ibrated determinations agreed to within the experimental error of ±10%, hence no further calibrations were carried out on the remaining olefins. Calibrations made a significant difference in the ethyl vinyl ether run and the value in Table I is the corrected calibrated value. Relative rates were calculated by means of the given equation[7] and are reported in Table I.

Preparation and Identification of Authentic Adducts. All authentic adducts were prepared by reaction of 1.0–2.0 g (5–10 mmol) of the triflate and 0.8–1.7 g (7–15 mmol) of *t*-BuOK with the appropriate pure olefin at −20 °C for 24–48 h. The reaction mixtures were taken up in pentane, washed once with water, and dried over anhydrous $MgSO_4$, the solvent was distilled off, and the product was collected from the residue by preparative GC and identified by spectral means. Adducts with ethyl vinyl ether, cyclohexene, *cis*- and *trans*-2-butene, cyclooctene, 1-octene, and 2,3-dimethyl-2-butene have been previously prepared and reported.[3-5] The remaining adducts were obtained and characterized as follows.

Norbornylene Adduct. *exo*-3-Isopropylidenetricyclo-$[3.2.1.0^{2,4}]$octane was collected on column A at 75 °C: mass spectrum *m/e* 148 (M^+, 18), 105 (100); IR 1772 cm^{-1} (C=C); NMR (CCl_4) δ 0.77 (m, 2 H, cyclopropyl), 1.12 (bs, 2 H, CH_2), 1.39 (m, 4 H, 2 CH_2), 1.69 (m, 6 H, 2 CH_3), 2.30 (bs, 2 H, 2 CH).

2-Methyl-2-butene Adduct. 2-Isopropylidene-1,1,3-trimethylcyclopropane was collected on column C at 45 °C: mass spectrum *m/e* 124 (M^+, 47), 67 (100); IR 1775 cm^{-1} (C=C); NMR (CCl_4) δ 1.08 (s, 6 H, 2 CH_3), 1.12 (d, *J* = 5.2 Hz, 3 H, CH_3), 1.13 (m, 1 H), 1.74 (s, 6 H, 2 $CH_3C{=}C$).

1,3-Butadiene Adduct. 1-Isopropylidene-2-vinylcyclopropane was collected on column A at 50 °C: mass spectrum *m/e* 108 (M^+, 42), 93 (100); IR 1785 cm^{-1} (C=C); NMR (CCl_4) δ 1.17 (m, 2 H, cyclopropyl), 1.76 (m, 6 H, 2 CH_3), 2.41 (m, 1 H, cyclopropyl), 5.42 (m, 3 H, 3 HC=C).

1-Butene Adduct. 1-Ethyl-2-isopropylidenecyclopropane was collected on column C at 45 °C: mass spectrum *m/e* 110 (M^+, 13), 67 (100); IR 1782 cm^{-1} (C=C); NMR (CCl_4) δ 0.33–1.58 (m, 8 H, 3 cyclopropyl H, CH_3CH_2), 1.76 (bs, 6 H, 2 $CH_3C{=}C$).

Isobutylene Adduct. 1,1-Dimethyl-2-isopropylidenecyclopropane was collected on column A at 40 °C: mass spectrum *m/e* 110 (M^+, 58), 67 (100); IR 1788 cm^{-1} (C=C); NMR (CCl_4) δ 0.80 (m, 2 H), 1.13 (s, 6 H, 2 CH_3), 1.73 (m, 6 H, 2 $CH_3C{=}C$).

Acknowledgments. This investigation was supported by Public Health Service Research Grant 1-RO-1-CA16903-01 from the National Cancer Institute. We are grateful to Dr. James McCloskey for mass spectrometric determinations and to Dr. T. B. Patrick for helpful discussions and exchange of data.

Registry No.—1, 26265-75-8; *exo*-3-isopropylidenetricyclo$[3.2.1.0^{2,4}]$octane, 61558-31-4; 2-isopropylidene-1,1,3-trimethylcyclopropane, 61558-32-5; 1-isopropylidene-2-vinylcyclopropane, 35234-77-6; 1-ethyl-2-isopropylidenecyclopropane, 61558-33-6; 1,1-dimethyl-2-isopropylidenecyclopropane, 1121-36-4.

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Preparation of Allenyl Esters

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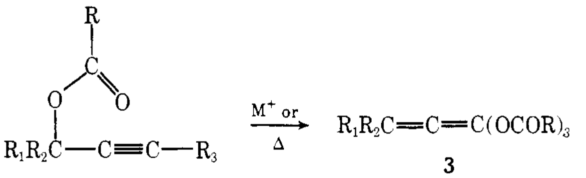
The formation of allenyl acetates and substituted benzoates by symmetry-allowed thermal rearrangement and by metal-catalyzed rearrangement is well documented.[2] The formation of allenyl[3] phosphonates, phosphinates, and phosphine oxides from thermal rearrangement of the corresponding propargyl phosphites, phosphonites, and phosphinites, respectively, is also well known.[4a-c] We wish to report the extension of these reactions to the preparation of the hitherto unknown allenyl dialkylphosphates, **1**,

$$R_1R_2C{=}C{=}C(R_3)OP(O)(OR)_2$$

1

as well as to describe our procedure for the preparation by silver-catalyzed rearrangement of these and other allenyl esters. This procedure affords yields comparable to those reported earlier while providing greater convenience. In addition we have prepared a number of new allenyl esters by thermal rearrangement of the isomeric propargyl compounds.

A variety of methods has been utilized to effect the silver ion catalyzed rearrangement of tertiary propargyl acetates[2,5a-c] and substituted nitrobenzoates,[2,5a] **2** → **3**. Reported yields vary from 40 to 65% depending upon the degree of substitution and the steric nature of the substituent groups, R_1, R_2, and R_3. Terminal alkynes generally give better yields than internal alkynes. Tertiary esters generally rearrange with higher yields and shorter reaction times than secondary esters. And, in our experience, the rearrangement will not tolerate the presence of an aromatic substituent at R_1, R_2, or R_3. Mixtures of **2** and **3** are often obtained. The reported procedures normally employ chlorobenzene or aqueous dioxane as the solvent and utilize up to 10 mol % amounts of $AgNO_3$, Ag_2CO_3, $AgClO_4$, $AgBF_4$, or AgOAc as the catalyst.



2 **3**

We required a number of allenyl esters in connection with a study of the acid- and base-catalyzed hydrolysis of allenyl-X substrates. Three disadvantages to earlier procedures became apparent in our first attempts to prepare several known allenyl acetates. It seemed to us that the choice of chlorobenzene or aqueous dioxane as a solvent did not facilitate the workup because of their relatively low volatility. Chlorobenzene was particularly troublesome in this respect. We preferred a solvent of high volatility but noted that the use of acetone by Benn[6] to effect the rearrangement of steroidal tertiary alkynyl acetates required reaction times of 96 h to acquire high yields. Secondly, the use of large quantities of Ag^+ salts very often resulted in the precipitation of silver acetylides during the reaction and workup, thus necessitating several tedious filtrations or extractions with CN^- to redissolve the propargyl ester and allow a reasonably clean purification procedure. Finally, the material thus obtained required lengthy purification by column chromatography with subsequent distillation or recrystallization.

We chose to perform the reaction in dichloromethane because of its high volatility and the similarity of its dielectric

Table I. Silver Perchlorate Catalyzed Rearrangement of Propargyl Esters in CH_2Cl_2 at 35 °C
$R_1R_2C(X)C{\equiv}C\text{-}R_3 \rightarrow R_1R_2C{=}C{=}C(X)R_3$

Registry no.	X	R_1	R_2	R_3	Compd	% yield
61570-74-9	CH_3CO_2	CH_3	CH_3	CH_3	**7**[a]	46
1604-29-1		CH_3	CH_3	H	**8**	68
49575-87-3		$t\text{-}C_4H_9$	CH_3	H	**9**[b]	63
33420-21-2		$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	H	**10**	70 (90)[c]
16169-82-7		CH_3	H	H	**11**[d]	13
3848-49-5		Ph	Ph	H		No reaction[e]
61570-75-0	$(C_2H_5O)_2P(O)O$	CH_3	CH_3	CH_3	**12**[f]	62
17423-44-8		CH_3	CH_3	H	**13**	54
61570-76-1		$t\text{-}C_4H_9$	CH_3	H	**14**	47
61570-77-2		$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	H	**15**[g]	43
42969-21-1	$p\text{-}NO_2PhCO_2$	CH_3	CH_3	CH_3	**16**[h]	46
42969-18-6		CH_3	CH_3	H	**17**[i]	37
61570-78-3	$3,5\text{-}(NO_2)_2PhCO_2$	CH_3	CH_3	H	**18**[j]	35
61570-79-4	CF_3CO_2	CH_3	CH_3	H	**19**[k]	33
53487-52-8	$p\text{-}CH_3PhSO_2O$	CH_3	H	H	**20**[l]	

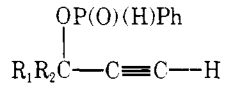
[a] Obtained as a 54:46 mixture of propargyl and allenyl isomers by NMR; column chromatography yielded a mixture of 86% allenyl acetate. [b] Reaction time of 5 h. [c] Second number indicates percent conversion to allenyl acetate during preparative GC at 225 °C. [d] Purified by preparative GC at 110 °C. [e] Thermal rearrangement led to decomposition; silver ion rearrangement returned starting material. [f] Attempts to purify a 62:38 allenyl:propargyl mixture resulted in decomposition and/or hydrolysis. [g] Thermal rearrangement in silicone oil at 135 °C for 30 min. [h] $AgBF_4$, product recrystallized from hexane yielded 46:54 allenyl:propargyl mixture. [i] $AgBF_4$, product recrystallized from hexane. [j] $AgBF_4$, 5 h reaction time. [k] 33% rearrangement by preparative GC at 85 or 110 °C. [l] $AgBF_4$, 12 h reaction time; recrystallization three times from pentane yielded a 40:60 allenyl:propargyl mixture by NMR.

Table II. Analytical Data for Allenyl Esters

			^1H NMR data[c]			
Compd[a]	Bp/mp, °C	IR[b]	1[d]	2[d]	3[d]	Ref
7	35–37 (2 mm)	1975	—	1.74 (s, 6) 1.99 (s, 3)	1.83 (s, 3)	This work
8	50 (3 mm)	3060, 1980	7.03 (m, *1*, J = 2 Hz)	1.79 (d, 6, J = 2 H)	2.05 (s, 3)	5a
9	42 (0.3 mm)	3050, 1960	7.12 (d, 1 J = 2 Hz)	1.79 (d, 3, J = 2 Hz) 1.09 (s, 9)	2.02 (s, 3)	13
10		3035, 1955	7.10 (s, 1)	1.18 (s, 18)	2.00 (s, 3)	This work
11		3050, 1980	7.15 (m, 1) 5.65 (m, 1)	1.88 (m, 3)	2.07 (s, 3)	This work
12[e]		1975		1.45 (s, 6) 1.79 (s, 3)	4.01 (m, 4, $POCH_2$–) 1.38 (t, 6, J = 7 Hz, –CH_2CH_3)	This work
13[f]	105 (0.5 mm)	3025, 1960	6.33 (m, 1)	1.82 (d, 6, J = 2 Hz)	4.05 (m, 4, $POCH_2$–) 1.34 (t, 6, J = 7 Hz, –CH_2CH_3)	This work
14	77 (8Cμ)	3025, 1960	6.38 (m, 1)	1.78 (d, 3, J = 2 Hz) 1.10 (s, 9)	4.02 (m, 4, $POCH_2$–) 1.32 (t, 6, J = 7 Hz, –CH_2CH_3)	This work
15	98–99 (25 μ)	3025, 1940	6.47 (d, 1)	1.24 (s, 18)	4.04 (m, 4, $POCH_2$) 1.33 (t, 6, J = 7 Hz, –CH_2CH_3)	This work
16	51–52[g]	1980[h]		1.82 (s, 6) 2.03 (s, 3)	8.15 (s, 4)	This work
17	105[i]	1975[h]	7.32 (m, 1, J = 2 Hz)	1.87 (d, 6, J = 2 Hz)	8.16 (s, 4)	5a
18	114	1970[h]	7.30 (m, 1, J = 2 Hz)	1.92 (d, 6, J = 2 Hz)	9.06 (s, 3)	This work
19		3050, 1970	8.71 (m, 1, J = 2 Hz)	1.88 (d, 6, J = 2 Hz)		This work
20		1975	6.44 (m, 1) 5.58 (m, 1)	1.58 (m, 3)	7.40 (m, 4) 2.40 (m, 3)	This work

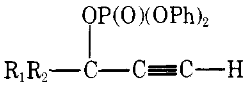
[a] See Table I for key to compound identity. [b] Allenic C–H stretch if observable given first; second entry is C=C=C absorption in cm^{-1}. [c] Neat liquids except solids in $CDCl_3$; shifts vs. internal Me_4Si in δ. [d] Column 1 = allenic proton shifts; C-1 first, C-3 second. Column 2 = proton shifts of alkyl substituents at C-3 in order of increasing mass; alkyl substituents at C-1 listed next. Column 3 = proton shifts of alkyl or aromatic substituents in ester moiety. [e] IR and NMR data assigned from spectra of crude reaction mixtures nad comparison with propargyl isomer. [f] Anal. Calcd for $C_9H_{21}PO_4$: C, 49.09; H, 7.73; P, 14.09. Found: C, 48.87; H, 7.78. [g] From hexane. [h] In CCl_4. [i] Lit. 108–111 °C.

constant, 8.9, to that of chlorobenzene, 5.6, as well as for the high solubility of the propargyl esters being used. The results obtained at 35 °C using reaction times of 1.75–2.75 h and 2.5 mol % $AgClO_4$ or $AgBF_4$ are summarized in Table I. The workup consisted of washing with aqueous ammonia, drying, rotary evaporation, and purification by distillation, recrystallization, or preparative GLC. In general our procedure provides a convenient method for the preparation of 3,3-disubstituted terminal allenyl acetates, nitrobenzoates, and diethyl phosphates. Monosubstituted allenyl esters and disubstituted allenyl trifluoroacetates and tosylates required lengthy separation procedures but are indeed formed in this reaction. The trifluoroacetates and tosylates are not stable for more than a few days at 0 °C. All other esters showed marked darkening after 1 month at 0 °C but can be purified by recrystallization or preparative GC. Repeated attempts to rearrange tertiary propargyl phenyl phosphinates, **5**, or diphenyl phosphates, **6**, were unsuccessful.



$$\mathrm{R_1R_2}\overset{\mathrm{OP(O)(H)Ph}}{\overset{|}{\mathrm{C}}}\mathrm{-C\equiv C-H}$$

5



$$\mathrm{R_1R_2-}\overset{\mathrm{OP(O)(OPh)_2}}{\overset{|}{\mathrm{C}}}\mathrm{-C\equiv C-H}$$

6

Preliminary results indicate that 3,3-dimethylallenyl acetate undergoes hydrolysis to 3-methyl-2-butenal at 45 °C at pH 7.8 with a half-life of 100 min. The corresponding diethyl phosphate appears to be even more reactive under the same conditions.

Experimental Section

Infrared spectra were recorded using a Perkin-Elmer Model 337 infrared spectrophotometer. Preparative gas–liquid chromatography was performed on a Hewlett-Packard chromatograph, Model 5750, using 8 ft × 0.5 in. SE-30 columns. The ^1H NMR spectra were run on an Hitachi Perkin-Elmer R-20B nuclear magnetic resonance spectrometer, 60 Hz. Melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

Propargyl Esters. Acetates of secondary and tertiary propargyl alcohols were prepared according to the method of Hennion et al.[7] Diethyl phosphates were prepared by treatment of the alkoxide salt with diethyl chlorophosphate according to reported procedures.[8,9] Nitrobenzoates were prepared according to Hennion et al.[10] Propargyl tosylates and trifluoroacetates were prepared according to reported procedures.[11,12]

General Procedure for Ag^+-Catalyzed Rearrangement of Propargyl Esters. Propargyl ester (50 mmol) dissolved in 50 mL of CH_2Cl_2 is allowed to react at 35 °C under N_2 in the presence of 1.5 mmol of $AgClO_4$ or $AgBF_4$ until the appearance of a red-brown color (usually 1.75–2.75 h). Continued reaction leads to lower yields. The mixture is then diluted with 50 mL of ether and washed with 2 × 75 mL of 10% aqueous ammonia and 2 × 100 mL of H_2O before drying over K_2CO_3 and rotary evaporation. Distillation or recrystallization followed by preparative GC (8 ft × 0.5 in., SE-30) or column chromatography on neutral alumina (10 ft × 0.5 in.) with pentane afforded the desired allenyl ester in the yields reported. Variations for specific compounds and requisite analytical data are to be found in Table II.

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Registry No.—**7**, 61570-65-8; **8**, 17458-90-1; **9**, 17458-93-4; **10**, 61570-66-9; **11**, 50989-92-9; **12**, 61570-67-0; **13**, 61570-68-1; **14**, 61570-69-2; **15**, 61570-70-5; **16**, 42969-38-0; **17**, 42969-35-7; **18**, 61570-71-6; **19**, 61570-72-7; **20**, 61570-73-8.

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Pyrolysis of the Lithium Salts of the *p*-Toluenesulfonylhydrazones of 8,9-Dehydro-2-adamantanone and 2,4-Dehydro-5-homoadamantanone

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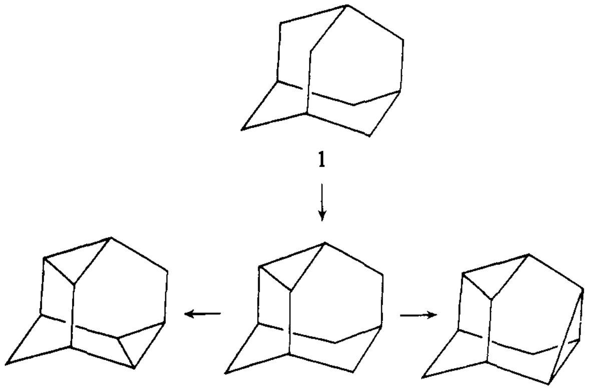
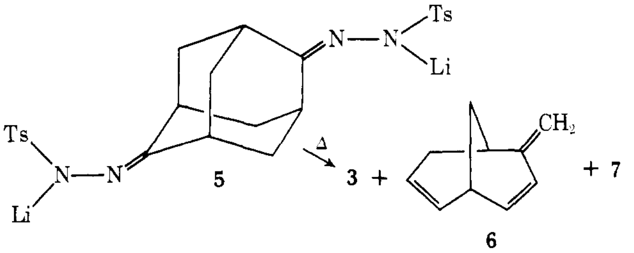
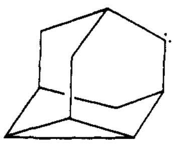
Adamantane (**1**) (T_d symmetry) allows for only one "nonbridgehead" dehydroadamantane (**2**). By contrast, two nonbridgehead didehydroadamantanes, **3** and **4**, are possible.



Geluk and de Boer have reported that thermolysis of the dilithium salt of 2,6-adamantanedione bistosylhydrazone (**5**) gives a mixture of three volatile $C_{10}H_{12}$ hydrocarbons: **3**, 2-methylenebicyclo[3.3.1]nona-3,6-diene (**6**), and an unknown compound **7** in yields of 12, 9, and 3%, respectively.[1] These authors have suggested that the reaction proceeds via carbene **8**.[1] 2,4,6,9-Bisdehydroadamantane (**3**) has also been obtained in ca. 30% yield by pyrolysis of diazirine **9**.[2]





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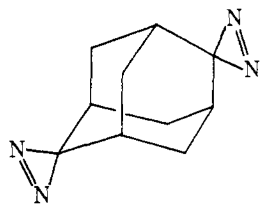

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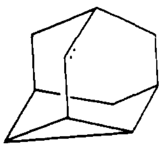
In principle, hydrocarbon **3** might also be generated from carbene **10**. Although Isaev and co-workers have reported that pyrolysis of diazirine **11** leads to a mixture of products containing **3** in ca. 30% yield,[2] Geluk and de Boer observed that pyrolysis of **12** only affords a condensate that consists of a



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