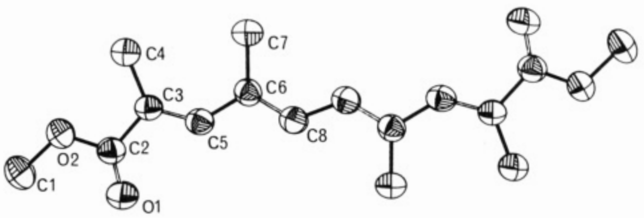
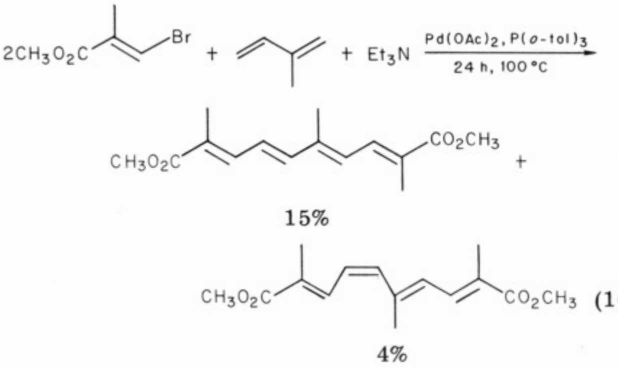


Figure 2. Structure of (*E,E,E,E*)-dimethyl 2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate.

and a much more soluble, yellow isomer (4%) believed to be the *E,E,Z,E* compound (eq 16). The structures of these

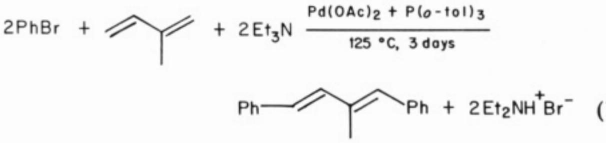


(16)

isomers are based upon a crystal structure of the first isomer (Figure 1) and NMR (^{1}H and ^{13}C) and UV spectra. The structures were incorrectly assigned in a preliminary paper.[4]

The reaction of (*E,Z*)-2,4-hexadiene with the (*E*)-bromo ester also produces (at least) two isomeric tetraenes. The less soluble, major product (34%) was found to be the *E,E,E,E* isomer by X-ray crystallography. The structure found is shown in Figure 2. A second isomer (6%) was found to be symmetrical, as is the other isomer, by ^{1}H and ^{13}C NMR. The lower λ_{max} and intensity of the absorption [λ_{max} 325 nm (ϵ 15150) vs. λ_{max} 354 nm (ϵ 41860)] and comparison of the ^{1}H NMR absorptions indicate that it is the *E,Z,Z,E* isomer. It is not surprising that at least two isomeric tetraenes are formed since four isomeric trienes are produced. It is likely, in fact, that other isomeric tetraenes are produced also, but because of their probable higher solubility they were not isolated.

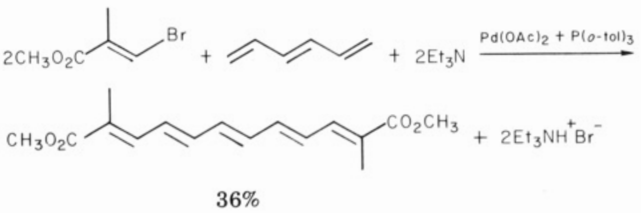
The question naturally arises as to whether aromatic halides will doubly arylate dienes as the bromo ester does. We have found it possible to diphenylate isoprene in 22% yield with palladium in one step by reacting 2 equiv of bromobenzene with isoprene and triethylamine (eq 17).



(17)

The reaction, however, stopped at only about 50% reaction of the bromobenzene probably because a very stable π-allylic palladium complex was formed.

Pentaenes. One pentaene was prepared by the double vinylation of 1,3,5-hexatriene with (*E*)-methyl 3-bromo-2-methylpropenoate under the same conditions as were employed in the 1,3-diene reactions (eq 18). The reaction



(18)

gave the *all-trans*-pentaene diester in 36% yield as orange-red needles. The structure was assigned on the basis of the NMR and UV spectra and its molecular weight.

Summary. The palladium-catalyzed reaction of vinylic bromides with dienes and an amine may be used to form trienes, in some cases tetraenedioates, and in one case a pentaenedioate. The reactions work best when an ester or carboxyl group is conjugated with a double bond in one of the reactants. Equilibration of isomers occurs under the reaction conditions, giving the most stable isomers either exclusively or, at least, partly. A variety of trienes have been prepared while only (*E*)-methyl 3-bromo-2-methylpropenoate has been found to divinylate dienes and 1,3,5-hexatriene. While the yields of the tetraene- and pentaenedioates are only modest, the reaction is easy to perform, and reactants are readily available, making this a useful synthetic method for preparing some polyene esters.

Experimental Section

Materials. Most of the dienes and other reagents used in this study were obtained from commercial sources as described previously.[5] The (*E*)-methyl 3-bromo-2-methylpropenoate[6] and (*E*)-2,4-pentadienoic acid[7] were prepared by literature methods. The physical properties of the products prepared are given in Table II (supplementary material).

(*E,E*)-7-Methyl-2,4,6-octatrienoic Acid. A mixture of 1.0 g (10 mmol) of (*E,E*)-2,4-pentadienoic acid,[7] 1.35 g (10 mmol) of 1-bromo-2-methyl-1-propene,[8] 3 g (30 mmol) of triethylamine, 67.2 mg (0.3 mmol) of Pd(OAc)$_2$ and 122 mg (0.6 mmol) of tri-*o*-tolylphosphine was heated at 100 °C for 24 h in a steam bath in a capped, heavy-walled Pyrex tube. After cooling, the reaction mixture was treated with 50 g of water and 6 g of sodium bicarbonate. After the gas evolution ceased, the solution was extracted with ether. The separated aqueous phase was then acidified with 10% aqueous hydrochloric acid to a pH of 5–6. An oil separated which was extracted with ether. The extracts were dried, and the solvent was removed under reduced pressure. A brown solid remained. Recrystallization from ether–pentane gave 0.79 g (52%) of an off-white solid, mp 128–131 °C. Another crystallization gave 40% product, mp 130–132 °C. Anal. Calcd for $C_9H_{12}O_2$: C, 79.37; H, 8.88. Found: C, 79.54; H, 9.02. The infrared spectrum in KBr had strong absorptions at 3300–2800, 1700, 1610, 1430, 1385, 1315, 1270, 1165, 1000, 830, and 700 cm^{-1}.

3-Methyl-7-phenyl-2,4,6-heptatrienoic Acid. A mixture of 10 mmol of (*E*)-2-bromostyrene, 10 mmol of (*Z*)-3-methyl-2,4-pentadienoic acid,[9] 0.10 mmol of Pd(OAc)$_2$, 0.20 mmol of tri-*o*-tolylphosphine, and 60 mmol of triethylamine was prepared in a Pyrex tube. The tube was capped after being flushed with argon and then heated at 100 °C in a steam bath for 2 h. The cooled

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Table I. Preparation of Polyenes from Methyl 3-Bromo-2-methylpropenoate[a]

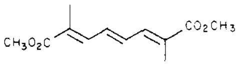
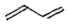
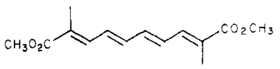
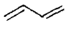
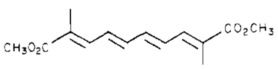
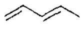
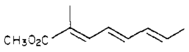
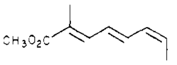
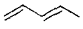
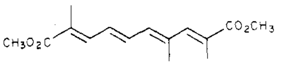
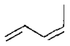
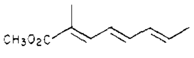
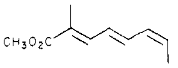
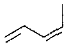
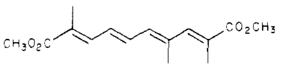
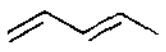
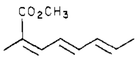
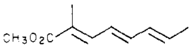
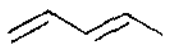
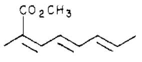
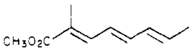
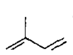
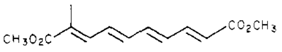
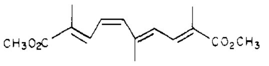
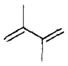
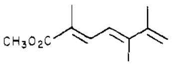
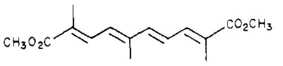
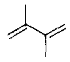
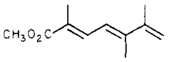
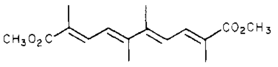
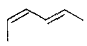
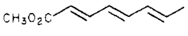
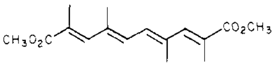
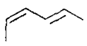
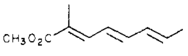
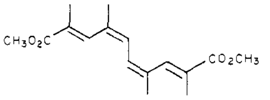
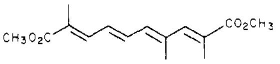
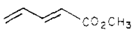
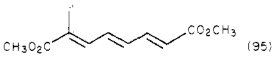
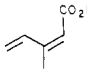
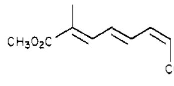
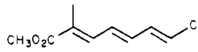
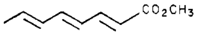
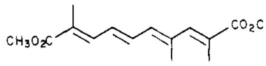
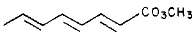
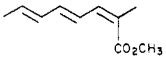
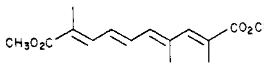
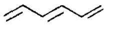
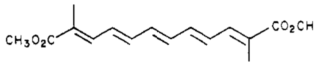
methyl 3-bromo-2-methylpropenoate isomer	diene or triene reactant	bromo ester/polyene reactant ratio	reaction		products (% yield)
			temp, °C	time	
E	=	2	100	10 h	 (35)
E		1	100	6 h	 (44)
E		2	100	6 h	 (52)[c]
E		0.8	100	24 h	 (66)  (7)
E		2.1	125	15 h	 (21)
E		0.8	100	23 h	 (57)  (6)
E[b]		2.1	100 then 125	24 then 26	 (8)
Z		0.7	100	42 h	 (41)  (13)
Z		2.0	100	150 h	 (28)  (9)
E	[c]	2.1	100	24 h	 (15)  (4)
E		0.4	100	110 h	 (47)  (12)
E		1.6	100	110 h	 (15)
					 (37)
E		1.0	100	4 days	 (4 isomers, 31)  (10)[c]
E		2	100	4 days	 (4 isomers, 25)  (6)  (34)
E		0.8	100	3 h	 (95)

Table I (*Continued*)

methyl 3-bromo-2-methyl-propenoate isomer	diene or triene reactant	bromo ester/ polyene reactant ratio	reaction temp °C	reaction time	products (% yield)
E		1.0	100	1.5 h	 (16)  (39)
E		0.9	100	24 h	 (28)
Z		0.9	100	145 h	recovered 70% of the reactant triene
E	 75% *Z,E,E*/ 25% *E,E,E*	1.0	100	54 h	[d]  (13)
E		2	100	24 h	 (36)

[a] Carried out with 1 mol % (based upon the bromoester) of $Pd(OAc)_2$ and 2 mol % of tri-*o*-tolylphosphine as a catalyst, unless otherwise noted, in the presence of excess triethylamine. [b] About 10% starting bromo ester was recovered. [c] The catalyst was 3 mol % palladium acetate and 6 mol % tri-*o*-tolylphosphine. [d] Assuming the triene was totally the *Z,E,E* isomer.

reaction mixture was treated with water and sodium bicarbonate, and the product was isolated as in the previous reaction. There was obtained a 40% yield of a mixture of 70% *E,E,E* acid and 30% *Z,E,E* acid as determined from the NMR spectrum of the mixture.

Monomethyl Ester of 2,6-Dimethyl-2,4,6-octatrienedioic Acid. A mixture of 10 mmol of (*E*)-methyl 3-bromo-2-methylpropenoate, 10 mmol of (*Z*)-3-methyl-2,4-pentadienoic acid, 60 mmol of triethylamine, 0.10 mmol of $Pd(OAc)_2$, and 0.20 mmol of tri-*o*-tolylphosphine was prepared in an argon-flushed tube and heated at 100 °C for 1.5 h. Isolation of the products as in the preceding examples gave a 55% yield of a 30:70 mixture of the 2*E*,4*E*,6*E* and 2*E*,4*E*,6*Z* isomers of the half-acid ester as determined from the NMR spectrum of the mixture.

2,4-Pentadienal Diethyl Acetal. 5-Piperidino-3-pentenal diethyl acetal [bp 96–98 °C (0.40 mm)] was prepared in 40% yield according to the published procedure for preparing the dimethyl acetal by employing acrolein diethyl acetal in place of the dimethyl acetal.[3] The amino acetal (15.2 g, 63 mmol) was dissolved in 15 mL of absolute ethanol and cooled in an ice bath while 5.25 mL (84 mmol) of methyl iodide was added. The solution was stirred at room temperature for 15 h. Evaporation of the solvent under reduced pressure gave the quaternary salt as a light brown liquid. The liquid was dissolved in 160 mL of water, 23.2 g (100 mmol) of freshly prepared silver oxide was added, and the mixture was stirred at 60 °C for 1 h. After the mixture cooled, the silver salts were removed by filtration, washed well with 50 mL of water and filtered again. The combined filtrates were distilled at 170 mm and 40 °C to remove the water and then warmed to 90 °C at 170 mm. A two-phase distillate was obtained. The organic layer was separated by extraction with ether (2 × 100 mL). After the mixture was dried the ether was distilled and then the product, bp 63–64 °,c (11 mm). The yield was 5.91 g (61%). The product appeared to be a mixture of cis and trans isomers from its NMR spectrum.

Palladium-Catalyzed Vinylation of 2,4-Pentadienal Acetals. Mixtures of 50 mmol of the vinylic bromide, 62.5 mmol of the acetal, 125 mmol of piperidine, 0.50 mmol of $Pd(OAc)_2$, and 1.00 mmol of tri-*o*-tolylphosphine were prepared in Pyrex bottles, and the bottles were capped after being flushed with argon. The mixtures were warmed and mixed until homogeneous and then placed in a steam bath. Samples were removed periodically and analyzed by GLC. When the vinylic bromide had completely reacted, the mixtures were cooled and mixed with excess aqueous sodium hydroxide and ether. The ether layers were separated, dried, and distilled under reduced pressure to yield the trienal acetals and piperidino dienal acetals.

Methyl 2,5-Dimethyl-7-phenyl-2,4,6-heptatrienoate. A mixture of 12 mmol of 3-methyl-1-phenyl-1,3-butadiene,[2] 10 mmol of (*E*)-methyl 3-bromo-2-methylpropenoate, 30 mmol of triethylamine, 0.10 mmol of $Pd(OAc)_2$, and 0.20 mmol of tri-*o*-tolylphosphine in a capped Pyrex bottle was heated at 100 °C for 44 h. After the mixture cooled, excess 10% aqueous hydrochloric acid was added, and the products were extracted with ether. After the mixture was dried and the solvent removed, a brown oil was obtained. This was purified by chromatography on silica gel. Unreacted diene eluted first followed by the product. Evaporation of the solvent left an oil which crystallized when it was dissolved in methanol and cooled. The solid obtained [mp 87–89 °C; 1.5 g (63%)] was shown by NMR to be a 85:15 mixture of *E,E,E* to *E,Z,E* isomers. After the mixture was heated at 130 °C for 14 h, its composition remained unchanged.

General Procedure for the Preparation of Polyene Diesters from Methyl 3-Bromo-2-methylpropenoate and Conjugated Dienes. Mixtures of 25 mmol of the bromo ester and either 12.5 mmol of the diene for the preparation of tetraenes or 30 mmol of the diene for the preparation of trienes, with 75 mmol of triethylamine, 0.112 g (0.5 mmol) of $Pd(OAc)_2$, and 0.304 g (1.0 mmol) of tri-*o*-tolylphosphine, were heated in capped bottles at 100 °C until analysis by GLC showed the absence of the bromo ester or until the bromo ester no longer decreased on further heating. The cooled reaction mixtures were treated with excess cold 10% hydrochloric acid, and the products were extracted with ether. The extracts were washed with water and then with aqueous sodium bicarbonate. The ether solutions were dried, and the solvent was removed under reduced pressure. The residue was then generally chromatographed on alumina to separate the trienes and tetraenes. Alternatively, the residues could be dissolved in methanol, and on cooling the tetraenes generally crystallized from solution. The mother liquors could then be concentrated to give other isomers or evaporated and the residues chromatographed. If only the trienes were of interest, the residues could be distilled under reduced pressure.

Dimethyl 2,7-Dimethylocta-2,4,6-trienedioate. A mixture of 3.58 g (20 mmol) of (*E*)-methyl 3-bromo-2-methylpropenoate, 6.06 g (60 mmol) of triethylamine, 0.0224 g (0.1 mm) of palladium acetate, and 0.061 g (0.2 mmol) of tri-*o*-tolylphosphine was prepared in a 200-mL heavy-walled Pyrex bottle. A magnetic stirring bar was added, and the bottle was capped and flushed with nitrogen and then with ethylene. The bottle was pressured to 30 psi with ethylene with stirring and then placed in a 100 °C oil bath. The mixture was stirred magnetically at 100 °C for 10

h. After being cooled and vented, the bottle was opened, and the contents were diluted with ether and 10% NaOH. The ether layer was separated, and the aqueous phase was extracted with chloroform. The combined ether and chloroform layers were dried with magnesium sulfate, and the solvents were removed under reduced pressure. Methanol was added to the residual oil, and crystals separated. These were collected and recrystallized from methanol to afford 0.8 g (35%) of triene diester, mp 139–140 °C.

Methyl (*Z*)-3-Bromo-2-methylpropenoate. 1,3-Dibromo-2-methylpropene was first prepared by NBS bromination of 1-bromo-2-methyl-1-propene.[8] A mixture of 110 g (0.815 mol) of the bromide, 147 g (0.825 mol) of NBS, 2 g of benzoyl peroxide, and 1 L of carbon tetrachloride was heated to boiling with stirring under a reflux condenser. After 1 h the mixture was cooled, the succinimide was removed by filtration, and the filtrate was distilled. There was obained 116 g (67%) of the dibromide, bp 73–75 °C (18 mm). This compound was a mixture of 60% *E* and 40% *Z* isomers as determined by ^{1}H NMR.

The dibromide was then hydrolyzed to the bromo alcohol. A mixture of 116 g of the dibromide, 95 g of potassium carbonate monohydrate, and 1 L of water was heated at 80 °C with good stirring for 18 h under a reflux condenser. The cooled solution was saturated with sodium chloride and extracted with several portions of ether. The extracts were dried, and the ether was distilled and then the alcohol, bp 91–94 °C (18 mm). There was obtained 67.4 g (82%) of the *E* and *Z* mixture. The pure *Z* isomer was obtained by fractional distillation of the mixture through a spinning-band column; bp 80 °C (19 mm).

The alcohol was then oxidized to the aldehyde. To a mechanically stirred suspension of 37 g (0.425 mmol) of manganese dioxide freshly prepared by the method of Attenburrow[10] at 0 °C in 100 mL of hexane was added a solution of 12.82 g (85 mmol) of the *Z* alcohol in 30 mL of hexane over a period of 20–25 min. The cooling bath was removed, and stirring was continued for 8 h. The manganese residues were then removed by filtration through Celite, and the solids were throughly rinsed with additional hexane. Concentration of the hexane gave the crude aldehyde.

Further oxidation to the ester was achieved by dissolving the crude aldehyde in 30 mL of methanol and adding the solution to a stirred suspension of 30 g of manganese dioxide,[10] 2 g of sodium cyanide (hood!) and 1.8 g of acetic acid in 100 mL of methanol at 0 °C. After the mixture was stirred for 3 h, another 30-g portion of manganese dioxide was added along with 1 mL of acetic acid. Stirring was continued for a total of 18–20 h, and the insoluble salts were removed by filtraton. The solids were washed well with ether. The combined organic solutions were concentrated to about 80 mL, extracted with water, and dried. The solvent was removed under reduced pressure, and the residue was distilled to yield 5.51 g (36%) of the colorless (*Z*)-bromo ester, bp 76 °C (43 mm).

2-Methyl-1,4-diphenyl-1,3-butadiene. A mixture of 15.7 g (100 mmol) of bromobenzene, 3.4 g (50 mmol) of isoprene, 30.0 g (300 mmol) of triethylamine, 0.224 g (1 mmol) of palladium acetate, and 0.608 g (2 mmol) of tri-*o*-tolylphosphine was prepared in a 200-mL heavy-walled Pyrex bottle, and the bottle was capped. The bottle was warmed with shaking until homogeneous and then heated at 125 °C in an oil bath for 3 days, at which time the reaction had stopped with only about 50% of the bromobenzene reacted as judged by analyses by GLC. The cooled reaction mixture was diluted with ether and 10% aqueous sodium hydroxide. The ether layer was separated, washed with water, dried, and concentrated under reduced pressure. The residue remaining was chromatographed on alumina with 10% ether–pentane to remove the bromobenzene. The crude product was recrystallized from hexane by cooling the mixture in dry ice to give 2.42 g (22%) of colorless crystals of the product, mp 78–80 °C.

Dimethyl 2,11-Dimethyldodeca-2,4,6,8,10-pentaenedioate. A mixture of 0.80 g (10 mmol) of hexatriene,[11] 3.58 g (20 mmol) of (*E*)-methyl 3-bromo-2-methylpropenoate, 6.06 g (60 mmol) of triethylamine, 0.0224 g (0.1 mmol) of palladium acetate, and 0.061 g (0.2 mmol) of tri-*o*-tolylphosphine was prepared in a 200-mL heavy-walled Pyrex bottle. The bottle was capped, shaken until homogeneous, and heated in a steam bath for 24 h, at which time GLC analyses showed that the bromo ester had all reacted. The cooled reaction mixture was diluted with ether and aqueous 10% sodium hydroxide. The ether layer was separated, and the aqueous phase was extracted with ether and then with chloroform. The combined organic layers were dried with magnesium sulfate, and the solvents were removed under reduced pressure. Methanol was added to the residual oil, and the crystals which formed were removed by filtration. Recrystallization from methanol afforded 0.72 g (36%) of the orange-red crystalline pentaene diester, mp 157–158 °C.

X-ray Crystallographic Analyses. General Methods. All data were collected on a Nicolet R3 automated diffractometer at 23 °C. The structures were solved and refined by using the Nicolet crystallographic software package SHELXTL. The unit cell parameters were obtaining from the angular settings of 25 reflections (20° ≤ 2θ ≤ 30°) by using Mo K_α radiation (λ = 0.710 73 Å).

Dimethyl (*E*,*E*,*E*,*E*)-2,4,7,9-Tetramethyl-2,4,6,8-decatraenedioate. A pale yellow crystal (0.12 × 0.22 × 0.35 mm) was found to belong to the monoclinic space group $P2_1/n$ (a nonstandard setting for $P2_1/c$) with a = 8.346 (1) Å, b = 7.231 (1) Å, c =12.811 (3) Å, β = 95.49 (2)°, V = 769.6 (3) Å^3, and Z = 2 (two halves of the molecule are related by an inversion center). A single form of the reflection data (3° ≤ 2θ ≤ 45°) for $+h,+k,\pm l$ was collected which yielded 674 independent reflections for $F_o \geq 3\sigma F_o$. All atoms, including hydrogen atoms, were located, and the nonhydrogen atoms were refined with anisotropic thermal parameters (hydrogen atoms, isotropic). At convergence, $R(F)$ = 5.04% and $R_w(F)$ = 5.12%. A final difference map showed only a well-scattered background with no peaks greater than 0.4 e/Å^3.

Dimethyl (*E*,*E*,*E*,*E*)-2,5,9-Trimethyl-2,4,6,8-decatetraenedioate. A pale orange crystal (0.21 × 0.31 × 0.38 mm) of moderate crystallographic quality was found to belong to the monoclinic space group $P2_1/c$, with a = 7.246 (3) Å, b = 8.165 (3) Å, c = 24.965 (8) Å, β = 95.17 (3)°, V = 1490.9 Å^3, and Z = 4. A single form of the data, $+h,+k,\pm l$, was collected (3° ≤ 2θ ≤ 45°) which yielded 1209 independent reflections for $F_o \geq 3\sigma F_o$. All nonhydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were added to the structure as fixed contributions in idealized positons (C–H = 0.96 Å) with isotropic thermal parameters 20% larger than the carbon atoms to which they were attached. At convergence $R(F)$ = 9.6% and $R_w(F)$ = 10.8%. A final difference map showed no unusual features (highest peak 0.3 e/Å^3).

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Registry No. (*E*)-2,4-Pentadienoic acid, 21651-12-7; 1-bromo-2-methyl-1-propene, 3017-69-4; triethylamine, 121-44-8; palladium diacetate, 3375-31-3; tri-*o*-tolylphosphine, 6163-58-2; (*E*,*E*)-7-methyl-2,4,6-octatrienoic acid, 81714-82-1; (2*E*,4*E*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienoic acid, 64245-74-5; (2*Z*,4*E*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienoic acid, 81714-81-0; (*E*)-β-bromostyrene, 588-72-7; methyl (*E*)-3-bromo-2-methylpropenoate, 40053-01-8; (*Z*)-1-bromo-1-butene, 31849-78-2; (*E*)-2,4-pentadienal dimethyl acetal, 67356-82-5; piperidine, 110-89-4; (2*E*,6*Z*)-4-piperidino-2,6-nonadienal dimethyl acetal, 84695-22-7; (3*E*,6*Z*)-2-piperidino-3,6-nonadienal dimethyl acetal, 84695-23-8; (2*E*,4*E*,6*E*)-nonatrienal dimethyl acetal, 84695-24-9; 2-bromopropene, 557-93-7; (2*E*)-2,4-pentadienal diethyl acetal, 75773-17-0; (3*E*)-6-methyl-2-piperidino-3,6-heptadienal diethyl acetal, 81714-94-5; (2*E*,4*E*)-6-methyl-2,4,6-heptatrienal diethyl acetal, 81714-93-4; bromoethene, 593-60-2; propenal dimethyl acetal, 6044-68-4; propenal diethyl acetal, 3054-95-3; (*E*)-5-piperidino-3-pentenal dimethyl acetal, 76251-68-8; (*E*)-5-piperidino-3-pentenal diethyl acetal, 81714-80-9; styrene, 100-42-5; (*E*)-1-phenyl-3-methyl-1,3-butadiene, 68036-69-1; methyl (2*E*,4*E*,6*E*)-2,5-dimethyl-7-phenyl-2,4,6-heptatrienoate, 84695-25-0; methyl (2*E*,4*Z*,6*E*)-2,5-dimethyl-7-phenyl-2,4,6-heptatrienoate, 84695-26-1; acrylic acid, 79-10-7; 1-methyl (2*E*,4*E*)-2-methyl-

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pentadiendioate, 84695-27-2; phenyl bromide, 108-86-1; (*E*,*E*)-3-methyl-1,4-diphenyl-1,3-butadiene, 23637-43-6; methyl (*Z*)-3-bromo-2-methylpropenoate, 84695-28-3; (*E*)-1,3-dibromo-2-methylpropene, 28357-78-0; (*Z*)-1,3-dibromo-2-methylpropene, 28357-77-9; (*E*)-3-bromo-2-methylprop-2-en-1-ol, 84695-29-4; (*Z*)-3-bromo-2-methylprop-2-en-1-ol, 84695-30-7; (*Z*)-3-bromo-2-methylpropenal, 84695-31-8; ethene, 74-85-1; 1,3-butadiene, 106-99-0; (*Z*)-1,3-pentadiene, 1574-41-0; (*E*)-1,3-pentadiene, 2004-70-8; dimethyl (2*E*,4*E*,6*E*)-2,7-dimethyl-2,4,6-octatrienoate, 84695-32-9; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,9-dimethyl-2,4,6,8-decatetraendioate, 84695-33-0; methyl (2*E*,4*E*,6*E*)-2-methyl-2,4,6-octatrienoate, 81714-88-7; methyl (2*E*,4*E*,6*Z*)-2-methyl-2,4,6-octatrienoate, 81714-89-8; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,4,9-trimethyl-2,4,6,8-decatetraenedioate, 81715-00-6; 2-methyl-1,3-butadiene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; methyl (2*Z*,4*E*,6*E*)-2-methyl-2,4,6-octatrienoate, 84695-34-1; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,5,9-trimethyl-2,4,6,8-decatetraenedioate, 81714-98-9; dimethyl (2*E*,4*E*,6*Z*,8*E*)-2,5,9-trimethyl-2,4,6,8-decatetraenedioate, 84773-41-1; methyl (2*E*,4*E*)-2,5,6-trimethyl-2,4,6-heptatrienoate, 81714-92-3; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,5,6,9-tetramethyl-2,4,6,8-decatetraenedioate, 81724-46-1; (*E*,*Z*)-2,4-hexadiene, 5194-50-3; methyl (*E*)-2,4-pentadienoate, 2409-87-2; methyl (2*E*,4*E*,6*E*,8*E*)-2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate, 84695-35-2; methyl 2,4-dimethyl-2,4,6-octatrienoate, 81714-91-2; methyl (2*E*,4*Z*,6*Z*,8*E*)-2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate, 84695-36-3; dimethyl (2*E*,4*E*,6*E*)-2-methyl-2,4,6-octatrienedioate, 81714-83-2; (*Z*)-3-methyl-2,4-pentadienoic acid, 30288-18-7; (*E*)-1,3,5-hexatriene, 821-07-8; 1-methyl (2*E*,4*E*,6*Z*)-2,6-dimethyl-2,4,6-octatrienedioate, 84695-37-4; 1-methyl (2*E*,4*E*,6*E*)-2,6-dimethyl-2,4,6-octatrienedioate, 84695-38-5; dimethyl (2*E*,4*E*,6*E*,8*E*,10*E*)-2,11-dimethyl-2,4,6,8,10-dodecapentaenedioate, 84695-39-6.

Supplementary Material Available: Table II containing the physical properties, NMR spectra, and molecular weights of the products prepared and crystallographic data for (*E*,*E*,*E*)-dimethyl 2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate (Tables III and IV) and (*E*,*E*,*E*,*E*)-dimethyl 2,5,9-trimethyl-2,4,6,8-decatetraenedioate (Tables V and VI) (7 pages). Ordering information is given on any current masthead page.

Structure of ω-Arylalkyl Radicals: A ^{13}C CIDNP Investigation

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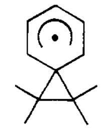
Thermolysis of a series of ω-arylalkanoyl *m*-chlorobenzoyl (and acetyl) peroxides at ~100 °C in cyclohexanone and in hexachloroacetone was studied by using ^{13}C chemically induced dynamic nuclear polarization. Analysis of the observed ^{13}C polarizations indicate that all the three radicals (β-arylethyl, γ-arylpropyl and δ-arylbutyl) have open-chain structures with no evidence for aryl participation resulting in spirocycloalkylcyclohexadienyl radicals.

Introduction

The 1,2-migration of phenyl groups in phenylethyl cations involving bridged species is well-known. For example, ionization of β-phenylethyl chloride under superacid conditions leads to the bridged ethylenebenzenium ion, which has been well characterized by spectroscopic means.[1] Analogous aryl migrations in β-arylethyl radicals are also of interest in reference to the structure of the intermediates. Such 1,2-aryl migrations have been shown to proceed best when a tertiary or a benzylic radical is formed or when steric compression at the β-carbon is relieved.[2–5]

An ESR spectroscopic study of the β-phenylethyl and neophyl radicals at low temperature[6] showed no resolvable hyperfine interaction with the aromatic hydrogens, indicating the absence of the spirocyclic radicals 1 and 2.


1


2

Recently, Ingold et al.[7] have estimated that the ring opening of radical 1 to the open-chain β-phenylethyl radical would be endothermic by ca. 17 kcal/mol. Radical 1 generated by hydrogen atom abstraction from spiro[2.5]-octa-4,6-diene could not be detected[7] by means of ESR spectroscopy even at temperature as low as 100 K. Instead, the ESR spectrum of the cyclopropyl ring-opened radical was obtained. However, 1 was identified by using optical detection methods by means of its absorption and fluorescence at ca. 560 nm, which is characteristic of cyclohexadienyl moiety.

In a recent study of the rearrangements of β-arylated nitroparaffins in the presence of sodium methylmercaptide, Kornblum et al.[8,9] proposed the intermediacy of spirocyclic free radicals such as 2.

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