benzoic acid (170 mg, 0.93 mmol, 7%), identified in the same way. The third fraction was a pale yellow syrup that did not crystallize but was analytically pure (2.30 g, 8.03 mmol, 57%): $^1$H NMR ($CDCl_3$) $\delta$ 3.53 (br s, 3, 2-$OCH_3$), 3.86 (s, 3, 3-$OCH_3$), 6.93-7.71 (m, 6, Ar H). When the NMR probe was heated to 100 °C the resonance at $\delta$ 3.53 became a sharp singlet.

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 66.99; H, 4.82.

**Alizarin Dimethyl Ether (12b).** A sample of **15** (0.63 g, 2.2 mmol) was cooled in ice while 6 mL of concentrated sulfuric acid was added slowly with stirring. The resulting orange-brown solution was allowed to stand without further cooling for 4 h before pouring it on ice. The resulting yellow solid was recrystallized from acetone–ethanol as yellow needles (mp 207.5–208.5 °C, 0.32 g, 54%) which was again crystallized from ethanol: mp 210.5–211.5 °C (lit.[44] mp 210–211 °C); $^1$H NMR ($CF_3COOH$) $\delta$ 4.23 (s, 3, $OCH_3$), 4.26 (s, 3, $OCH_3$), 7.64 (d, 1, Ar H), 8.03 (m, 2, Ar H), 8.43 (m, 3, Ar H); $^1$H NMR ($CDCl_3$)[45] $\delta$ 4.00 (s, 6, $OCH_3$), 7.22 (d, 1, $J$ = 8 Hz, Ar H), 7.60-7.80 (m, 2, Ar H), 8.02-8.30 (m, 3, Ar H).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.55; H, 4.30.

(44) Perkin, A. G. *J. Chem. Soc.* **1907**, *91*, 2066.

(45) Cf.: Chan, A. W. K.; Crow, W. E. *Aust. J. Chem.* **1966**, *19*, 1701. The spectrum which we have observed differs from that reported by Chan and Crow for alizarin dimethyl ether mainly in that we have a single signal at $\delta$ 4.00 for the two methoxyl groups whereas Chan and Crow have resolved this into two separate signals at $\delta$ 3.94 and 4.00. The difference in our observations may be due to a concentration effect (we used a saturated solution), but in any event our spectrum using trifluoroacetic acid shows that the two methoxyl groups are not equivalent.

**2-(3,4,5-Trimethoxybenzoyl)-4,5-(methylenedioxy)benzoic Acid (20).** 6-Bromopiperonylic acid[30] (25 mmol) was subjected to halogen–metal exchange with butyllithium for 2 h at −100 °C, following the general procedure. 3,4,5-Trimethoxybenzoyl chloride (25 mmol) was added, following the usual procedure. The yellow suspension was stirred for 30 min at −100 °C and then allowed to rise to 25 °C and stirring was continued for an additional 17 h. The solution was worked up in the usual way; the product, which precipitated on acidification of the bicarbonate solution, was purified by crystallization from ethanol, affording 3.84 g (67% yield) of fluffy colorless needles: mp 211–214.5 °C; $^1$H NMR ($CD_3SOCD_3$) $\delta$ 3.67 (br s, 9, $OCH_3$), 6.06 (s, 2, $OCH_2O$), 6.67–6.84 (m, 3, Ar H), 7.18 (br s, 1, *o*-HOOCAr**H**); $^{13}$C NMR ($CD_3SOCD_3$) $\delta$ 55.88, 60.16, 102.72, 106.30, 107.53, 108.70, 124.29, 132.61, 148.33, 150.74, 152.82, 166.53, 194.14. One more recrystallization from ethanol afforded an analytical sample, mp 214–215.5 °C (lit.[28] mp 215.5 °C).

Anal. Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 59.91; H, 4.40.

**Acknowledgment.** This research was supported in part by Biomedical Research Support Grant 5507-RR-07070-13.

**Registry No.** 1, 57901-57-2; **2a**, 98-88-4; **2b**, 100-07-2; **2c**, 1711-05-3; **2d**, 21615-34-9; **5a**, 85-52-9; **5b**, 1151-15-1; **5c**, 2159-36-6; **5d**, 1151-04-8; **8a**, 2159-48-0; **8b**, 76250-90-3; **10**, 22921-68-2; 11, 76250-91-4; **12b**, 6003-12-9; **14**, 7169-06-4; **15**, 76250-92-5; **19**, 4521-61-3; **20**, 7470-99-7; bromobenzene, 108-86-1; triphenylcarbinol, 76-84-6; butylbenzene, 104-51-8; *o*-bromotoluene, 95-46-5; 2-methylbenzophenone, 131-58-8; bis(2-methylphenyl)phenylmethanol, 6324-60-3; *o*-bromobenzonitrile, 2042-37-7; valerophenone, 1009-14-9; 2-cyanobenzophenone, 37774-78-0; 6-bromopiperonylic acid, 60546-62-5.

# Palladium-Catalyzed Three Carbon Chain Extension Reactions with Acrolein Acetals. A Convenient Synthesis of Conjugated Dienals

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*Received June 2, 1980*

A variety of vinylic halides has been found to react with acrolein or methacrolein acetals and amines with palladium catalysts to form 5-amino 3-enal acetals and/or dienal acetals. The reaction products yield 2,4-dienals on treatment with aqueous acids, in moderate to good yields. Crotonaldehyde dimethyl acetal also undergoes the reaction, but only in low yields. 3-Buten-2-one ethylene ketal reacted well under the same conditions, however, and Hofmann elimination and hydrolysis of the product amine gave (*E*,*E*)-3,5-heptadien-2-one in 90% yield.

The palladium-catalyzed reaction of vinylic halides with various olefinic compounds to form dienes and/or allylic amines[1,2] is a synthetically useful reaction. Recently we have reported three carbon chain extensions of aryl and vinylic halides forming unsaturated carboxylic acid derivatives using acrylic acid derivatives in the reaction.[2] It would be of synthetic value to be able to add to other three carbon functionalized moieties in a similar manner. In this report we describe the synthesis of aliphatic, diunsaturated aldehydes and ketones by this method.

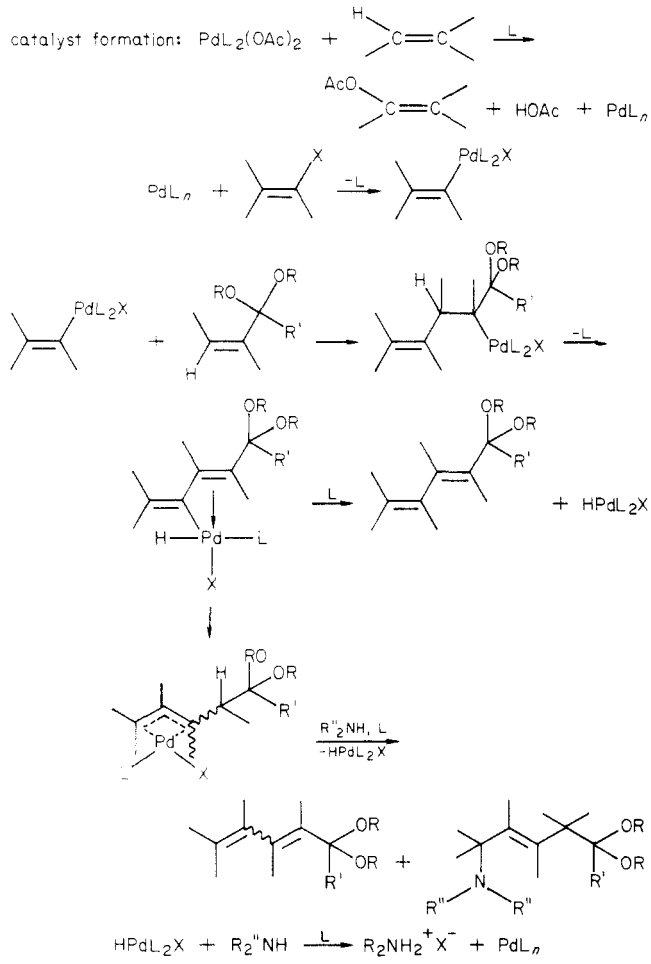
## Results and Discussion

As noted previously with aryl halide reactions,[3] unprotected $\alpha,\beta$-unsaturated aldehydes and ketones do not usually react well with organic halides because of competing polymerization, aldol condensation, and 1,4-addition reactions. Accordingly, as before, we have used the protected acetals or ketals. Also, as would have been expected from earlier results, the reaction with unsaturated acetals and ketals proceeded much faster and more cleanly with nucleophilic secondary amines as bases than with triethylamine, in the absence of an activating ester substituent.[2] With secondary amines, the major products are usually amino acetals or ketals, sometimes along with minor amounts of dienal acetals or dienone ketals. The hydrogens $\alpha$ to the acetal or ketal groups in the intermediate palladium complexes, apparently, are not reactive enough for the elimination to conjugated dienes to occur easily. It is interesting and of synthetic advantage that the competing formation of esters by way of intermediate ketene acetals observed in the related aromatic halide reactions[3] is generally much less important and often insignificant in the reactions with vinylic halides and nucleophilic secondary amines. The following major reaction

(1) B. A. Patel and R. F. Heck, *J. Org. Chem.*, **43**, 3898 (1978).
(2) R. F. Heck, *Acc. Chem. Res.*, **12**, 146 (1979), and references therein.
(3) T. C. Zebovitz and R. F. Heck, *J. Org. Chem.*, **42**, 3907 (1977).

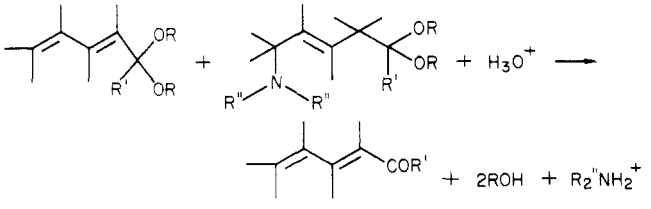
0022-3263/81/1946-1061$01.25/0 

Scheme I

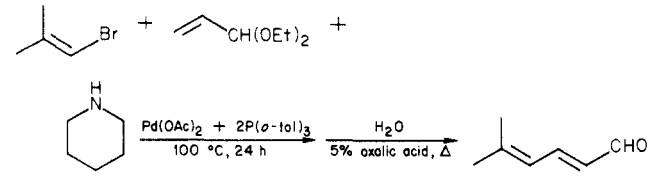


paths are believed to be involved in our reactions (Scheme I).

Both the dienal acetals or ketone ketals and the amino acetal or ketal products generally yield conjugated dienals or dienones on treatment with aqueous acid. However, problems arise with some compounds (see below).

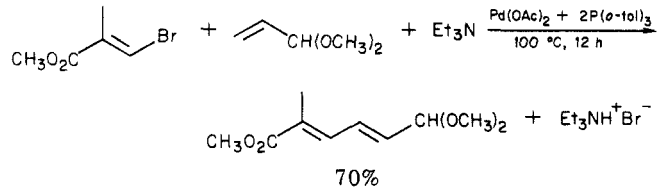


Numerous examples of the reaction have been studied. In some cases the reaction mixtures were hydrolyzed without isolation of the acetals or ketals. The results are summarized in Table I. The stereochemical assignments were made on the basis of proton NMR spectra. Some decoupling experiments at 250 MHz were necessary to confirm structures. A specific case is described below. The NMR data on the products prepared is given in Table III (Supplementary Material). Reactions of acrolein dimethyl acetal and diethyl acetal, methacrolein dimethyl acetal, crotonaldehyde dimethyl acetal, and 3-buten-2-one ethylene ketal with one or more of the following vinylic bromides were carried out: vinyl bromide, (*E*)- and (*Z*)-1-bromo-1-propene, 2-bromo-1-butene, (*E*)-2-bromo-2-butene, 1-bromo-2-methyl-1-propene, (*E*)-methyl 3-bromo-2-methylpropenoate, 2-bromo-3-methyl-2-butene, and (*Z*)-1-bromo-1-hexene. Piperidine and morpholine, and in one case triethylamine, were employed as the bases. The piperidine and morpholine appear similar in most reactions, but an accurate comparison was obtained only in the reaction of 1-bromo-2-methyl-1-propene with acrolein diethyl acetal. Here piperidine gave a 17% higher yield than morpholine did of 5-methyl-2,4-hexadienal after hydrolysis of the crude reaction mixtures (76% vs. 59%).



76%

Triethylamine was used only in the reaction of (*E*)-methyl 3-bromo-2-methylpropenoate with acrolein dimethyl acetal where the ester group facilitates the elimination.[1]

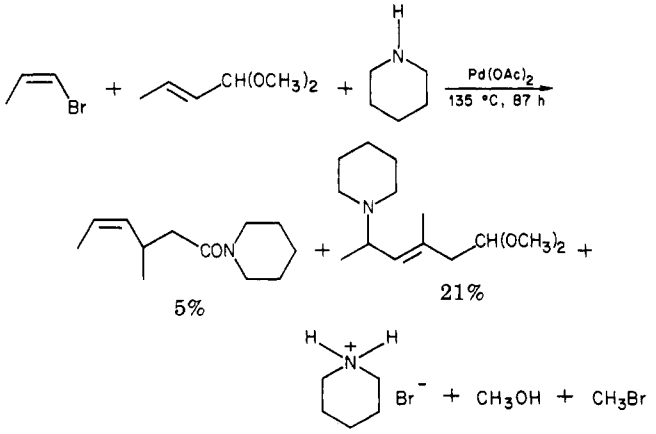


70%

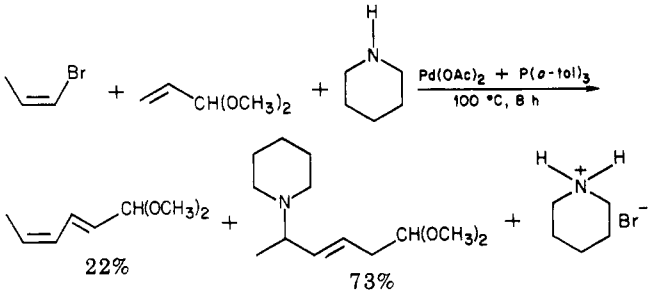
We have used as catalysts both palladium acetate alone and in conjunction with tri-*o*-tolylphosphine. The phosphine must be used when triethylamine is the base, but with morpholine or piperidine the phosphine is not necessary. The addition of the phosphine sometimes caused a higher yield of products to be formed than with palladium acetate alone, however. Other times better yields were obtained without the phosphine. The effect is unpredictable at this time. We have used tri-*o*-tolylphosphine because of the advantages noted previously,[4] but triphenylphosphine probably would be comparable in most of these reactions. In general, reactions of the vinylic bromides with the acrolein acetals went in higher yields than those with methacrolein acetal and 3-butene-2-one ethylene ketal. Considerably lower yields were obtained with crotonaldehyde dimethyl acetal. Only two reactions were attempted with the last compound: reactions with vinyl bromide and with (*Z*)-1-bromo-1-propene. It is not surprising that the vinyl bromide reacted poorly because the amine adduct expected to be formed would be about as reactive as the starting material and the dienal acetal would be more reactive. In this case the yield was not determined because it was very low (less than 10%). The products were isolated by preparative gas chromatography and definitely identified, however. The corresponding (*Z*)-1-bromo-1-propene reaction was the only reaction in which a product from the possible ketene acetal intermediate was observed. The reaction was very slow, requiring 4 days at 100 °C to reach completion. The ketene intermediate gave the piperidine amide of *cis*-3-methyl-5-hexenoic acid (~5%), apparently formed from the methyl ester expected as the initial product[3] and piperidine. The expected piperidino acetal also was formed, but only in ~21% yield. The remainder of the reaction mixture was a nonvolatile dark viscous liquid.

The other reactions in Table I, in general, proceeded to amino acetals or ketals and/or dienal acetals or dienone ketals in considerably better yields and are preparatively useful methods. It is interesting that in the reactions of (*E*)- and (*Z*)-1-bromo-1-propene with acrolein dimethyl acetal and piperidine that both isomers gave the same yields of dienal acetals and amine adduct, but that the dienal acetals were different isomers and the amine ad-

(4) C. B. Ziegler, Jr., and R. F. Heck, *J. Org. Chem.*, 43, 2941 (1978).



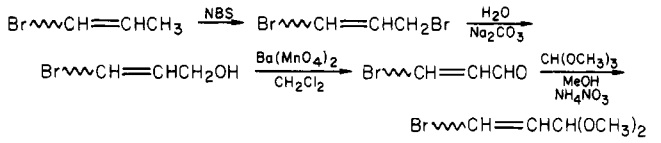
ducts were the same. The assignment of stereochemistry to these products is based upon their proton NMR spectra. Hydrolysis of the two isomeric dienal acetals with dilute acid at room temperature produced two dienals. The isomers obtained from both (*Z*)- and (*E*)-1-bromo-1-propenes showed a doublet of doublets for the proton on C-3 with $J_1 = 15.5$ Hz and $J_2 = 11.0$ Hz, indicating a trans $\alpha,\beta$ double bond in both compounds. We could not determine the coupling constants for the other double bond but since equilibration with warm dilute acid converted the isomer from the (*Z*)-bromide into the other one we feel confident in assigning the *E,E* stereochemistry to the more stable product and the *E,Z* stereochemistry to the other one. The amine adduct is clearly the *E* isomer since at 250 MHz decoupling of the tertiary allylic hydrogen caused the vinyl H on C-4 to become a doublet with $J = 15.5$ Hz. (See Table III for chemical shift data). These results are consistent with a mechanism in which the dienal acetals are arising from a direct elimination and are not coming from the $\pi$-allylic intermediate while the amine adduct arises from the equilibrated $\pi$-allylic intermediate. The amine adducts are the *E* isomers since the $\pi$-allylic complexes are most stable with the largest groups in syn positions.



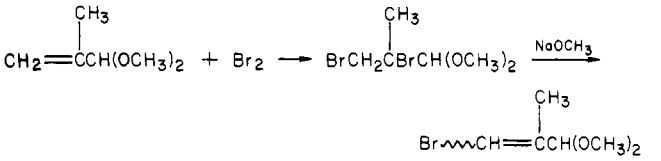
The reaction is limited in scope by steric effects in the vinylic halide as well as in the acetal or ketal. (*Z*)-3-Iodo- and 3-bromo-3-hexene both fail to give detectable amounts of the expected products with either acrolein or crotonaldehyde dimethyl acetals. The only product found was dimerized halide, 4,5-diethyl-3,5-octadiene, in low yield.

The reverse combination of reactants to form the dienal and amino enal acetals was investigated briefly. This is the reaction of 3-bromoacrolein dimethyl acetal with 1-hexene and related reactions with 3-bromomethacrolein dimethyl acetal.

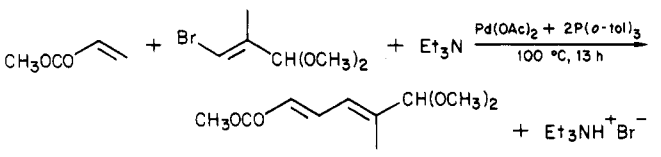
3-Bromoacrolein dimethyl acetal was prepared from 1-bromo-1-propene by first NBS bromination to 1,3-dibromopropene (mixture of *E* and *Z* isomers), hydrolysis to 3-bromo-2-propen-1-ol, oxidation to the aldehyde with barium permanganate, and finally reaction with trimethyl orthoformate to form the acetal. Unfortunately, the bromo acetal is relatively unstable. It slowly decomposed even at 5 °C over a period of a few weeks. It was reacted



with 1-hexene under the usual reaction conditions. It appeared to react normally, but the reaction mixture was very dark and it contained a mixture of about 6 or 7 products as determined by GLC. This bromide also failed to form volatile products when it was reacted with the usually reactive 3-buten-2-ol under similar conditions. The instability of the bromide and the relatively inconvenient method of synthesis make this compound unattractive for general use and it was not investigated further. The corresponding methallyl derivative, however, was easily prepared by bromination–dehydrobromination of methacrolein dimethyl acetal and it was more stable than the parent compound above. The bromo acetal was a mixture



of stereoisomers from which the *E* isomer could be separated by fractional distillation. This compound proved to have limited value in our acetal synthesis as we had anticipated from our previous results.[1] The compound behaved like 1-bromo-2-methyl-1-propene in that it gave mixtures of regioisomers when it was reacted with piperidine and 1-hexene (four dienes and very little amine adduct). Presumably this would be a problem with other alkenes with electron-donating substituents also. The compound did react selectively with methyl acrylate with triethylamine as the base to form a single isomeric product.



90%

**Hydrolysis of Amino Acetals and Ketals.** The most useful feature of the vinylic bromide–enal acetal or enone ketal–amine reaction is that the products can be hydrolyzed to conjugated dienals or dienones. The selectivity with which hydrolysis of the acetals and ketals occurs varies with the structure of the compound involved, however. The amine adducts obtained from the acrolein acetal reactions hydrolyzed easily to the dienals with warm 5% oxalic acid. The corresponding adducts from methacrolein and crotonaldehyde acetals largely rearranged under the same hydrolysis conditions to give 5-amino 2-enals which were resistant to loss of the amine even at 100 °C in 5% oxalic acid. A similar problem was encountered with the amine adduct obtained from the 3-buten-2-one ethylene ketal, (*Z*)-1-bromo-1-propene and piperidine. We attempted to convert these materials to the dienals and dienones in several other ways. Stronger acids and lower temperatures did not help. The reaction of the amines with methyl chloroformate occurred readily and the crude chloro enal acetals were converted by steam distillation from the 5% oxalic acid into dienals, but significant amounts of volatile side products were also formed. The quaternary ammonium salts made by reaction with methyl iodide could be hydrolyzed more easily than the amines, but these too produced large amounts of side products in addition to the desired aldehydes. Finally, we simply

Table I. Palladium-Catalyzed Reactions of Unsaturated Acetals and Ketals with Vinylic Halides and Amines[a]

| acetal or ketal | vinylic halide | amine[b] | catalyst, $PR_3/Pd(OAc)_2$ | temp, °C | time, h | products (% yield)[d] |
|---|---|---|---|---|---|---|
| $CH_2$=CHCH$(OCH_3)_2$[c] | $CH_2$=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 20 | (*E*)-P*$CH_2$CH=CH$CH_2$CH$(OCH_3)_2$ (57) |
| $CH_2$=CHCH$(OCH_3)_2$ | $CH_2$=C$(CH_3)$Br | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 1 | 100 | 22 | (*E*)-$CH_2$=C$(CH_3)$CH=CHCH$(OCH_3)_2$ (31), (*E*)-P*$CH_2$C$(CH_3)$=CH$CH_2$CH$(OCH_3)_2$ (60) |
| $CH_2$=CHCH$(OCH_3)_2$ | $CH_2$=C$(CH_3)$Br | P*H | $Pd(OAc)_2$ | 100 | 18 | (*E*)-$CH_2$=C$(CH_3)$CH=CHCHO (42)[e] |
| $CH_2$=CHCH$(OCH_3)_2$ | (*E*)-$CH_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 9 | (*E,E*)-$CH_3$CH=CHCH=CHCH$(OCH_3)_2$ (23), (*E*)-$CH_3$CH(P*)CH=CH$CH_2$CH$(OCH_3)_2$ (72) |
| $CH_2$=CHCH$(OCH_3)_2$ | (*Z*)-$CH_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 8 | (*E,Z*)-$CH_3$CH=CHCH=CHCH$(OCH_3)_2$ (22), (*E*)-$CH_3$CH(P*)CH=CH$CH_2$CH$(OCH_3)_2$ (73) |
| $CH_2$=CHCH$(OCH_3)_2$ | (*E*)- + (*Z*)-$CH_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 24 | (*E,E*)-$CH_3$CH=CHCH=CHCHO (75)[e] |
| $CH_2$=CHCH$(OCH_3)_2$ | $CH_3CH_2CBr$=$CH_2$ | MH | 1% $Pd(OAc)_2$ | 125 | 48 | MC$H_2$C$(C_2H_5)$=CH$CH_2$CH$(OCH_3)_2$ (84) |
| $CH_2$=CHCH$(OCH_3)_2$ | (*E*)-$CH_3$CH=CBrC$H_3$ | MH | 1% $Pd(OAc)_2$ | 100 | 6 days | (*E*)-MCH$(CH_3)$C$(CH_3)$=CH$CH_2$CH$(OCH_3)_2$ (78) |
| $CH_2$=CHCH$(OCH_3)_2$ | $(CH_3)_2$C=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 18 | (*E*)-$CH_2$=C$(CH_3)$CH=CH$CH_2$CH$(OCH_3)_2$ (20), (*E*)-$(CH_3)_2$C=CHCH=CHCH$(OCH_3)_2$ (20), (*E*)-P*$(CH_3)_2$CCH=CH$CH_2$CH$(OCH_3)_2$ (40) |
| $CH_2$=CHCH$(OCH_3)_2$ | $(CH_3)_2$C=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 18 | (*E*)-$(CH_3)_2$C=CHCH=CHCHO (76)[e] |
| $CH_2$=CHCH$(OEt)_2$ | $(CH_3)_2$C=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 24 | (*E*)-$(CH_3)_2$C=CHCH=CHCHO (76)[e] |
| $CH_2$=CHCH$(OEt)_2$ | $(CH_3)_2$C=CHBr | MH | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 19 | (*E*)-$(CH_3)_2$C=CHCH=CHCHO (59)[e] |
| $CH_2$=CHCH$(OCH_3)_2$ | (*E*)-$CH_3O_2$CC$(CH_3)$=CHBr | $Et_3N$ | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 12 | (*E,E*)-$CH_3O_2$CC$(CH_3)$=CHCH=CHCH$(OCH_3)_2$ (70) |
| $CH_2$=CHCH$(OCH_3)_2$ | $(CH_3)_2$C=C(Br)$CH_3$ | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 145 | 3.5 days | (*E*)-$CH_2$=C$(CH_3)$C$(CH_3)$=CH$CH_2$CH$(OCH_3)_2$ (45), (*E*)-P*C$(CH_3)_2$C$(CH_3)$=CH$CH_2$CH$(OCH_3)_2$ (13) |
| $CH_2$=CHCH$(OCH_3)_2$ | (*Z*)-$CH_3(CH_2)_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 24 | $CH_3(CH_2)_3$CH=CHCH=CHCH$(OCH_3)_2$[f] (28), (*E*)-$CH_3(CH_2)_3$CH(P*)CH=CH$CH_2$CH$(OCH_3)_2$ (60) |
| $CH_2$=CHCH$(OCH_3)_2$ | (*Z*)-$CH_3(CH_2)_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 16 | (*E,E*)-$CH_3(CH_2)_3$CH=CHCH=CHCHO (76)[e,g] |
| $CH_2$=C$(CH_3)$CH$(OCH_3)_2$ | (*Z*)-$CH_3$CH=CHBr | P*H | $Pd(OAc)_2$ | 100 | 14 | (*E*)-P*CH$(CH_3)$CH=CHCH$(CH_3)$CH$(OCH_3)_2$ (57) |
| $CH_2$=C$(CH_3)$CH$(OCH_3)_2$ | (*Z*)-$CH_3(CH_2)_3$CH=CHBr | P*H | $Pd(OAc)_2$ | 100 | 6.5 days | (*E,E*)-$CH_3(CH_2)_3$CH=CHCH=C$(CH_3)$CHO[e] (40) |
| (*E*)-$CH_3$CH=CHCH$(OCH_3)_2$ | $CH_2$=CHBr | P*H | $Pd(OAc)_2$ | 100 | 39 | (*E,Z*)-P*$CH_2$CH=C$(CH_3)$$CH_2$CH$(OCH_3)_2$ (very low)[h] |
| (*E*)-$CH_3$CH=CHCH$(OCH_3)_2$ | (*Z*)-$CH_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 100 | 4 days | (*E*)-$CH_3$(P*)CHCH=C$(CH_3)$$CH_2$CH$(OCH_3)_2$ (~21%), (*Z*)-$CH_3$CH=CHCH$(CH_3)$$CH_2$COP* (~5%) |
| $CH_2$=CHC$(O_2C_2H_4)CH_3$ | (*Z*)-$CH_3$CH=CHBr | P*H | $\frac{P(o\text{-tol})_3}{Pd(OAc)_2}$ = 2 | 125 | 4 days | (*Z,E*)-$CH_3$CH=CHCH=CHC$(O_2C_2H_4)CH_3$ (16), (*E*)-P*CH$(CH_3)$CH=CH$CH_2$C$(O_2C_2H_4)CH_3$ (47) |

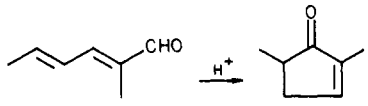
[a] Reactants: 12.5 mmol of acetal or ketal, 10 mmol of vinylic halide, 30 mmol of amine, 0.10 mmol of palladium acetate, and 0.20 mmol of triarylphosphine, if used. Reaction mixtures were heated in capped tubes or bottles for the times and at the temperatures shown. [b] P*H = piperidine, MH = morpholine. [c] 30 mmol of acrolein dimethyl acetal used. [d] Yields of isolated products. [e] Product isolated after steam distillation of the reaction mixture from excess 5% oxalic acid solution. [f] Two isomers. [g] 90% *E,E* and 10% of another isomer. [h] Yield not determined accurately. Products were isolated by preparative GLC only.

Table II. Dienals and Dienones Obtained from Isolated Amine Adducts or Dienal Acetals

| amine adduct or dienal acetal | method | aldehyde (% yield) |
|---|---|---|
| (*E*)-*n*-$C_4H_9CH(P^*)CH{=}CHCH_2CH(OCH_3)_2$ | 5% oxalic acid, 100 °C | *n*-$C_4H_9CH{=}CHCH{=}CHCHO$ (79)[a] |
| (*E*)-$P^*CH_2C(C_2H_5){=}CHCH_2CH(OCH_3)_2$ | 5% oxalic acid, 100 °C | $CH_2{=}C(C_2H_5)CH{=}CHCHO$ (54)<br>$CH_3CH{=}C(CH_3)CH{=}CHCHO$ (2 isomers) (19) |
| (*E*)-$P^*CH(CH_3)CH{=}CHCH(CH_3)CH(OCH_3)_2$ | Hofmann + 5% oxalic acid, 25 °C | $CH_3CH{=}CHCH{=}C(CH_3)CHO$ (74)[b] |
| (*E*)-$P^*CH(CH_3)CH{=}CHCH_2C(O_2C_2H_4)CH_3$ | Hofmann + 5% oxalic acid, 100 °C | $CH_3CH{=}CHCH{=}CHCOCH_3$ (57)[c] |
| (*E*)-$P^*CH(CH_3)C(CH_3){=}CHCH_2CH(OCH_3)_2$ | 5% oxalic acid, 50 °C | $CH_3CH{=}C(CH_3)CH{=}CHCHO$ (83)[d] |
| (*E*)-$(CH_3)_2C{=}C(CH_3)CH{=}CHCH(OCH_3)_2$ | 10% oxalic acid, 30 °C | (*E*)-$(CH_3)_2C{=}C(CH_3)CH{=}CHCHO$ (80) |

[a] About 90% of the *E,E* isomer and 10% of another one. [b] Greater than 90% one isomer. [c] About 90% pure. [d] About an 87:13 mixture of two isomers (presumably *E,E* and *E,Z*, respectively).

carried out the Hofmann elimination of the quaternary ammonium hydroxides and hydrolyzed the acetals or ketal obtained with aqueous oxalic acid, usually to get reasonably pure dienones and dienals in acceptable yields. Some of the dienals are quite sensitive to acid-catalyzed rearrangements, polymerization, and/or cyclization. For example, 2-methyl-2,4-hexadienal is cyclized to 2,5-dimethyl-2-cyclopentenone fairly easily even with hot 5%




oxalic acid and, therefore, hydrolysis of the acetal is best carried out at room temperature. The aldehydes and ketone obtained from the isolated amine adducts are listed Table II. It should be remembered that the amine adducts, in general, are produced along with dienal acetals or dienone ketals in the original reactions and higher yields of dienals and dienones can be obtained if these materials are hydrolyzed with products obtained with the amines.

3-Methyl-2,4-hexadienal was also obtained by way of the Hofmann elimination, but this product was obtained as a mixture with two other similar materials (~60% pure). Since the yield of amine adduct in the first step was only 21% this reaction is not attractive as a method for preparing this aldehyde.

## Experimental Section

**Materials. Vinylic Halides.** Vinyl bromide (Aldrich), 2-bromo-1-propene (Chem. Samples), (*E,Z*)-bromo-1-propene (Pfaltz & Bauer), 2-bromo-1-butene (Pfaltz & Bauer), and (*Z*)-2-bromo-2-butene (Columbia) were commercial products and were used as received. The (*E*)- and (*Z*)-1-bromo-1-propene isomers were separated by fractional distillation. 1-Bromo-2-methyl-1-propene[5] and (*E*)-methyl 2-methyl-3-bromopropenoate[6] were made according to the literature. The other halides were prepared as described below.

**Acetals and Ketals.** Acrolein dimethyl acetal (Aldrich) was a commercial product used as received. Acrolein diethyl acetal,[7] crotonaldehyde dimethyl acetal,[8] and 3-buten-2-one ethylene ketal were prepared by the literature methods.[3] Methacrolein dimethyl acetal was prepared by the phosphoric acid catalyzed reaction of the aldehyde with trimethyl orthoformate, bp 103–110 °C, 50% yield.

**Miscellaneous.** The morpholine (Fisher), piperidine (Aldrich), and triethylamine (Aldrich) were used as received. Palladium acetate and tri-*o*-tolylphosphine were obtained as described previously.[1]

**(*Z*)-1-Bromo-1-hexene.**[9] 1-Hexyne, 41 g (0.5 mol), was placed in a 500-mL three-necked flask equipped with a stirrer, gas inlet tube, and a condenser. The flask was cooled in a dry ice–acetone bath, stirred, and irradiated with ultraviolet light while 40 g of hydrogen bromide gas was passed into the stirred 1-hexyne over a period of 3 h. The reaction mixture was then warmed to room temperature, washed with aqueous sodium carbonate, dried over magnesium sulfate, and distilled through a spinning-band fractionating column at 15-mm pressure. There was obtained 57 g (70%) of (*Z*)-1-bromo-1-hexene, bp 33–34 °C (15 mm).

**2-Bromo-3-methyl-2-butene.**[10] Bromine, 78 g (0.49 mol), was added dropwise with stirring to 34 g (0.49 mol) of 2-methyl-2-butene (Aldrich) in 100 mL chloroform at 0 °C. The mixture then was stirred at room temperature for 30 min and the solvent was removed under reduced pressure. The crude dibromide obtained was added slowly to a solution of 70 g (1.25 mol) of potassium hydroxide in 140 mL of ethylene glycol at 110 to 125 °C. The product was allowed to distill from the reaction mixture through a short Vigreux column. The distillate was dried and shown to be pure by its NMR spectrum. The yield was 60% of theory.

**(*E,Z*)-3-Bromopropenal Dimethyl Acetal.** A mixture of 13.7 g (0.10 mol) of 3-bromo-2-propen-1-ol,[11] 200 mL of methylene chloride, 38.0 g (0.101 mol) of barium permanganate, and a spatula full of cetyltrimethylammonium bromide was stirred vigorously until analysis by GLC showed the absence of the starting alcohol (1–7 days). The mixture was then filtered through Celite and the solids were rinsed several times with fresh methylene chloride. The combined filtrates were used directly to form the acetal because of the bromo aldehyde decomposed on attempted isolation. To the methylene chloride solution of the aldehyde was added 11.7 g (0.11 mol) of trimethyl orthoformate, 5 mL of methanol, and 0.35 g of ammonium nitrate. The mixture was stirred at room temperature until GLC analysis showed the absence of aldehyde (1–4 days). The reaction mixture was then washed with dilute ammonium hydroxide and water. The organic phase was dried with sodium carbonate and then distilled to give 9.0 g (50%) of the bromo acetal, bp 45–53 °C (12 mm).

**(*E*)-3-Bromo-2-methylpropenal Dimethyl Acetal.** Methacrolein dimethyl acetal was brominated in methylene chloride solution at dry ice temperature. After removal of the solvent, the crude dibromide, 41.4 g (0.15 mol), was mixed with a solution of 3.9 g (0.17 mol) of sodium metal dissolved in 100 mL of dry methanol and the mixture was heated under a reflux condenser overnight. The solution was filtered to remove sodium bromide and distilled. There was obtained 15 g (70%) of the bromo acetal, bp 58–60 °C (15 mm). This material was about 90% *E* isomer and 10% *Z*. A 95% pure sample of the *E* isomer was obtained by fractional distillation of the mixture at 15 mm through a spinning-band column.

**3-Buten-2-one Ethylene Ketal.** A solution of 73.5 g (0.7 mol) of 3-chloro-2-butanone (Aldrich), 34.7 g (0.7 mol) of ethylene glycol, 0.45 g (0.0024 mol) of *p*-toluenesulfonic acid monohydrate, and 1 L of benzene was heated to boiling and the water was removed from the reaction mixture by azeotropic distillation with a Dean–Stark trap. About 23 h were required. The benzene was then distilled and the residue was distilled to give 63 g (60%) of the chloro ketal, bp 58–60 °C (20 mm).

The chloro ketal, 46 g (0.3 mol), was added dropwise to a solution of 100 g of potassium hydroxide in 200 mL of ethylene glycol heated to 150 °C. The product was allowed to distill from the reaction mixture as it was formed. The distillate was dried

(5) H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974).
(6) P. Caubere, *Bull. Soc. Chim. Fr.*, 144 (1964).
(7) J. A. V. Allan, *Org. Synth.*, **32**, 5 (1952).
(8) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **18**, 516 (1935).
(9) An *E,Z* mixture of 1-bromo-1-hexene is obtained at higher temperatures as reported by C. A. Young, R. R. Vogt, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 1806 (1936).
(10) Preparation carried out by F. G. Stakem of these laboratories.
(11) L. F. Hatch and K. E. Harwell, *J. Am. Chem. Soc.*, **75**, 6002 (1953).

with magnesium sulfate to give 20.9 g (61%) of the ketal, bp 110–115 °C. The properties of the product were identical with those reported previously.[3]

**General Procedure for Reacting Vinylic Bromides with Unsaturated Acetals or Ketals and Amines.** A solution of 50 mmol of the vinylic bromide, 62.5 mmol of the acetal or ketal, 150 mmol of the amine, 0.50 mmol of palladium acetate, and (if used) 1.00 mmol of tri-*o*-tolylphosphine was prepared in a 200-mL heavy-walled Pyrex bottle. After a brief flushing with nitrogen the bottle was capped and heated in a steam bath with shaking initially until it was homogeneous. Heating was continued until analysis of a small sample of the reaction mixture showed the vinylic bromide had all reacted by GLC analysis. If the reaction was very slow more catalyst could be used or the reaction temperature could be increased to as high as 145 °C. After completion of the reaction as judged by the disappearance of the bromide, the mixture was cooled to room temperature and treated with aqueous sodium hydroxide, and the products were extracted with several portions of ether. The extracts were dried with magnesium sulfate and distilled under reduced pressure.

The purified amine adducts could then be hydrolyzed to the aldehydes by treatment with excess 5% aqueous oxalic acid. Steam distillation generally proved to be a good way to separate the aldehydes from the oxalic acid solution although some decomposition of the aldehyde and/or isomerization may occur under these conditions. Alternatively, the total reaction mixture from the vinylic bromide reaction could be steam distilled from excess 5% aqueous oxalic acid and the organic part of the distillate separated and distilled to give the aldehyde.

**(*E*,*E*)-2-Methyl-2,4-hexadienal.** A mixture of 12.1 g (0.10 mol) of (*Z*)-1-bromo-1-propene, 14.5 g (0.125 mol) of methacrolein dimethyl acetal, 30 mL (0.30 mol) of piperidine, and 0.224 g (0.001 mol) of palladium acetate was shaken until homogeneous in a capped 200-mL heavy-walled Pyrex bottle and heated in a steam bath for 14 days. At this time analysis of the solution by GLC showed the bromopropene had all reacted. The cooled reaction mixture was diluted with ether and excess aqueous potassium hydroxide. The mixture was shaken in a separatory funnel and the ether phase was separated. The aqueous layer was extracted again with ether and the combined ether phases were dried with magnesium sulfate and then distilled under reduced pressure. There was obtained 13.7 g (57%) of 2-methyl-5-piperidino-3-hexenal dimethyl acetal, bp 78–90 °C (0.2 mm).

The acetal, 6.03 g (0.025 mol), was dissolved in 50 mL of ether and 5 mL (0.080 mol) of methyl iodide was added. After the mixture was stirred at room temperature for 18 h, the ether was decanted from the dark yellow insoluble viscous quaternary salt which had formed. The salt was taken up in 100 mL of distilled water and stirred with the silver oxide freshly prepared from 8.5 g (0.050 mol) of silver nitrate and 2.0 g (0.050 mol) of sodium hydroxide in aqueous solution (washed until neutral). After being stirred at 60 °C for 1 h, the quaternary hydroxide solution was filtered from the silver salts and the residue was stirred with 100 mL of 60 °C water for 15 min and filtered again. The combined aqueous filtrates were then distilled under aspirator vacuum. After most of the water had been removed a second phase appeared in the distillate. Distillation was continued until the heating bath temperature reached 90 °C under 20 mm of pressure. The two-phase distillate was extracted with three portions of ether. The extracts were dried with magnesium sulfate and concentrated to give 3.3 g (84%) of crude dienal acetal. The acetal was hydrolyzed by stirring with 50 mL of 5% aqueous oxalic acid at room temperature for 5 min. Extraction of the product with ether, washing the extracts with aqueous sodium bicarbonate, drying with magnesium sulfate, and concentrating gave 2.02 g (74% yield based upon the amino acetal) of 2-methyl-2,4-hexadienal. The product was an 80:20 mixture of two isomers, presumably *E*,*E* and *Z*,*E*, based upon the NMR spectrum of the mixture. The aldehyde(s) is thermally unstable and even steam distillation from neutral solution resulted in a 25% loss of the product. Steam distillation did not change the isomer ratio.

**(*Z*)-3-Methyl-4-hexenoyl Piperidide and 3-Methyl-2,4-hexadienal.** A mixture of 6.05 g (50 mmol) of *cis*-1-bromopropene, 7.25 g (62.5 mmol) of crotonaldehyde dimethyl acetal, 15 mL (150 mmol) of piperidine, 0.336 g (1.5 mmol) of palladium acetate, and 0.912 g (3.0 mmol) of tri-*o*-tolylphosphine was prepared in a 200-mL heavy-walled Pyrex bottle. The bottle was capped after a brief flushing with nitrogen and then heated in a steam bath for 4 days. At this time GLC analyses showed the bromopropene had all reacted. The cooled reaction mixture was diluted with ether and aqueous potassium hydroxide. The ether layer was separated and the aqueous phase was extracted with fresh ether. The combined ether layers were dried with magnesium sulfate. The ether was removed under reduced pressure and the residual oil was distilled. The fraction with bp 75–103 °C (0.3 mm), 3.0 g, was a mixture of 20% of the amide (5% yield) and 80% of the amino acetal (21% yield).

The 3.0 g of the amide–acetal mixture in 50 mL of dry ether was treated with 2 mL (32 mmol) of methyl iodide, mixed well, and left at room temperature for 24 h. The ether solution was then decanted from the viscous quaternary ammonium salt. Evaporation of the ether solution gave quite pure piperidide, 0.52 g (5%). The quaternary salt was dissolved in 50 mL distilled water and stirred with freshly prepared silver oxide (from 3.54 g, 20.8 mmol, of silver nitrate) at 60 °C and treated as in the previous example to give 0.94 g (58%) of an isomeric mixture of acetals (~70% one isomer). Steam distillation of the mixture from 100 mL of 5% oxalic acid gave 0.42 g of product which by GLC contained 60% 3-methyl-2,4-hexadienal (22%).

**Acknowledgment.** This project was supported by a grant from the National Science Foundation. The palladium acetate used was kindly loaned to us by the Matthey Bishop Company, Inc.

**Registry No.** $CH_2$=$CHCH(OCH_3)_2$, 6044-68-4; $CH_2$=$CHCH(OEt)_2$, 3054-95-3; $CH_2$=$C(CH_3)CH(OCH_3)_2$, 23230-91-3; (*E*)-$CH_3CH$=$CHCH(OCH_3)_2$, 18318-79-1; $CH_2$=$CHC(O_2C_2H_4)CH_3$, 26924-35-6; $CH_2$=$CHBr$, 593-60-2; $CH_2$=$C(CH_3)Br$, 557-93-7; (*E*)-$CH_3CH$=$CHBr$, 590-15-8; (*Z*)-$CH_3CH$=$CHBr$, 590-13-6; $CH_3CH_2C$-$Br$=$CH_2$, 23074-36-4; (*E*)-$CH_3CH$=$CBrCH_3$, 3017-71-8; $(CH_3)_2C$=$CHBr$, 3017-69-4; (*E*)-$CH_3O_2CC(CH_3)$=$CHBr$, 40053-01-8; $(CH_3)_2$-$C$=$C(Br)CH_3$, 3017-70-7; (*Z*)-$CH_3(CH_2)_3CH$=$CHBr$, 13154-12-6; P*H, 110-89-4; MH, 110-91-8; $Pd(OAc)_2[P(o\text{-}tol)_3]_2$, 69073-98-9; Pd-$(OAc)_2P(o\text{-}tol)_3$, 76269-80-2; $Pd(OAc)_2$, 3375-31-3; (*E*)-P*$CH_2CH$=$CHCH_2CH(OCH_3)_2$, 76251-68-8; (*E*)-$CH_2$=$C(CH_3)CH$=$CHCH$-$(OCH_3)_2$, 76251-69-9; (*E*)-P*$CH_2C(CH_3)$=$CHCH_2CH(OCH_3)_2$, 76251-70-2; (*E*)-$CH_2$=$C(CH_3)CH$=$CHCHO$, 20432-43-3; (*E*,*E*)-$CH_3CH$=$CHCH$=$CHCH(OCH_3)_2$, 72908-61-3; (*E*)-$CH_3CH(P^*)$-$CH$=$CHCH_2CH(OCH_3)_2$, 75066-94-3; (*E*,*Z*)-$CH_3CH$=$CHCH$=$CHCH(OCH_3)_2$, 72908-59-9; (*E*,*E*)-$CH_3CH$=$CHCH$=$CHCHO$, 4488-48-6; $MCH_2C(C_2H_5)$=$CHCH_2CH(OCH_3)_2$, 76251-71-3; (*E*)-$MCH(CH_3)C(CH_3)$=$CHCH_2CH(OCH_3)_2$, 76251-72-4; (*E*)-$CH_2$=$C$-$(CH_3)CH$=$CHCH_2CH(OCH_3)_2$, 76251-73-5; (*E*)-$(CH_3)_2C$=$CHCH$=$CHCH(OCH_3)_2$, 76251-74-6; (*E*)-P*$(CH_3)_2CCH$=$CHCH_2CH$-$(OCH_3)_2$, 75066-97-6; (*E*)-$(CH_3)_2C$=$CHCH$=$CHCHO$, 17424-21-4; (*E*,*E*)-$CH_3O_2CC(CH_3)$=$CHCH$=$CHCH(OCH_3)_2$, 76251-75-7; (*E*)-$CH_2$=$C(CH_3)C(CH_3)$=$CHCH_2CH(OCH_3)_2$, 76251-76-8; (*E*)-P*$C$-$(CH_3)_2C(CH_3)$=$CHCH_2CH(OCH_3)_2$, 76251-77-9; $CH_3(CH_2)_3CH$=$C$-$HCH$=$CHCH(OCH_3)_2$, 76251-78-0; (*E*)-$CH_3(CH_2)_3CH(P^*)CH$=$CHCH_2CH(OCH_3)_2$, 76251-79-1; (*E*,*E*)-$CH_3(CH_2)_3CH$=$CHCH$=$CHCHO$, 5910-87-2; P*$CH(CH_3)CH$=$CHCH(CH_3)CH(OCH_3)_2$, 76251-80-4; (*E*,*E*)-$CH_3(CH_2)_3CH$=$CHCH$=$C(CH_3)CHO$, 76251-81-5; (*E*)-P*$CH_2CH$=$C(CH_3)CH_2CH(OCH_3)_2$, 76251-82-6; (*Z*)-P*$CH_2CH$=$C(CH_3)CH_2CH(OCH_3)_2$, 76251-83-7; (*E*)-$CH_3(P^*)$-$CHCH$=$C(CH_3)CH_2CH(OCH_3)_2$, 76251-84-8; (*Z*)-$CH_3CH$=$CHCH$-$(CH_3)CH_2COP^*$, 76251-85-9; (*Z*,*E*)-$CH_3CH$=$CHCH$=$CHC$-$(O_2C_2H_4)CH_3$, 76251-86-0; (*E*)-P*$CH(CH_3)CH$=$CHCH_2C(O_2C_2H_4)$-$CH_3$, 76281-98-6; (*E*)-P*$CH_2C(C_2H_5)$=$CHCH_2CH(OCH_3)_2$, 76251-87-1; (*E*)-P*$CH(CH_3)C(CH_3)$=$CHCH_2CH(OCH_3)_2$, 76251-88-2; (*E*)-$(CH_3)_2C$=$C(CH_3)CH$=$CHCH(OCH_3)_2$, 76251-89-3; (*E*)-$CH_2$=$C(C_2H_5)CH$=$CHCHO$, 76251-90-6; (*E*,*E*)-$CH_3CH$=$CHCH$=$C$-$(CH_3)CHO$, 54716-17-5; (*E*,*E*)-$CH_3CH$=$CHCH$=$CHCOCH_3$, 18402-90-9; (*E*,*E*)-$CH_3CH$=$C(CH_3)CH$=$CHCHO$, 76251-91-7; (*E*,*Z*)-$CH_3CH$=$C(CH_3)CH$=$CHCHO$, 76251-92-8; (*E*)-$(CH_3)_2C$=$C(CH_3)$-$CH$=$CHCHO$, 76251-93-9; (*E*,*E*)-$CH_3O_2CCH$=$CHCH$=$C(CH_3)CH$-$(OCH_3)_2$, 76232-30-9; (*Z*,*E*)-$CH_3CH$=$CHCH$=$CHCHO$, 54716-12-0; (*E*)-$MC(CH_3)_2C(CH_3)$=$CHCH_2CH(OCH_3)_2$, 76251-94-0; (*E*)-P*$CH$-$(CH_3)CH_2CH$=$C(CH_3)CHO$, 76251-95-1; *n*-$C_4H_9CH(P^*)CH$=$CHCH(CH_3)CH(OCH_3)_2$, 76251-96-2; (*E*,*E*)-$CH_3CH$=$CHCH$=$CHC(O_2C_2H_4)CH_3$, 76251-97-3; (*E*)-$CH_3CH$=$CHC(=CH_2)CH_2CH$-$(OCH_3)_2$, 76251-98-4; 2,5-dimethyl-2-cyclopentenone, 4041-11-6; methacrolein, 78-85-3; trimethyl orthoformate, 149-73-5; 1-hexyne, 693-02-7; 2-methyl-2-butene, 513-35-9; (*E*)-3-bromopropenal dimethyl acetal, 76251-99-5; (*Z*)-3-bromopropenal dimethyl acetal,

76252-00-1; 3-bromo-2-propen-1-ol, 37675-33-5; (*E*)-3-bromo-2-methylpropenal dimethyl acetal, 76232-48-9; 2,3-dibromo-2-methylpropanal dimethyl acetal, 76252-01-2; (*Z*)-3-bromo-2-methylpropenal dimethyl acetal, 76252-02-3; 3-chloro-2-butanone, 4091-39-8; ethylene glycol, 107-21-1; 3-chloro-2-butanone ethylene ketal, 40609-93-6; 2-methyl-2,4-hexadienal dimethyl acetal, 76252-03-4; (*Z,E*)-2-methyl-2,4-hexadienal, 54716-14-2; 3-methyl-2,4-hexadienal dimethyl acetal, 76252-04-5; 3-methyl-2,4-hexadienal, 59502-64-6.

**Supplementary Material Available:** Table III containing the physical properties, NMR spectral data, and molecular weights of the products prepared (9 pages). Ordering formation is given on any current masthead page.

# Palladium-Catalyzed Synthesis of 2,4-Dienoic Acid Derivatives from Vinylic Halides

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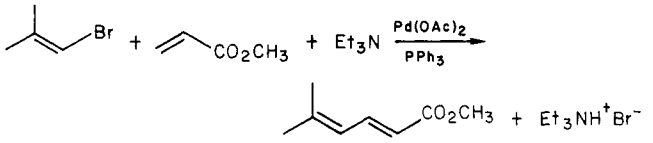
*Received September 17, 1980*

A wide variety of vinylic bromides and iodides have been coupled with acrylic, methacrylic, crotonic, and maleic esters and in some cases with the free acids, nitriles, and amides. In general, good yields of the 2,4-dienoic acid derivatives were obtained. The stereochemistry of the products was determined and the factors influencing the stereoselectivity of the reaction were studied.

Esters of 2,4-dienoic acids have been shown to be easily formed by the palladium-catalyzed reaction of 1-iodo- and 1-bromo-1-hexene, 1-bromo-2-methyl-1-propene, and methyl 3-bromo-2-methylacrylate with methyl acrylate in the presence of triethylamine.[1] Vinyl iodide and 2-

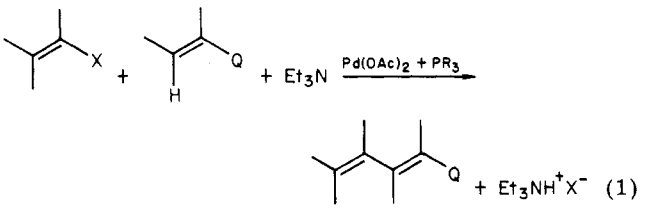



bromopropene in the reaction gave only Diels–Alder adducts of the dienoate products with methyl acrylate. Since the general reaction could be of significant synthetic value, we have investigated it in more detail with respect to the influence of substituents in the reactants on the rates, yields, and the stereochemistry of the products. We have also included examples of reactions of acrylonitrile, acrylamide, and methacrylamide which were not investigated previously.

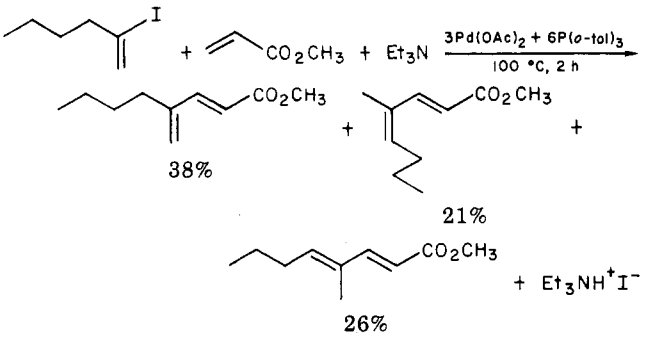
## Results and Discussion

A variety of vinylic halides were allowed to react with acrylic acid, methyl acrylate, acrylonitrile, acrylamide, (*E*)-crotonic acid, (*E*)-methyl crotonate, methyl methacrylate, and methacrylamide in the presence of triethylamine and (usually) a palladium acetate–tri-*o*-tolylphosphine catalyst. The *o*-tolyl catalyst usually gives higher reaction rates than a triphenylphosphine catalyst. The results are summarized in Table I. The reactions carried out are listed with the unsaturated acids first, followed by esters, nitriles, and amides. Within each of these groups reactants are arranged in order of increasing numbers of carbon atoms present. Esters were used most frequently because of their availability and the ease of analysis of their reaction products by GLC.

In general, the reactions proceeded as found in our previous work to give good yields of conjugated dienoic acids or their derivatives according to eq 1. Exceptions




to this general reaction occurred with the least hindered reactants, (*E*)-2-bromo-2-butene, 2-bromo-1-hexene, and 1-bromocyclohexene, in their reactions with methyl acrylate, where major or exclusive products were Diels–Alder adducts of the expected dienoate esters with methyl acrylate. Rearranged dienoate esters were major products in the reaction of 2-iodo-1-hexene with methyl acrylate.




**Reactivity.** The rates of the reactions generally decrease as the number and/or the size of the alkyl substituents on either of the double bonds of the reactants increase. The electron-withdrawing carbomethoxyl group in (*E*)-methyl 3-bromo-2-methylpropenoate, on the other hand, significantly increases the reactivity of the halide in the reaction relative to 1-bromo-1-propene. Unfortunately, 3-bromoacrylic acid and its esters, nitrile, or amides cannot be used in this reaction, presumably because of facile dehydrohalogenation and polymerization of the resulting acetylene under the reaction conditions.

Acrylic acid and its ester and amide all have a similar reactivity but acrylonitrile is less reactive. Methyl methacrylate and methacrylamide are much less reactive than

(1) H. A. Dieck and R. F. Heck, *J. Org. Chem.*, **40**, 1083 (1975).

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