h at room temperature (chromatography conditions of trioxide **3a**) led to recovery of the trioxide **3a** as confirmed by ^{1}H NMR.

Thermal Stability of Syn,Anti Trioxide 3b. Heating a solution of 0.1 mmol of **3b** in 1 mL of toluene in a sealed tube for 1 h at 190 °C (thermolysis conditions of *anti*-**2b** → **3b**) gave unchanged **3b** as confirmed by ^{1}H NMR.

Silica Gel Stability of Syn,Anti Trioxide 3b. Stirring a solution of 0.1 mmol of **3b** in 10 mL of CH_2Cl_2 in the presence of silica gel for 3 h at room temperature (chromatography conditions of trioxide **3b**) afforded **3b** unchanged as confirmed by ^{1}H NMR.

Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant CHE-78-12621), and the National Institutes of Health (Grants GM-00142-04 and RR-8102-07) for financial support.

References and Notes

(1) Part 99 in the Cyclic Peroxides Series.
(2) NIH Career Development Awardee, 1975-1980.
(3) (a) Boche, J.; Runquist, O. *J. Org. Chem.* **1968**, *33*, 4285. (b) Maheshwari, K. K.; De Mayo, P.; Wiegand, D. *Can. J. Chem.* **1970**, *48*, 3265.
(4) Adam, W. *Angew. Chem.* **1974**, *86*, 683.
(5) Vogel, E.; Altenbach, H. J.; Sommerfeld, C. D. *Angew. Chem.* **1972**, *84*, 986.
(6) (a) Forster, C. H.; Berchthold, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 7939. (b) *J. Org. Chem.* **1975**, *40*, 3743.
(7) (a) Adam, W.; Balci, M. *Angew. Chem.* **1978**, *90*, 1014. (b) Asao, T.; Yaglhara, M.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2131. (c) Mori, H.; Takeshita, H. *Chem. Lett.* **1978**, 395.
(8) Takeshita, H.; Kanamori, H.; Hatsui, T. *Tetrahedron Lett.* **1973**, 3139.
(9) Adam, W.; Balci, M. Gordon Research Conference, Holderness School, June 1979.
(10) Prinzbach, H.; Rücker, C. *Angew. Chem.* **1976**, *88*, 611.
(11) Adam, W.; Balci, M. *J. Am. Chem. Soc.* **1979**, *101*, 7537, 7542.
(12) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.
(13) Kornblum, M.; de la Mare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 980.
(14) Houben-Weyl. "Methoden der Organischen Chemie," Vol. 7/2c; Georg Thieme Verlag: Stuttgart, 1977; p 2180.
(15) Schiess, P.; Wisson, M. *Helv. Chim. Acta* **1974**, *57*, 980.

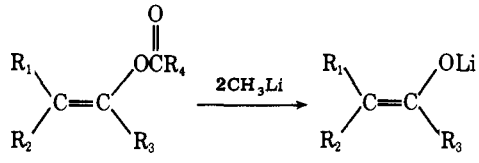
Mercury in Organic Chemistry. 17. A Convenient Stereospecific Synthesis of Enol Esters from Vinylmercurials

R. C. Larock,*[1] K. Oertle, and K. M. Beatty

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received July 23, 1979*

Abstract: The room temperature reaction of vinylmercurials, mercury carboxylates, and a catalytic amount of palladium acetate provides a novel stereospecific route to a variety of enol carboxylates. The mercuration and subsequent palladium-catalyzed esterification of internal acetylenes afford trans ene diacetates in a convenient one-pot procedure. Lead tetraacetate also reacts with vinylmercurials to afford enol acetates.

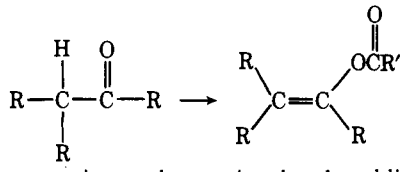
Enol esters have proven to be extremely valuable intermediates in organic synthesis. Epoxidation[2-11] or halogenation[12-20] of these compounds affords α-acyloxy- or α-halocarbonyl compounds. Photolysis,[21] reduction,[22] acylation, and rearrangement[23-36] all result in carbon-carbon bond formation. One especially important application of enol esters lies in their facile conversion to regio- and stereospecific lithium enolates upon treatment with methyllithium (eq 1).[37-43] Very



(1)

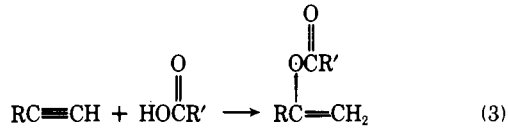
few general methods are available for the stereospecific generation of such enolates in spite of their widespread utility in organic synthesis.

Unfortunately, relatively few methods are presently available for the synthesis of enol esters. The most widely practiced technique involves the treatment of aldehydes or ketones under either acid or basic conditions with the appropriate acid anhydride or chloride (eq 2).[2,7,12,13,16,17,30,37-39,42-61] Other major

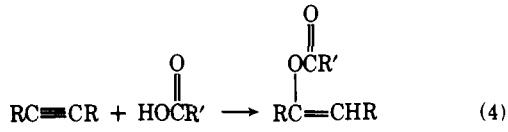


(2)

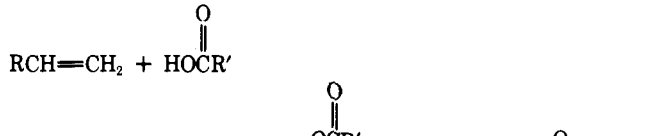
methods for preparing enol esters involve the addition of carboxylic acids to alkynes[62-81] (eq 3 and 4) and the palladium-promoted acetoxylation of olefins (eq 5 and 6).[82,83] Although limited in scope, vinyl acetate can be arylated using arenes,[84-86] triarylphosphines,[87] or arylmercurials[88-90] and palladium catalysts (eq 7).



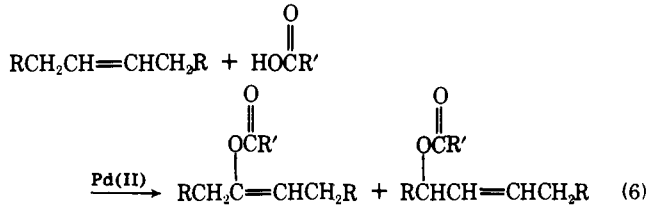
(3)



(4)



(5)



(6)

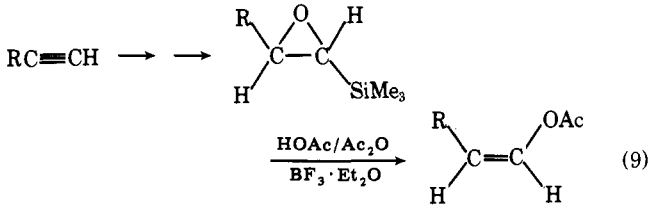
0002-7863/80/1502-1966$01.00/0

$$H_2C{=}CHOAc \rightarrow ArCH{=}CHOAc \quad (7)$$

Finally, the thermal decomposition of vinylmercury carboxylates also results in enol ester formation (eq 8).[91-94] Unfortunately, none of these methods affords enol esters of high regio- and stereospecificity, and low yields are not uncommon.

$$(RCH{=}CH)_2Hg + HOCR' \longrightarrow (RCH{=}CHHgOCR') \xrightarrow{\Delta} RCH{=}CHOCR' + Hg \quad (8)$$

Prior to the present work, only one method has been reported for the stereospecific formation of enol esters. This method utilizes the regio- and stereospecific acid-catalyzed ring opening and elimination of α,β-epoxysilanes formed by hydrosilation and epoxidation of terminal acetylenes (eq 9).[95]

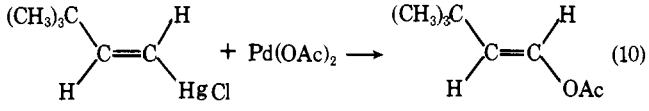


(9)

Unfortunately, no evidence has been provided to indicate whether α,β-epoxysilanes formed from internal acetylenes react in a similar manner.

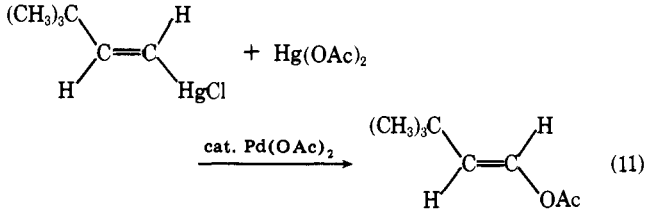
Results and Discussion

Synthesis of Enol Esters. During an examination of the reactions of vinylmercurials and palladium salts,[96,97] a new method for the synthesis of enol esters was discovered which appeared particularly promising. Preliminary studies indicated that *trans*-3,3-dimethyl-1-butenylmercuric chloride reacts with 1 equiv of palladium acetate at room temperature in tetrahydrofuran (THF) to form *trans*-1-acetoxy-3,3-dimethyl-1-butene in 25-30% yield (eq 10). It was subsequently observed



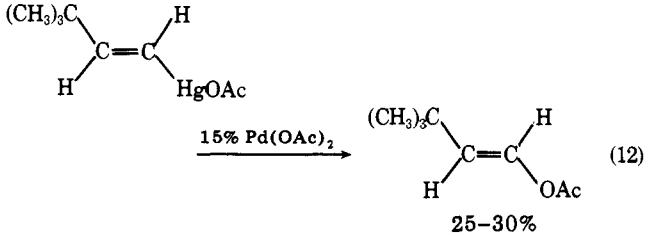
(10)

that this reaction could be made catalytic in palladium and the yield vastly improved if mercuric acetate was added in equivalent amounts (eq 11). Although vinylmercuric acetates are



(11)

known to decompose to enol acetates,[91-94] relatively high temperatures are required and cis-trans mixtures result. In the presence of catalytic amounts of palladium acetate this same reaction proceeds catalytically and stereospecifically at room temperature, but the yields are still lower than when the vinylmercuric chloride and mercuric acetate are used (eq 12).



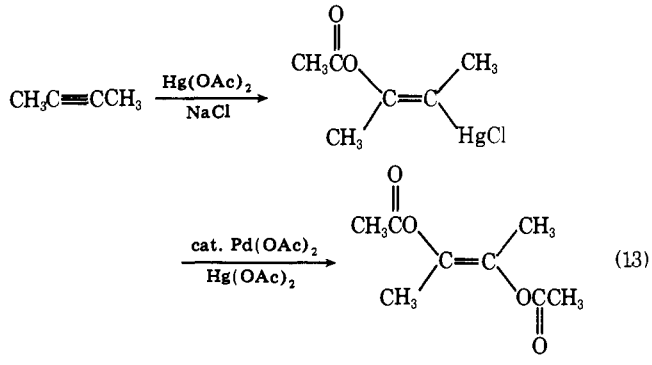
(12)

25-30%

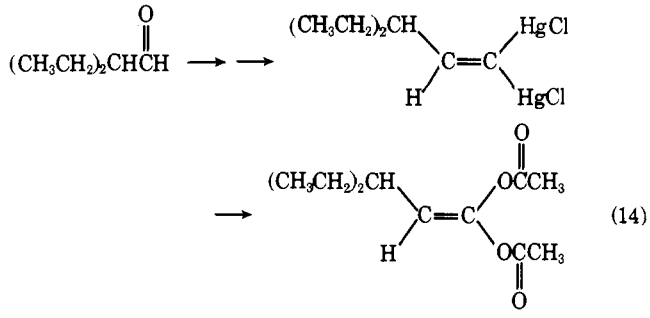
Our reaction proceeds smoothly at room temperature and affords high yields of the corresponding enol acetate in greater than 99% stereospecificity. In the absence of palladium acetate, the vinylmercuric chloride and mercuric acetate give no vinyl acetate product.

These results prompted a closer study of the reaction of vinylmercuric chlorides with mercury and palladium carboxylates. *trans*-3,3-Dimethyl-1-butenylmercuric chloride was chosen as a model system. Instead of mercuric carboxylates, less toxic and cheaper copper salts were also examined as possible reoxidants for the palladium in these reactions. However, copper acetate, copper acetate plus sodium acetate, and copper chloride plus sodium acetate all gave only very low yields (<20%) of enol acetate. It would appear that the mercury salts serve as more than a simple reoxidant for palladium, and are intimately involved in the mechanism of enol ester formation. Next, the most suitable quantity of $Pd(OAc)_2$ for this system was determined. Although 0.5% catalyst gave the same yields as 1 and 5% (77% yield), concentrations of less than 1% $Pd(OAc)_2$ were not used in subsequent work in order to facilitate accurate weighings. Under these conditions 24-48 h reaction time was required for the reaction to reach completion.

The scope of this new stereospecific enol ester synthesis was then examined using the optimum reaction conditions with a wide assortment of vinylmercurials. The results are summarized in Table I. Most reactions were complete in 24-48 h. By increasing the amount of catalyst, the reaction rates and yields increased in some cases. Aryl-substituted vinylmercuric chlorides seem to react faster and produce higher yields of enol esters than the alkyl-substituted compounds. No major difficulties were encountered in using more highly hindered di- and trisubstituted vinylmercurials. Especially encouraging was the ability to prepare ene diacetates from readily available β-acetoxyvinylmercurials[98-104] (eq 13) and dimercurials[105] (eq 14).



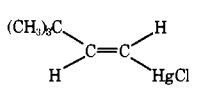
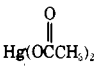
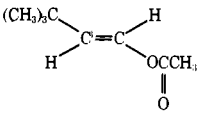
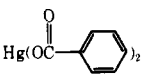
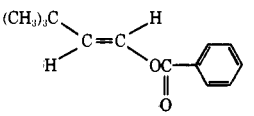
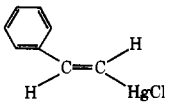
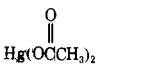
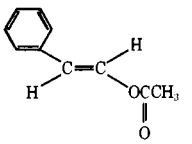
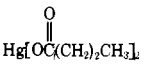
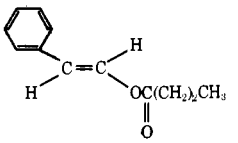
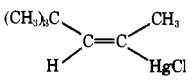
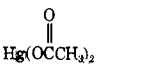
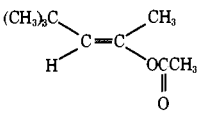
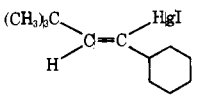
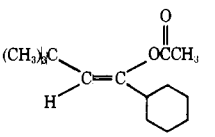
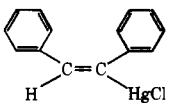
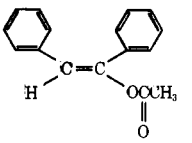
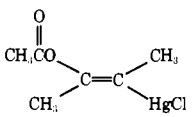
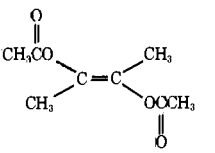
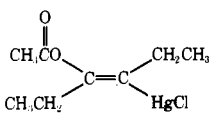
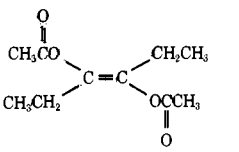
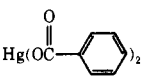
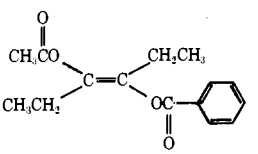
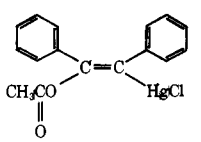
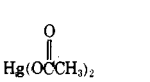
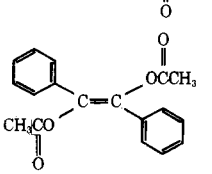
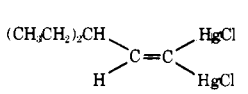
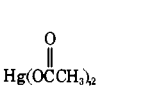
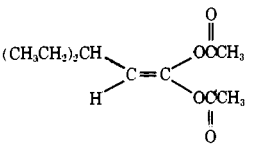
(13)



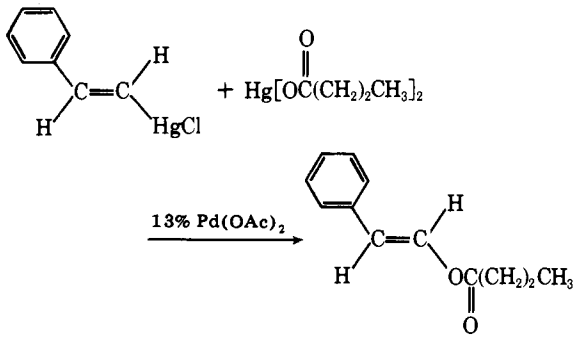
(14)

One can also readily prepare enol esters of other carboxylic acids. For example, using *trans*-styrylmercuric chloride, mercuric butyrate, and 13% palladium acetate, the corresponding styryl butyrate ester was obtained in 72% yield (eq 15). In similar fashion *trans*-1-benzoyloxy-3,3-dimethyl-1-butene was prepared using mercuric benzoate (eq 16). In this case approximately statistical amounts of the corresponding

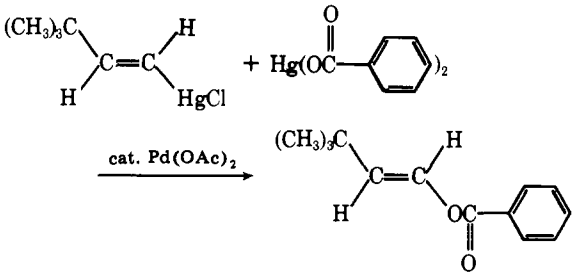
Table I. Synthesis of Enol Esters

entry	vinylmercurial	mercuric carboxylate	enol ester	% $Pd(OAc)_2$ catalyst	time, h	% yield[a]
1				0.5	48	77
				1	12	70
					24	75
					48	77 (42)
				5	24	77
				5	48	45[b]
				16	48	(50)
				22	48	71[c]
2				1	48	100 (72)
				4	48	50 (47)
				13	48	72
3				1	48	77 (58)
				5	24	97
4				15	48	(68)
5				1	48	(87)
6				1	96	36
				5	48	60 (35)
				10	48	60
7				10	48	80
				18	48	86
				17	48	(31)
8				100	64 (70 °C)	26
9				6	48	(89)

[a] Yield determined by gas-liquid phase chromatography (GLC) using an internal standard; isolated yield in parentheses. [b] ~4% yield of *trans*-1-acetoxy-3,3-dimethyl-1-butene. [c] ~15% yield of *trans*-1-acetoxy-3,3-dimethyl-1-butene.

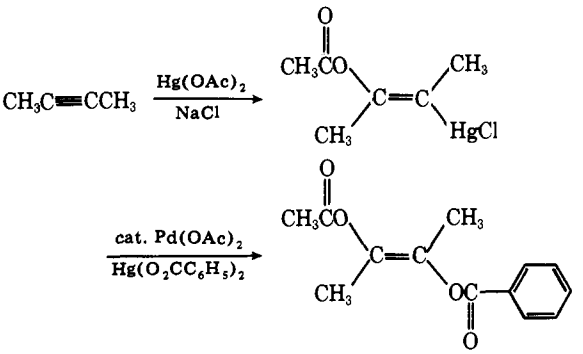


(15)



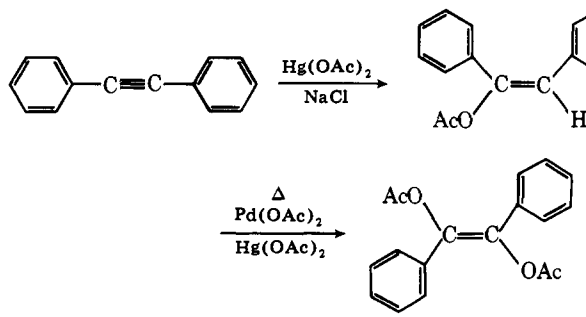
(16)

enol acetate were also observed. In the synthesis of both the benzoate and butyrate esters larger amounts of palladium acetate catalyst were required in order to obtain high yields of the desired esters. Finally, it is noteworthy that mixed ene diesters can be prepared via mercuration-esterification of internal acetylenes (eq 17).



(17)

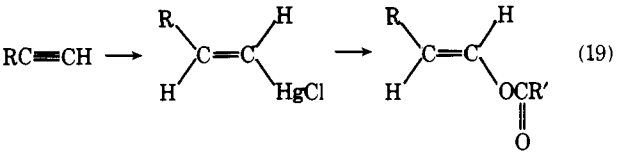
The esterification reaction failed in two instances. The cis addition compound of diphenylacetylene and mercuric acetate[98,100,103,104] gave only very low yields of ene diacetate even when 1 full equiv of palladium acetate was used and elevated temperatures were employed (eq 18). Furthermore, the



(18)

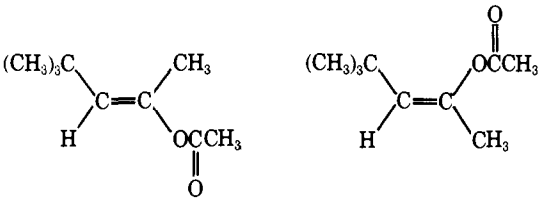
product that was isolated was observed to be the pure trans isomer as determined by comparison with an authentic sample prepared by an alternate route. All attempts to prepare enol esters of trifluoroacetic acid also failed. Four different vinylmercurials were examined in this reaction without success.

In view of the very limited number of stereospecific procedures for the synthesis of enol esters, we have closely examined the stereochemistry of the products formed by our procedure. With the one exception noted above, the reaction appears to proceed with complete retention of configuration. In the reactions of the vinylmercurials derived from terminal acetylenes via hydroboration-mercuration (entries 1 and 2),[106,107] pure trans products were established by analysis of their NMR spectra (eq 19). For disubstituted vinylmercurials, careful



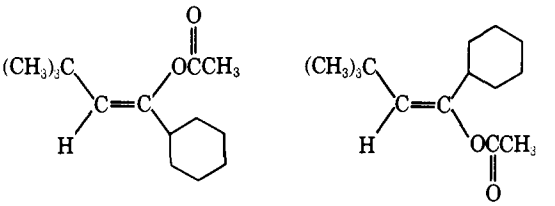
(19)

examination of the mercury-hydrogen coupling constants of the vinylmercurials[108,109] and calculation of the anticipated chemicals shifts[110] of the enol acetate products established the stereochemical configurations reported in Table I. For example, hydroboration-mercuration of 4,4-dimethyl-2-pentyne affords the *E* vinylmercurial shown (entry 3),[107] as evidenced by the cis mercury-hydrogen coupling constant of $J = 362$ Hz. Similarly, the mercury-hydrogen coupling constant of $J = 584$ Hz for (*Z*)-1-cyclohexyl-3,3-dimethyl-1-iodomercuri-1-butene (entry 4), prepared by accidental modification of a literature procedure, clearly establishes the *Z* configuration of this vinylmercurial. Each vinylmercurial gave only one isomerically pure product as determined by gas chromatography, thin layer chromatography, and nuclear magnetic resonance spectroscopy. Comparison of the calculated[110] and observed vinyl hydrogen NMR chemical shifts for each of the anticipated enol ester products indicated that these reactions proceed with complete retention of configuration.



calculated: δ 5.03
found: δ 5.04

δ 4.79

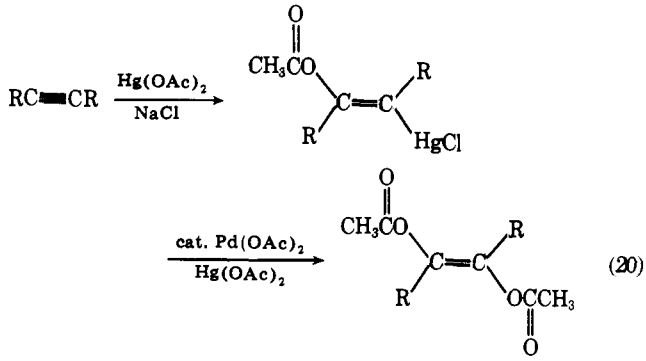


calculated: δ 4.72
found: δ 4.75

δ 5.02

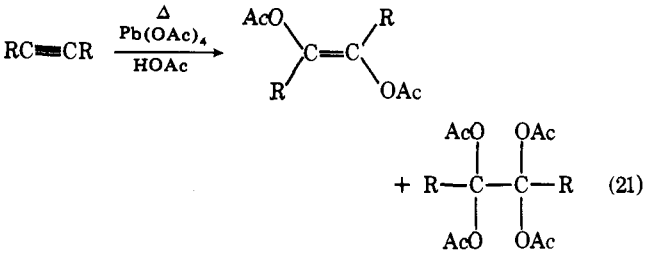
The esterification of *cis*-stilbenylmercuric chloride (entry 5) also proceeds with strict retention of configuration as established by comparison with an authentic sample of the corresponding enol acetate. Analysis of the diesters derived from 2-butyne and 3-hexyne (entries 6 and 7) by gas chromatography, thin layer chromatography, and NMR spectroscopy indicates that only one isomer is formed. In these cases the product of complete retention is presumed, though not firmly established. The complete retention of configuration observed in all but one reaction so far examined suggests that this esterification reaction affords a valuable new tool for the determination of the configuration of vinylmercurials and provides a very useful new stereospecific enol ester synthesis.

The ease with which 2-butyne and 3-hexyne are transformed into the corresponding trans ene diacetates via mercuration-esterification (eq 20) suggested that this reaction sequence might be consolidated to provide a convenient direct synthesis of ene diacetates. At present these compounds are available from the reaction of alkynes and lead tetraacetate,[111] but the procedure affords only low yields and the products are fre-



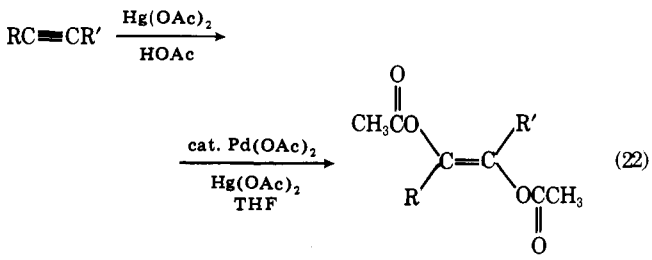
(20)

quently contaminated by the corresponding tetraacetates (eq 21). As anticipated we have been able to effect the desired



(21)

transformation directly from internal acetylenes using mercuric acetate in acetic acid, followed by palladium acetate and mercuric acetate in THF (eq 22). The results are summarized

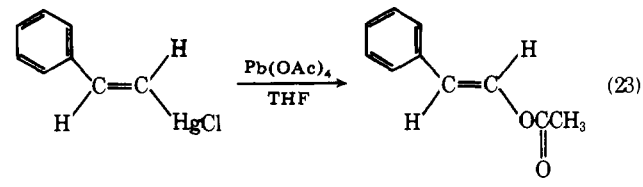


(22)

in Table II. Attempts to effect this transformation completely in acetic acid gave only low yields of the desired diacetates. Better yields were also obtained if only 1 equiv of mercuric acetate was used in the mercuration step, and the second equiv added during the esterification step. A close examination of the yields in Table II indicates that the yields of diacetate drop off drastically as steric hindrance about the triple bond increases. The ene diacetates obtained from 3-hexyne and diphenylacetylene were identical in all respects with those obtained earlier from the corresponding isolated β-acetoxyvinylmercurials. Since the mercuration of 1-phenyl-1-propyne has been reported to give a trans addition compound,[101,102] we assume that the isolated ene diacetate is also the trans compound. The stereochemistry of the other two ene diacetates is assumed to be trans, though not proven so. This approach to ene diesters is obviously restricted to relatively unhindered acetylenes in which case the procedure is simple and the yields are high. All attempts to prepare ene triacetates from terminal acetylenes were unsuccessful.

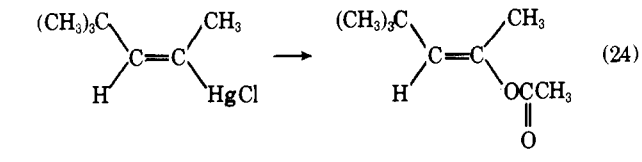
We have also briefly examined an alternate route to simple enol esters from vinylmercurials. We have discovered that vinylmercurials will also readily react at room temperature with lead tetraacetate in THF (eq 23-25). Unfortunately, the reaction does not appear to offer any advantages over the palladium-catalyzed procedure. The yields with more highly substituted vinylmercurials are lower and the reaction is not as clean. No improvement in yield was observed with the adduct derived from diphenylacetylene either.

The palladium procedure has also been examined on a variety of other organomercurials to see if it might provide a general method for the stereospecific replacement of mercury



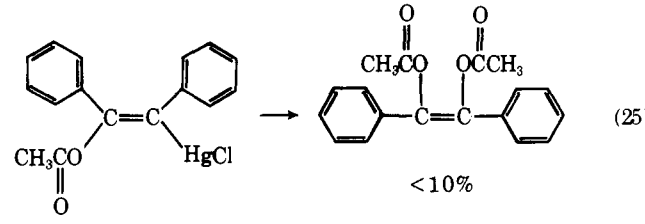
(23)

80% isolated



(24)

< 37%



(25)

<10%

by an acetate group. *n*-Butylmercuric chloride gave neither *n*-butyl acetate nor octane. Not surprisingly, phenylmercuric chloride gave some biphenyl.[112-115] Similarly, dialkynylmercurials gave low yields of the corresponding diyne (eq 26).

$$(RC{\equiv}C)_2Hg \rightarrow RC{\equiv}CC{\equiv}CR \qquad (26)$$

Finally, although we have no direct evidence to bear on the subject, it is perhaps worth commenting on possible mechanisms for these palladium-catalyzed esterification reactions. Two possible mechanisms come readily to mind. One involves the generation of a vinylpalladium acetate which then undergoes stereospecific reductive elimination to the corresponding enol ester and palladium metal, which is subsequently reoxidized to palladium(II) by the mercuric acetate present (Scheme I). The ability of vinylmercuric carboxylates to decompose to the corresponding enol esters[91-94] lends credence to this palladium analogy, as do numerous previous literature reports on the oxidation of alkyl-,[116-119] aryl-,[120-128] and allylpalladium[129,130] acetates to the corresponding organic acetates. It is also possible that the mercuric acetate actually oxidizes the vinylpalladium(II) acetate to a palladium(IV) species, which only then eliminates the enol acetate. A stereospecific addition-elimination mechanism may also be envisioned (Scheme II). Quite obviously, further mechanistic work is desirable.

One thing is clear, however. The above procedure provides a much-needed convenient new procedure for the stereospecific synthesis of enol esters. In combination with the hydroboration-mercuration of acetylenes, it affords a novel procedure

Scheme I

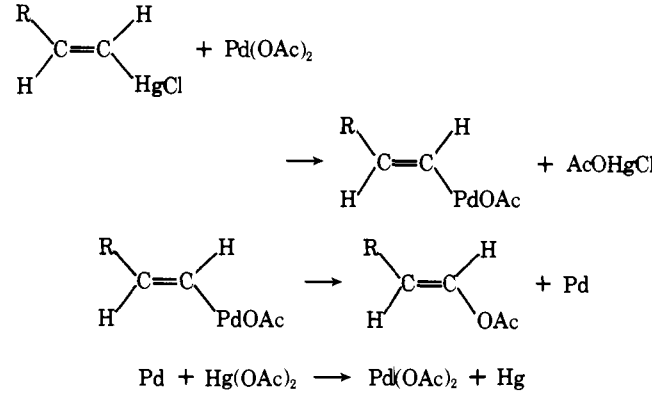
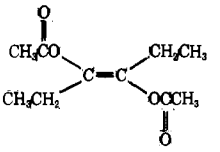
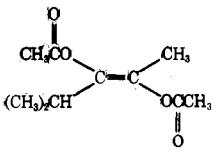
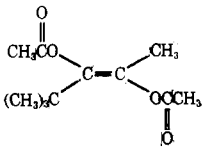
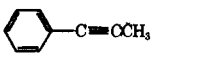
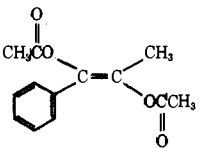
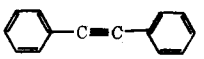
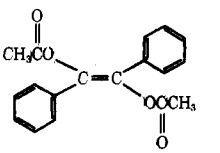
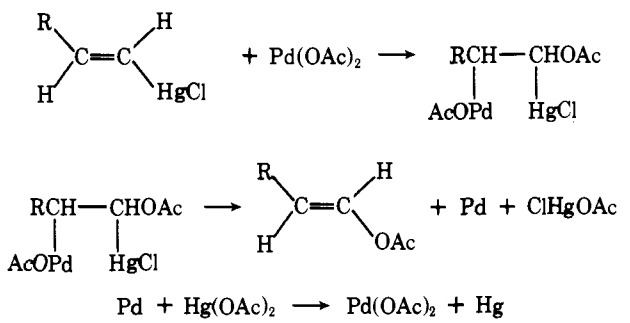


Table II. Direct Synthesis of Ene Diacetates

entry	acetylene	product	mercuration conditions	% $Pd(OAc)_2$	% yield[a]
1	$CH_3CH_2C{\equiv}CCH_2CH_3$		20 h, 0 °C 3 h, 25 °C	12	80-86
2	$(CH_3)_2CHC{\equiv}CCH_3$		24 h, 25 °C	15	40-45
3	$(CH_3)_3CC{\equiv}CCH_3$		17 h, 25 °C	15	7
4			70 h, 25 °C	16 18	(85) 69
5			2-3 h, 95 °C	10-17	(5-8)

[a] Isolated yield; GLC yield in parentheses.

Scheme II



for the anti-Markownikoff esterification of terminal acetylenes, which nicely complements present methods for the conversion of acetylenes to enol esters.

Experimental Section

Equipment. All infrared spectra were obtained on a Beckman IR 4250 spectrophotometer. ^1H NMR spectra were obtained on Varian A-60 and HA-100 instruments. Mass spectra were recorded on an AEI MS 902 and a Finnegan 4023 GC/MS combination. A Varian 920 gas chromatograph with a thermal conductivity detector was used for all GLC analyses. All GLC yields were determined by the use of hydrocarbon internal standards and appropriate correction factors calculated from authentic samples.

Reagents. All chemicals were used directly as obtained commercially unless otherwise noted. THF was distilled from calcium hydride under nitrogen. The following reagents were used without prior purification: 3-hexyne (Farchan), 4-methyl-2-pentyne (Farchan), 4,4-dimethyl-2-pentyne (Farchan), 1-phenyl-1-propyne (Farchan), diphenylacetylene (Eastman), acetic acid (Fisher), mercuric acetate (Fisher), and palladium acetate (Matthey Bishop). Mercuric trifluoroacetate,[132] mercuric butyrate,[133] and anhydrous mercuric benzoate[133] were prepared according to literature procedures.

The majority of the vinylmercurials were prepared by published hydroboration-mercuration procedures.[106,107] 1,1-Bis(chloromercuri)-3-ethyl-1-pentene was prepared from the corresponding diboron compound.[105] *trans*-2-Acetoxy-3-chloromercuri-2-butene[98-100] and *cis*-1-acetoxy-2-chloromercuri-1,2-diphenylethylene[98,100,103,104] were prepared according to literature procedures. *trans*-3-Acetoxy-4-chloromercuri-3-hexene was prepared similarly: 73% yield; mp 64.5-65.5 °C; ^1H NMR ($DCCl_3$) δ 1.03 (3 H, t, J = 7 Hz, CH_3), 1.10 (3 H, t, J = 7 Hz, CH_3), 2.16 (3 H, s, O_2CCH_3), 2.0-2.55 (4 H, m, CH_2); IR (max) ($HCCl_3$) 2950, 2920, 2860, 1750, 1650, 1455, 1370, 1160, 970 cm^{-1}. Anal. ($C_8H_{13}ClHgO_2$) C, H, Cl, Hg.

(*Z*)-1-Cyclohexyl-3,3-dimethyl-1-iodomercuri-1-butene was prepared by accidental modification of a literature procedure.[134] To 58 mmol of BH_3 in THF (miscalculation) was added at 0 °C 148 mmol of cyclohexene. After stirring for 10 h at room temperature, the slurry was cooled to 0 °C and 15.1 g (72.6 mmol) of 3,3-dimethyl-1-iodo-1-butyne was added. The clear solution was warmed to room temperature over a period of 2.5 h, then cooled to −78 °C. Over a period of 45 min 42 mL of 1.86 M *tert*-butyllithium in pentane was added dropwise and the solution warmed to room temperature for 30 min. The THF was removed under vacuum. The organoborane residue was extracted with pentane which was subsequently replaced by 30 mL of THF and the solution cooled to 0 °C. Mercuric acetate (23 g, 72 mmol) was added and the solution stirred for 1 h at room temperature before the entire reaction mixture was poured into an ice-cold sodium chloride solution. The THF was removed under vacuum and the precipitate collected and washed with water several times. Recrystallization from 95% ethanol afforded 15.3 g of a mixture of the vinylmercuric chloride and iodide. The iodide was the major product and could be obtained pure by chromatography on silica gel: mp 74-75 °C; R_f (hexane) 0.5; ^1H NMR ($DCCl_3$) δ 1.17 (9 H, s, $(CH_3)_3C$), 1.1-2.0 (11 H, br, cyclohexyl), 6.28 (1 H, s, vinyl, J_{Hg-H} = 584 Hz). Anal. ($C_{12}H_{21}HgI$) C, H, Hg.

Palladium-Catalyzed Synthesis of Enol Esters. The following preparation of *trans*-styryl acetate is representative of the procedure used in determining the isolated yields reported in Table I. To determine GLC yields, reactions were run on a 1-mmol scale using an appropriate hydrocarbon internal standard and correction factors calculated from authentic samples.

Mercuric acetate (1.61 g, 5.04 mmol) and 1.70 g (5.04 mmol) of

trans-styrylmercuric chloride[106] were added to 25 mL of THF and the reaction mixture was flushed with nitrogen. Palladium acetate (1%, 0.05 mmol) was added and the reaction mixture stirred for 48 h. Charcoal was added and the solution filtered through Celite which was then washed with 50 mL of ether. The organic solvents were removed under reduced pressure and the residue was extracted several times with ether. The extracts were then washed carefully with saturated sodium chloride solution and 2 M sodium thiosulfate and dried over anhydrous sodium sulfate. Removal of the solvent and distillation afforded 584 mg (72%) of a colorless oil: bp 80°C (0.25 mm) (lit.[89] bp 87–97 °C (1.5 mm), cis-trans mixture); ^{1}H NMR[89] ($DCCl_3$) δ 2.10 (3 H, s, O_2CCH_3), 6.33 (1 H, d, J = 13 Hz, vinyl), 7.25 (5 H, s, C_6H_5), 7.80 (1 H, d, J = 13 Hz, vinyl); IR (max) ($HCCl_3$) 3090, 3030, 1765, 1660, 1365, 1095, 920 cm^{-1}; MS *m/e* 162.067 03 ± 6.5 ppm (calcd for $C_{10}H_{10}O_2$, 162.068 08).

The following enol esters were isolated in identical fashion.

trans-1-Acetoxy-3,3-dimethyl-1-butene: bp 80 °C (50 mm); ^{1}H NMR[135] ($DCCl_3$) δ 1.08 (9 H, s, $(CH_3)_3C$), 2.03 (3 H, s, O_2CCH_3), 5.42 (1 H, d, J = 13 Hz, vinyl), 7.08 (1 H, d, J = 13 Hz, vinyl); IR (max)[135] ($HCCl_3$) 3100, 2960, 2900, 2860, 1745, 1670, 1475, 1370, 935 cm^{-1}; MS *m/e* 142.098 99 ± 2.8 ppm (calcd for $C_8H_{14}O_2$, 142.099 38).

(*E*)-2-Acetoxy-4,4-dimethyl-2-pentene: bp 70 °C (40 mm); ^{1}H NMR (CCl_4) δ 1.14 (9 H, s, $(CH_3)_3C$), 1.90 (3 H, s, CH_3), 1.99 (3 H, s, O_2CCH_3), 5.04 (1 H, s, CH=C); IR (max) (CCl_4) 3020, 2960, 2870, 1755, 1690, 1370, 1115, 960, 895 cm^{-1}; MS *m/e* 156.113 71 ± 7.8 ppm (calcd for $C_9H_{16}O_2$, 156.115 03).

(*E*)-1-Acetoxy-1,2-diphenylethylene: purified by column chromatography, R_f (hexane/ether 1:1) 0.7, and identified as the pure *E* isomer by comparison with an authentic sample synthesized by an alternate procedure;[136] ^{1}H NMR (CCl_4) δ 2.03 (3 H, s, O_2CCH_3), 6.35 (1 H, s, CH=C), 7.0–7.45 (10 H, m, C_6H_5); IR (max) (CCl_4) 3080, 3060, 3020, 1770, 1665, 1445, 1365, 1205, 1180, 1050, 1025, 925 cm^{-1}; MS *m/e* 238.100 62 ± 5.2 ppm (calcd for $C_{16}H_{14}O_2$, 238.099 38).

(*Z*)-1-Acetoxy-1-cyclohexyl-3,3-dimethyl-1-butene: bp 60 °C (0.03 mm); ^{1}H NMR ($DCCl_3$) δ 1.04 (9 H, s, $(CH_3)_3C$), 1.0–2.1 (11 H, br m, cyclohexyl), 2.05 (3 H, s, O_2CCH_3), 4.75 (1 H, s, CH=C); IR (max) (CCl_4) 3040, 2940, 2860, 1760, 1685, 1455, 1370, 1230, 1200, 1020, 955 cm^{-1}; MS *m/e* 224.177 64 ± 0.01 ppm (calcd for $C_{14}H_{24}O_2$, 224.177 64); ^{13}C NMR ($DCCl_3$) δ 21.15, 26.19, 30.42, 31.39, 33.55, 42.07, 122.00, 151.50, 169.37.

trans-Styryl butyrate: bp 80 °C (0.1 mm); mp 44–45 °C; ^{1}H NMR (CCl_4) δ 1.01 (3 H, t, J = 7 Hz, CH_3), 1.70 (2 H, m, CH_2CH_3), 2.36 (2 H, t, J = 7 Hz, O_2CCH_2), 6.28 (1 H, d, J = 13 Hz, CH=C), 7.23 (5 H, s, C_6H_5), 7.83 (1 H, d, J = 13 Hz, OCH=C); IR (max) (CCl_4) 3080, 3070, 3020, 2960, 2930, 2870, 1755, 1660, 1200, 1145, 1105, 925 cm^{-1}; MS *m/e* 190.099 39 ± 0.5 ppm (calcd for $C_{12}H_{14}O_2$, 190.099 38).

trans-1-Benzoyloxy-3,3-dimethyl-1-butene: bp 80 °C (0.3 mm); ^{1}H NMR (CCl_4) δ 1.13 (9 H, s, $(CH_3)_3C$), 5.57 (1 H, d, J = 13 Hz, CH=C), 7.26 (1 H, d, J = 13 Hz, OCH=C), 7.35–8.15 (5 H, m, C_6H_5); IR (max) (CCl_4) 3090, 2960, 2895, 2860, 1740, 1675, 1605, 1350, 1105, 1055, 1010, 920 cm^{-1}; MS *m/e* 204.114 76 ± 1.4 ppm (calcd for $C_{13}H_{16}O_2$, 204.115 03).

trans-2,3-Diacetoxy-2-butene: bp 60 °C (0.02 mm); mp 54–55 °C; ^{1}H NMR ($DCCl_3$) δ 1.80 (6 H, s, CH_3C=), 2.18 (6 H, s, O_2CCH_3); IR (max) ($HCCl_3$) 3000, 2920, 2850, 1770, 1430, 1370, 1160, 1125, 1010, 945, 860 cm^{-1}; MS *m/e* 172.073 60 ± 0.22 ppm (calcd for $C_8H_{12}O_2$, 172.073 56).

trans-3,4-Diacetoxy-3-hexene: bp 70 °C (0.02 mm); mp 45–47 °C; ^{1}H NMR (CCl_4) δ 0.95 (6 H, t, J = 7.5 Hz, CH_3), 2.08 (6 H, s, O_2CCH_3), 2.10 (4 H, q, J = 7.5 Hz, CH_2); IR (max) (CCl_4) 2980, 2940, 2880, 1770, 1465, 1370, 1195, 1150, 1020, 910, 865 cm^{-1}; MS *m/e* 200.104 810 ± 0.3 ppm (calcd for $C_{10}H_{16}O_4$, 200.104 867); ^{13}C NMR (CCl_4) δ 10.54, 20.56, 21.53, 142.07, 168.78.

(*E*)-3-Acetoxy-4-benzoyloxy-3-hexene: bp 115–120 °C (0.2 mm); ^{1}H NMR ($DCCl_3$) δ 1.00 (3 H, t, J = 7 Hz, CH_3), 1.04 (3 H, t, J = 7 Hz, CH_3), 2.22 (3 H, s, O_2CCH_3), 2.28 (2 H, q, J = 7 Hz, CH_2), 2.35 (2 H, q, J = 7 Hz, CH_2), 7.3–7.7 (3 H, m, aryl), 8.05–8.2 (2 H, m, aryl); IR (max) (CCl_4) 3060, 2980, 2940, 2880, 1760, 1745, 1600, 1455, 1370, 1220, 1155, 1090, 1065, 1050, 1025, 910 cm^{-1}; MS *m/e* 262.120 748 ± 0.89 ppm (calcd for $C_{15}H_{18}O_4$, 262.120 514); ^{13}C NMR ($DCCl_3$) δ 10.67, 20.61, 21.72, 128.56, 129.48, 130.06, 133.51, 142.29, 164.46, 168.88, 221.69, 223.12.

1,1-Diacetoxy-3-ethyl-1-pentene (1.42 mmol of 1,1-bis(chloromercuri)-3-ethyl-1-pentene was used): bp 60 °C (0.2 mm); ^{1}H NMR (CCl_4) δ 0.85–1.15 (6 H, m, CH_3), 1.15–1.9 (5 H, m, CH_2 and CH), 2.12 (3 H, s, O_2CCH_3), 2.14 (3 H, s, O_2CCH_3), 4.57 (1 H, d, J = 10 Hz, CH=C); IR (max) (CCl_4) 3010, 2960, 2920, 2870, 2850, 1785, 1710, 1455, 1425, 1365, 1200, 1185, 1140, 1095, 890 cm^{-1}; MS *m/e* 214.120 49 ± 0.13 ppm (calcd for $C_{11}H_{18}O_4$, 214.120 51).

trans-1,2-Diacetoxy-1,2-diphenylethylene: 100 mg of vinylmercurial employed, reaction run at 70 °C for 44 h, 22% yield by GLC analysis. Gas chromatographic isolation afforded the pure trans isomer, characterized by GLC and TLC comparison with an authentic sample prepared by an alternate procedure.[137]

Lead Tetraacetate Synthesis of Enol Acetates. The following preparation of *trans*-styryl acetate is representative of the procedure used for the synthesis of enol acetates from vinylmercurials and lead tetraacetate. *trans*-Styrylmercuric chloride (0.634 mmol) and lead tetraacetate (0.676 mmol) were added to 3 mL of THF under argon and the mixture was stirred for 48 h. The reaction mixture was taken up in ether and washed with saturated sodium chloride solution, 2 M sodium thiosulfate, and once again with saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the residue distilled to give 82 mg (80%) of *trans*-styryl acetate (bp 80 °C (0.02 mm), lit.[89] bp 87–97 °C (1.5 mm), for a cis-trans mixture).

Direct Synthesis of Ene Diacetates. The following preparation of *trans*-3,4-diacetoxy-3-hexene is representative of the general procedure used for the direct synthesis of ene diacetates from internal acetylenes. 3-Hexyne (830 mg, 10 mmol) was added with cooling to a solution of mercuric acetate (3.19 g, 10 mmol) in 15 mL of acetic acid. The reaction vessel was closed and stirring maintained for 24 h at room temperature. The acetic acid was removed under vacuum and three 10-mL portions of benzene were added and successively evaporated in order to remove all traces of acetic acid. The residue was taken up in 25 mL of THF and mercuric acetate (3.19 g, 10 mmol) and palladium acetate (260 mg, 1.18 mmol) were added. After the mixture was stirred for 48 h at room temperature, charcoal was added and the reaction mixture filtered through Celite. The Celite was washed with ether and the combined organic layers were washed several times with saturated sodium chloride solution and 2 M sodium thiosulfate and dried over anhydrous sodium sulfate. Removal of the solvent and distillation afforded 1.724 g of pure *trans*-3,4-diacetoxy-3-hexene[111] (bp 70 °C (0.02 mm)). All spectra were identical with those obtained earlier from the corresponding vinylmercuric chloride.

The following compounds were obtained in similar fashion.

(*E*)-1,2-Diacetoxy-1-phenyl-1-propene: bp 70 °C (0.2 mm); ^{1}H NMR (CCl_4) δ 1.95 (6 H, s, O_2CCH_3), 2.12 (3 H, s, CH_3), 7.1–7.4 (5 H, m, C_6H_5); IR (max) (CCl_4) 3040, 3000, 2900, 1750, 1420, 1355, 1170, 1090 cm^{-1}; MS *m/e* 234.088 68 ± 2.3 ppm (calcd for $C_{13}H_{14}O_4$, 234.089 22).

(*E*)-2,3-Diacetoxy-4-methyl-2-pentene: bp 55–60 °C (0.1 mm); ^{1}H NMR (CCl_4) δ 0.94 (6 H, d, J = 7 Hz, $C(CH_3)_2$), 1.67 (3 H, s, CH_3), 2.09 (3 H, s, O_2CCH_3), 2.12 (3 H, s, O_2CCH_3), 2.70 (1 H, septet, $CH(CH_3)_2$); IR (max) (CCl_4) 2995, 2950, 2895, 1765, 1375, 1205, 1190, 1150, 1060, 1010, 955, 880; MS *m/e* 200.104 35 ± 2.6 ppm (calcd for $C_{10}H_{16}O_4$, 200.104 86).

(*E*)-2,3-Diacetoxy-4,4-dimethyl-2-pentene: bp 80 °C (0.1 mm); ^{1}H NMR (CCl_4) δ 1.09 (9 H, s, $(CH_3)_3C$), 1.68 (3 H, s, CH_3), 2.09 (6 H, s, O_2CCH_3); IR (max) (CCl_4) 2970, 2920, 2870, 1760, 1480, 1365, 1195, 1180, 1105, 995, 940, 860 cm^{-1}; MS *m/e* 214.121 02 ± 2.4 ppm (calcd for $C_{11}H_{18}O_4$, 214.120 51).

(*E*)-1,2-Diacetoxy-1,2-diphenylethylene: the above procedure was used except that the mercuration was carried out at 95 °C for 3 h and the product collected by gas chromatography. Comparison with authentic samples of the cis and trans isomers prepared by an alternate literature procedure[137] established the trans stereochemistry.

Acknowledgments. The authors gratefully acknowledge the National Institutes of Health (AM-21795, GM-24254) and the A. P. Sloan Foundation for partial support of this research, and the National Science Foundation (CHE 76-80362) for funds used in the purchase of the Finnegan 4023 GC-mass spectrometer used in this work. Special thanks go to Matthey Bishop, Inc., for a generous loan of palladium acetate, and Professor D. Matteson for providing the 1,1-bis(chloromercuri)-3-ethyl-1-pentene.

References and Notes

(1) Alfred P. Sloan Foundation Fellow, 1977–1979.
(2) Mouserron, M.; Trinquier, M. *Bull. Soc. Chim. Fr.* **1947**, 598–605.
(3) Soloway, A. H.; Considine, W. J.; Fukushima, D. K.; Gallagher, T. F. *J. Am. Chem. Soc.* **1954**, *76*, 2941–2943.
(4) Leeds, N. S.; Fukushima, D. K.; Gallagher, T. F. *J. Am. Chem. Soc.* **1954**, *76*, 2943–2948.
(5) Gardner, P. D. *J. Am. Chem. Soc.* **1956**, *78*, 3421–3424.
(6) Shine, H. J.; Hunt, G. E. *J. Am. Chem. Soc.* **1958**, *80*, 2434–2435.
(7) House, H. O.; Thompson, H. W. *J. Org. Chem.* **1961**, *26*, 3729–3734.
(8) Williamson, K. L.; Johnson, W. S. *J. Org. Chem.* **1961**, *26*, 4563–4569.
(9) Draper, A. L.; Heilman, W. J.; Schaefer, W. E.; Shine, H. J.; Shoolery, J. N. *J. Org. Chem.* **1962**, *27*, 2727–2729.
(10) Williamson, K. L.; Coburn, J. I.; Herr, M. F. *J. Org. Chem.* **1967**, *32*, 3934–3937.
(11) Kirk, D. N.; Wiles, J. M. *Chem. Commun.* **1970**, 518–519.
(12) Bedoukian, P. Z. *J. Am. Chem. Soc.* **1944**, *66*, 1325–1327.
(13) Bedoukian, P. Z. *J. Am. Chem. Soc.* **1945**, *67*, 1430–1431.
(14) Bedoukian, P. Z. "Organic Syntheses", Collect. Vol. III; Wiley: New York, 1955; pp 127–129.
(15) Jones, E. R. H.; Wluka, D. J. *J. Chem. Soc.* **1959**, 907–910, 911–915.
(16) Hartshorn, M. P.; Jones, E. R. H. *J. Chem. Soc.* **1962**, 1312–1323.
(17) Hartshorn, M. P.; Wallis, A. F. A. *J. Chem. Soc.* **1962**, 3839–3841.
(18) Hartshorn, M. P.; Wallis, A. F. A. *Tetrahedron* **1965**, *21*, 273–280.
(19) Cambie, R. C.; Hayward, R. C.; Jurlina, J. L.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 126–130.
(20) Rozen, S.; Lerman, O. *J. Am. Chem. Soc.* **1979**, *101*, 2782–2784.
(21) Wexler, A.; Balchunis, R. J.; Swenton J. S. *J. Chem. Soc., Chem. Commun.* **1975**, 601–602.
(22) Schmitt, G.; Warwel, S.; Homminga, E.; Meltzow, W. *Justus Liebigs Ann. Chem.* **1972**, *763*, 75–82.
(23) Young, F. G.; Frostick Jr., F. C.; Sanderson, J. J.; Hauser, C. R. *J. Am. Chem. Soc.* **1950**, *72*, 3635–3642.
(24) Allan, R. J. P.; Forman, R. L.; Ritchie, P. D. *J. Chem. Soc.* **1955**, 2717–2725.
(25) Allan, R. J. P.; McGee, J.; Ritchie, P. D. *J. Chem. Soc.* **1957**, 4700–4708.
(26) Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 593–601.
(27) Yogev, A.; Gorodetsky, M.; Mazur, Y. *J. Am. Chem. Soc.* **1964**, *86*, 5208–5213.
(28) Gorodetsky, M.; Mazur, Y. *J. Am. Chem. Soc.* **1964**, *86*, 5213–5218.
(29) Banks, G. R.; Cohen, D.; Springall, H. D. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 513–514.
(30) Muir, W. M.; Ritchie, P. D.; Lyman, D. J. *J. Org. Chem.* **1966**, *31*, 3790–3793.
(31) Gorodetsky, M.; Mazur, Y. *Tetrahedron* **1966**, *22*, 3607–3615.
(32) Liston, A. J.; Toft, P. *J. Org. Chem.* **1968**, *33*, 3109–3113.
(33) Rothman, E. S.; Moore, G. G.; Speca, A. N. *Tetrahedron Lett.* **1969**, 5205–5206.
(34) Rothman, E. S.; Moore, G. G. *J. Org. Chem.* **1970**, *35*, 2351–2353.
(35) Wasserman, H. H.; Wentland, S. H. *Chem. Commun.* **1970**, 1–2.
(36) Dénes, V. I.; Ciurdaru, G. *Chem. Commun.* **1970**, 510.
(37) House, H. P.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 2502–2512.
(38) House, H. O. *Rec. Chem. Prog.* **1967**, *28*, 99–120.
(39) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1967**, *32*, 1741–1748.
(40) House, H. O.; Tefertiller, B. A.; Olmstead, H. D. *J. Org. Chem.* **1968**, *33*, 935–942.
(41) House, H. O.; Bare, T. M. *J. Org. Chem.* **1968**, *33*, 943–949.
(42) Whitlock Jr., H. W.; Overman, L. E. *J. Org. Chem.* **1969**, *34*, 1962–1963.
(43) House, H. O.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1971**, *36*, 2361–2371.
(44) House, H. O.; Reif, D. J. *J. Am. Chem. Soc.* **1955**, *77*, 6525–6532.
(45) Berkoz, B.; Chavez, E. P.; Djerassi, C. *J. Chem. Soc.* **1962**, 1323–1329.
(46) House, H. O.; Kramar, V. *J. Org. Chem.* **1963**, *28*, 3362–3379.
(47) Favre, H.; Liston, A. J. *Can. J. Chem.* **1964**, *42*, 268–276.
(48) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 1341–1348.
(49) Ferris, J. P.; Wright, B. G.; Crawford, C. C. *J. Org. Chem.* **1965**, *30*, 2367–2371.
(50) Smith, W. B.; Chen, T. K. *J. Org. Chem.* **1965**, *30*, 3095–3099.
(51) Edwards, B. E.; Rao, P. N. *J. Org. Chem.* **1966**, *31*, 324–327.
(52) Liston, A. J. *J. Org. Chem.* **1966**, *31*, 2105–2109.
(53) Liston, A. J.; Howarth, M. *J. Org. Chem.* **1967**, *32*, 1034–1041.
(54) Bellamy, A. J.; Whitham, G. H. *J. Chem. Soc. C* **1967**, 215.
(55) Liston, A. J.; Toft, P. *J. Org. Chem.* **1969**, *34*, 2288–2296.
(56) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336.
(57) Libman, J.; Sprecher, M.; Mazur, Y. *Tetrahedron* **1969**, *25*, 1679–1698.
(58) Libman, J.; Mazur, Y. *Tetrahedron* **1969**, *25*, 1699–1706.
(59) Favre, H.; Liston, A. J. *Can. J. Chem.* **1969**, *47*, 3233–3241.
(60) Toft, P.; Liston, A. J. *Chem. Commun.* **1970**, 111–112.
(61) Cousineau, T. J.; Cook, S. L.; Secrist III, J. A. *Synth. Commun.* **1979**, *9*, 157–163.
(62) Reppe, W. *Justus Liebigs Ann. Chem.* **1956**, *601*, 81–138.
(63) Hudrlik, P. F.; Hudrlik, A. M. *J. Org. Chem.* **1973**, *38*, 4254–4258.
(64) Wiley, R. H. In ref 14, pp 853–856.
(65) Hennion, G. F.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1934**, *56*, 1802–1803.
(66) Hennion, G. F.; Killian, D. B.; Vaughn, T. H.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1934**, *56*, 1130–1132.
(67) Bried, E. A.; Hennion, G. F. *J. Am. Chem. Soc.* **1938**, *60*, 1717–1719.
(68) Bol'shukhin, A. I.; Zhitorchuk, V. L. *Zh. Obshch. Khim.* **1955**, *25*, 1459–1462; *Chem. Abstr.* **1956**, *50*, 4832*c*.
(69) Bol'shukhin, A. I.; Egorov, A. G. *Zh. Obshch. Khim.* **1956**, *26*, 1121–1124; *Chem. Abstr.* **1956**, *50*, 16665*f*.
(70) Egorov, A. G. *Uch. Zap., Leningr. Gos. Pedagog. Inst. im. A. I. Gertsena* **1958**, *179*, 211–234; *Chem. Abstr.* **1961**, *55*, 3421*i*.
(71) Rothman, E. S.; Hecht, S. S.; Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1972**, *37*, 3551–3552.
(72) Henne, A. L.; Schmitz, J. V.; Finnegan, W. G. *J. Am. Chem. Soc.* **1950**, *72*, 4195–4197.
(73) Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 5555–5560.
(74) Lemaire, H.; Lucas, H. J. *J. Am. Chem. Soc.* **1955**, *77*, 939–945.
(75) Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 2124–2131.
(76) Evans, A. G.; Owen, E. D.; Phillips, B. D. *J. Chem. Soc.* **1964**, 5021–5023.
(77) Haas, H. C.; Schuler, N. W.; MacDonald, R. L. *J. Polym. Sci., Part A-1* **1969**, *7*, 3440–3442.
(78) Peterson, P. E.; Bopp, R. J.; Ajo, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 2834–2840.
(79) Peterson, P. E.; Duddey, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 2865–2866.
(80) Peterson, P. E.; Duddey, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4990–4996.
(81) Summerville, R. H.; Schleyer, P. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110–1120.
(82) Kitching, W.; Rappoport, Z.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1966**, *88*, 2054–2055.
(83) Schultz, R. G.; Gross, D. E. *Adv. Chem. Ser.* **1968**, *70*, 97–125.
(84) Reichenbacher, P. H.; Forsythe, T. M. U.S. Patent 3 878 074, 1957; *Chem. Abstr.* **1975**, *83*, 9570g.
(85) Moritani, I. French Patent 1 576 819, 1969; *Chem. Abstr.* **1970**, *72*, 90014w.
(86) Louvar, J. J.; Sparks, A. K. German Patent 2 041 563, 1971; *Chem. Abstr.* **1971**, *75*, 19989z.
(87) Yamane, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Tetrahedron* **1973**, *29*, 955–962.
(88) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5535–5538.
(89) Heck, R. F. *Organomet. Chem. Synth.* **1972**, *1*, 455–462.
(90) Heck, R. F. U.S. Patent 3 705 919, 1972; *Chem. Abstr.* **1973**, *78*, 58627m.
(91) Foster, D. J.; Tobler, E. *J. Org. Chem.* **1962**, *27*, 834–837.
(92) Foster, D. J.; Tobler, E. British Patent 945 177, 1963; *Chem. Abstr.* **1964**, *61*, 687*a*.
(93) Foster, D. J.; Tobler, E. U.S. Patent 3 153 074, 1964; *Chem. Abstr.* **1964**, *61*, 16093*d*.
(94) Sterlin, R. N.; Evplov, B. N.; Knunyants, I. L. *Zh. Vses. Khim. O.-va* **1967**, *12*, 591–593; *Chem. Abstr.* **1968**, *68*, 49706c.
(95) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993–1996.
(96) Larock, R. C. *J. Org. Chem.* **1976**, *41*, 2241–2246.
(97) Larock, R. C.; Riefling, B. *J. Org. Chem.* **1978**, *43*, 1468–1470.
(98) Borisov, A. E.; Vil'chevskaya, V. D.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1953**, *90*, 383–386; *Chem. Abstr.* **1954**, *48*, 4434*f*.
(99) Nesmeyanov, A. N.; Borisov, A. E.; Vil'chevskaya, V. D. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1954**, 1008–1018; *Chem. Abstr.* **1956**, *50*, 171*g*.
(100) Nesmeyanov, A. N.; Borisov, A. E.; Savel'eva, I. S.; Osipova, M. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1961**, 1249–1252; *Chem. Abstr.* **1962**, *56*, 1469*c*.
(101) Uemura, S.; Miyoshi, H.; Sohma, K.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1975**, 548–549.
(102) Spear, R. J.; Jensen, W. A. *Tetrahedron Lett.* **1977**, 4535–4538.
(103) Drefahl, G.; Schaaf, S. *Chem. Ber.* **1957**, *90*, 148–151.
(104) Drefahl, G.; Heublein, G.; Wintzer, A. *Angew. Chem.* **1958**, *70*, 166.
(105) Matteson, D. S.; Tripathy, P. B. *J. Organomet. Chem.* **1974**, *69*, 53–62.
(106) Larock, R. C.; Brown, H. C. *J. Organomet. Chem.* **1972**, *36*, 1–12.
(107) Larock, R. C.; Gupta, S. K.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 4371–4373.
(108) Wells, P. R.; Kitching, W.; Henzell R. F. *Tetrahedron Lett.* **1964**, 1029–1034.
(109) Moy, D.; Emerson, M.; Oliver, J. P. *Inorg. Chem.* **1963**, *2*, 1261–1264.
(110) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1974; p 223.
(111) Jadot, J.; Neuray, M. *Bull. Soc. R. Sci. Liège* **1961**, *30*, 34–51.
(112) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5535–5538, 5546–5548.
(113) Unger, M. O.; Fouty, R. A. *J. Org. Chem.* **1969**, *34*, 18–21.
(114) Kasahara, A.; Izumi, T.; Yodono, M.; Saito, R.; Takeda, T.; Sugawara, T. *Bull Chem. Soc. Jpn.* **1973**, *46*, 1220–1225.
(115) Izumi, T.; Lino, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2251–2252.
(116) Baird, W. C., Jr. *J. Org. Chem.* **1966**, *31*, 2411–2414.
(117) Henry, P. M. *J. Org. Chem.* **1967**, *32*, 2575–2580.
(118) Tamura, M.; Yasui, T. *Kogyo Kagaku Zasshi* **1969**, *72*, 568–571, 578–580, 581–585.
(119) Henry, P. M. *J. Org. Chem.* **1973**, *38*, 1681–1684.
(120) Davidson, J. M.; Triggs, C. *J. Chem. Soc. A* **1968**, 1331–1334.
(121) Tisue, T.; Downs, W. J. *Chem. Commun.* **1969**, 410.
(122) Henry, P. M. *J. Org. Chem.* **1971**, *36*, 1886–1890.
(123) Eberson, L.; Gomez-Gonzalez, L. *Chem. Commun.* **1971**, 263–264.
(124) Eberson, L.; Gomez-Gonzalez, L. *Acta Chem. Scand.* **1973**, *27*, 1162–1174, 1249–1254, 1255–1267.
(125) Arzoumandis, G. G.; Rauch, F. C. *J. Org. Chem.* **1973**, *38*, 4443–4445.
(126) Eberson, L.; Jönsson, L. *Chem. Commun.* **1974**, 885–886.
(127) Eberson, L.; Jönsson, L. *Acta Chem. Scand., Ser. B* **1974**, *28*, 597–

602.
(128) Eberson, L.; Jonsson, E. *Acta Chem. Scand., Ser. B* **1974**, *28*, 771-776.
(129) Takahashi, Y.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913-1916.
(130) Wolfe, S.; Campbell, P. G. C. *J. Am. Chem. Soc.* **1971**, *93*, 1499-1501.
(131) Kitching, W.; Sakakiyama, T.; Rappoport, Z.; Sleezer, P. D. *J. Am. Chem. Soc.* **1972**, *94*, 2329-2335.
(132) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1969**, *91*, 5646-5647.
(133) Mukaiyama, T.; Nambu, H.; Kuwajima, T. *J. Org. Chem.* **1963**, *28*, 917-920.
(134) Campbell, Jr., J. B.; Molander, G. A. *J. Organomet. Chem.* **1978**, *156*, 71-79.
(135) Bock, D. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814-2825.
(136) Noyce, D. S.; Meyers, A. M. *J. Org. Chem.* **1970**, *35*, 2460-2461.
(137) Fieser, L. F. *J. Chem. Educ.* **1954**, *31*, 291-297.

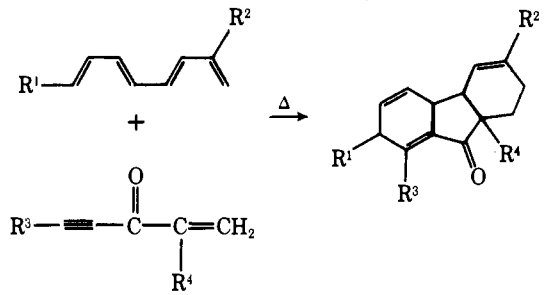
Timed Diels-Alder Reactions

George A. Kraus* and Michael J. Taschner

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received June 25, 1979*

Abstract: In this paper a unique approach to the synthesis of polycyclic ring systems is disclosed. The approach features an intermolecular Diels-Alder reaction followed by an intramolecular Diels-Alder reaction where the regiochemistry of addition is controlled by substituents on the bisdiene and bisdienophile. This methodology has been applied to the synthesis of the fluorenone ring system.

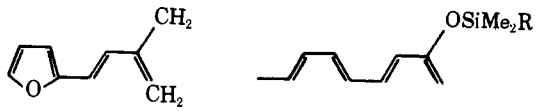
An efficient convergent strategy is vital for the practical synthesis of polycyclic systems. This postulate has motivated the creation of ingenious routes to steroids,[1] vitamins,[2] and alkaloids.[3] We have recently discovered a novel method, the general features of which are depicted below. In this polycy-



cloaddition (termed a "timed Diels-Alder") a tricyclic ring system is formed *regiospecifically* in a *single* reaction. In principle, a number of compounds might be formed. However, one of the diene units in the bisdiene is more reactive than the other unit. The same feature is true for the bisdienophile. Thus, the initial ring is created by cycloaddition of the more reactive diene and dienophile. The second and third rings are formed by the intramolecular cycloaddition of the less reactive diene and dienophile. At present, we have confined our study to the formation of the fluorenone ring system.

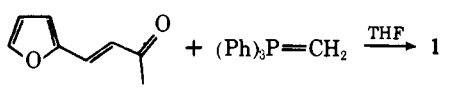
Results and Discussion

Synthesis of Reactants. The bisdienes used in this investigation were compounds **1** and **2**. The preparation of **1** was

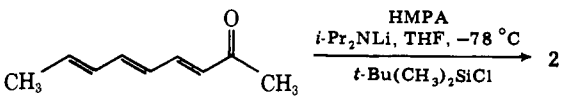


1 **2** (R = CH_3, *t*-Bu)

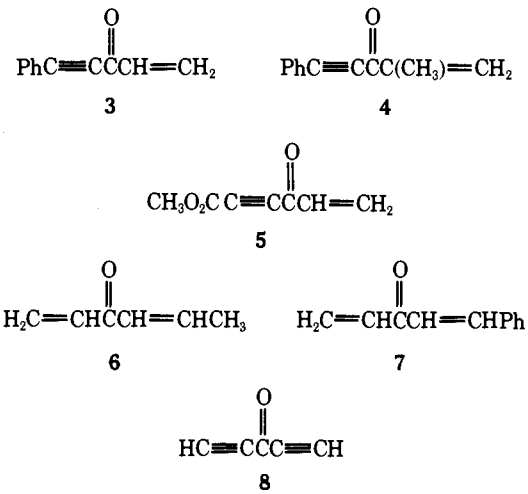
readily accomplished by the use of a Wittig reaction on 4-(2-furyl)-3-buten-2-one.[4] It could be purified by bulb to bulb



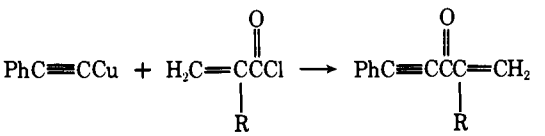
distillation or by filtration through silica gel. Bisdiene **2** could be synthesized by trapping the kinetic anion of 3,5,7-octatrien-2-one[5] with chlorodimethyl-*tert*-butylsilane or chlorotrimethylsilane. Both bisdienes were unstable to prolonged



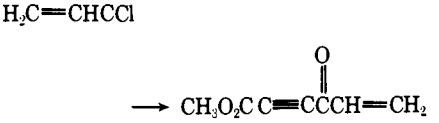
storage but could be stored for days under an inert atmosphere at 0 °C. The array of bisdienophiles employed in this study consisted of enynones **3**, **4**, and **5**, dienones **6** and **7**, and diynone



8. The enynones **3** and **4** were made by the coupling of cuprous



phenylacetylide with the requisite acid chloride according to the method of Normant.[6] Enynone **5** was similarly prepared.



0002-7863/80/1502-1974$01.00/0