114301-06-3; di-μ-chlorobis[(1,2,3-η)-2-*tert*-butyl-2-cyclohexen-1-yl]dipalladium, 114301-07-4; di-μ-chlorobis[(1,2,3-η)-1-methyl-2-cyclohexen-1-yl]dipalladium, 96981-64-5; di-μ-chlorobis[(1,2,3-η)-2-methyl-2-cyclohexen-1-yl]dipalladium, 32915-13-2; 1,2-dimethyl-1,4-cyclohexadiene, 17351-28-9; 1,4-dimethyl-1,4-cyclohexadiene, 4074-22-0; 1,5-dimethyl-1,4-cyclohexadiene, 4190-06-1; 1-isopropyl-4-methyl-1,4-cyclohexadiene, 99-85-4; 1,4-diisopropyl-1,4-cyclohexadiene, 114300-89-9; 1,2,3,4,5,8-hexahydronaphthalene, 36231-13-7; 2,3,4,7-tetrahydro-1*H*-indene, 7603-37-4; bicyclo[4.2.0]octa-1(6),3-diene, 38325-66-5; 1,2,4,5-tetramethyl-1,4-cyclohexadiene, 26976-92-1; 1,2,4-trimethyl-1,4-cyclohexadiene, 72985-36-5; 1,3,5-trimethyl-1,4-cyclohexadiene, 4074-23-1; 3-phenyl-1,4-cyclohexadiene, 4794-05-2; 1-*tert*-butyl-1,4-cyclohexadiene, 94625-86-2; 1-methyl-1,4-cyclohexadiene, 4313-57-9; 1,4-cyclohexadiene, 628-41-1; biphenyl, 92-52-4.

Supplementary Material Available: Melting points, IR, and elemental analyses (C, H) data for (η^3-cyclohexenyl)palladium complexes **7–16**, **18** and **20**, boiling points, IR, ^{13}C NMR, mass spectra, and elemental analyses (C, H) data for methyl cyclohexenecarboxylates **24–32**, and experimental details and NMR data for 1-isopropyl-4-methyl-1,4-cyclohexadiene, 1,4-diisopropyl-1,4-cyclohexadiene, 1,2,3,4,5,8-hexahydronaphthalene, 4,7-dihydroindan, 1,2,3,6-tetrahydrobenzocyclobutene, 1,2,4-trimethyl-1,4-cyclohexadiene, 1,3,5-trimethyl-1,4-cyclohexadiene, 3-phenyl-1,4-cyclohexadiene, 1-*tert*-butyl-1,4-cyclohexadiene, and 1-methyl-1,4-cyclohexadiene (11 pages). Ordering information is given on any current masthead page.

(Cycloalkylidenemethyl)triphenylphosphonium Salts as Versatile Intermediate Reagents

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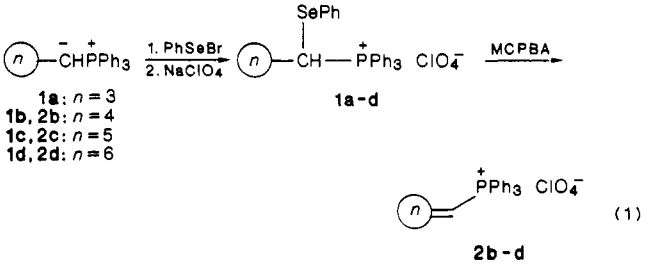
The (cycloalkylidenemethyl)triphenylphosphonium salts **2b–d** were synthesized in high yields by phenylselenylation of (cycloalkylmethylene)triphenylphosphoranes with benzeneselenenyl bromide to the [cycloalkyl(phenylseleno)methyl]triphenylphosphonium salts **1b–d** and subsequent oxidative elimination of the phenylseleno moiety, while the synthesis of the (cyclopropylidenemethyl)triphenylphosphonium salt **2a** was unsuccessful. Hydrolysis of **2b–d** in aqueous THF and methanol containing sodium hydroxide was studied. The reactions of the (cyclohexylidenemethyl)phosphonium salt **2d** and 1.1 equiv of butyllithium with aldehydes **9** gave alkenylcyclohexenes **10d–f** in 56–81% yields, whereas similar reactions using 1.5 equiv and 2 equiv of butyllithium produced allenes **11d–f** as major products together with small amounts of **10d,e**. Similar reactions of the (cyclopentylidenemethyl)phosphonium salt **2c** and butyllithium with **9** gave alkenylcyclopentenes **10a–c** in 56–80% yields, regardless of the amount of butyllithium used. The formation mechanism of **10** and **11** was discussed.

We have recently reported the synthesis and synthetic applications of 1-cycloalkenyltriphenylphosphonium salts.[1] Of these salts, the 1-cyclobutenyltriphenylphosphonium salt has been well-studied owing to its high reactivity and versatility.[2] On the other hand, (cycloalkylidenemethyl)triphenylphosphonium salts, a new type of related phosphonium salts, are similarly expected to be versatile intermediate reagents for the synthesis of functionalized cycloalkanes and fused cycloalkane compounds, but their syntheses have, to our knowledge, not been reported to date. Furthermore, in comparison with the 1-cycloalkenyltriphenylphosphonium salts, we became interested in the influence of ring sizes of the (cycloalkylidenemethyl)triphenylphosphonium salts on chemical and physical properties. We report herein the synthesis and synthetic utilization of small-ring to medium-ring (cycloalkylidenemethyl)phosphonium salts.

Results and Discussion

According to the established procedure,[1a,2a] the [cycloalkyl(phenylseleno)methyl]triphenylphosphonium salts **1a–d** were prepared in good yields from phenylselenylation of (cycloalkylmethylene)triphenylphosphoranes with benzeneselenenyl bromide. Oxidative elimination of the phenylseleno moiety in **1b–d** successfully produced the corresponding (cycloalkylidenemethyl)triphenylphosphonium perchlorates **2b–d**, while similar treatment of the [cyclopropyl(phenylseleno)methyl]triphenylphosphonium salt **1a** did not lead to the expected (cyclopropylidenemethyl)phosphonium salt **2a**; only an unidentified salt[3] was obtained. The structures of **2b–d** are



(1)

clearly derivable from their ^1H NMR (Experimental Section) and ^{13}C NMR spectral data (Table I). Thus, for **2d**, the ^1H NMR spectrum showed characteristically a vinylic proton at δ 6.15 as a doublet ($^2J_{P-H}$ = 23.7 Hz), and the ^{13}C NMR spectrum exhibited two olefinic carbons at δ 99.5 ($^1J_{^{31}P-^{13}C}$ = 88.5 Hz, C-1) and δ 178.0 (C-2), two allylic carbons to phosphorus at δ 35.0 ($^3J_{^{31}P-^{13}C}$ = 7.7 Hz, C-3)

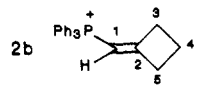
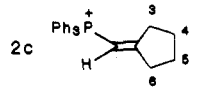
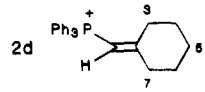
(1) (a) Saleh, G.; Minami, T.; Ohshiro, Y.; Agawa, T. *Chem. Ber.* **1979**, *112*, 355. (b) Minami, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1985**, *50*, 1278.

(2) (a) Minami, T.; Sako, H.; Ikehira, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1983**, *48*, 2569. (b) Minami, T.; Chikugo, T.; Hanamoto, T. *J. Org. Chem.* **1986**, *51*, 2210. (c) Minami, T.; Harui, N.; Taniguchi, Y. *J. Org. Chem.* **1986**, *51*, 3572. (d) Minami, T.; Okada, Y.; Nomura, R.; Hirota, S.; Nagahara, Y.; Fukuyama, K. *Chem. Lett.* **1986**, 613. (e) Okada, Y.; Minami, T.; Yahiro, S.; Kaku, H.; Ishiyama, M. *Nippon Kagaku Kaishi* **1987**, 1244.

(3) The ^{13}C NMR spectrum showed only sp^2 carbons at δ 111–137, which could not be assigned.

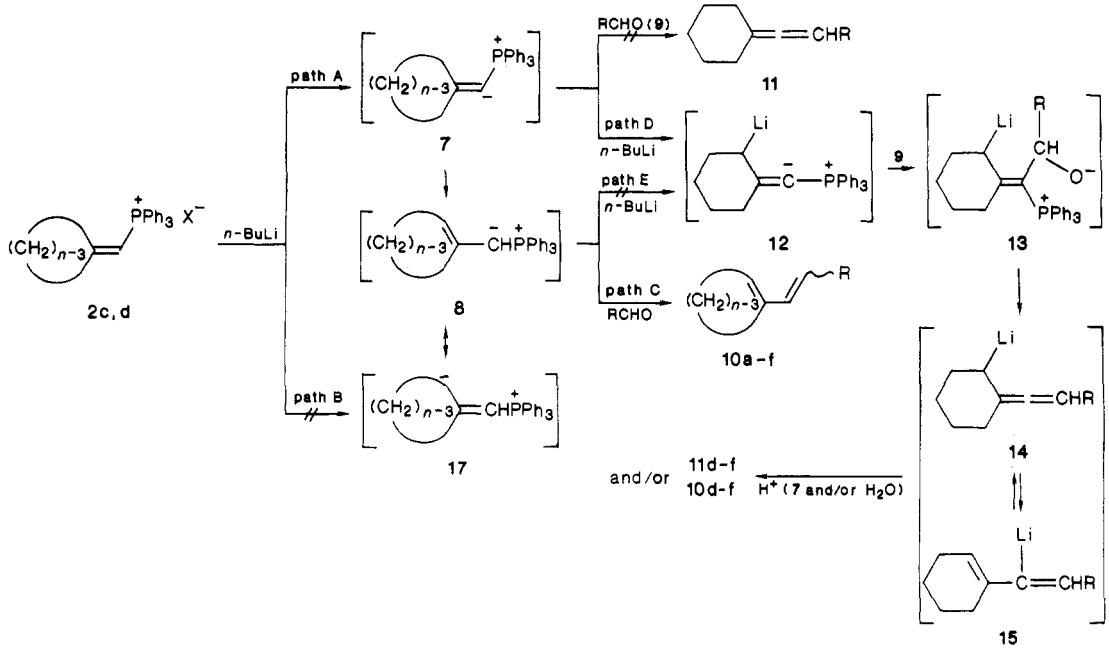
0022-3263/88/1953-2937$01.50/0

Table I. ^{13}C NMR Spectral Data of the (Cycloalkylidenemethyl)phosphonium Salts 2b–d

compd		^{13}C NMR chemical shifts,[a] ppm (^{31}P–^{13}C coupling const)						
		1	2	3	4	5	6	7
2b		97.3 (90.3)	182.3 (0)	33.4 (9.5)	16.7 (0)	36.6 (19.8)		
2c		96.7 (92.0)	183.9 (0)	34.4 (6.0)	25.0 (0)	26.7 (0)	39.3 (16.3)	
2d		99.5 (88.5)	178.8 (0)	35.0 (7.7)	26.8 (0)	24.5 (0)	28.1 (0)	39.9 (18.1)

[a] Chemical shifts for $CDCl_3$ solutions relative to Me_4Si.

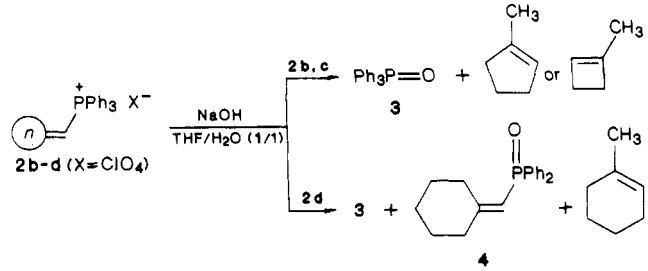
Scheme I



10a: $n=5$, R=Ph
10b: $n=5$, R=PhCH=CH
10c: $n=5$, R=Me_2C=CH
10d, 11d: $n=6$, R=Ph
10e, 11e: $n=6$, R=PhCH=CH
10f, 11f: $n=6$, R=Me_2C=CH

and δ 39.9 ($^3J_{^{31}P-^{13}C}$ = 18.1 Hz, C-7), and three sp^3 carbons at δ 26.8 (C-4), δ 24.5 (C-5), and δ 28.1 (C-6) whose assignments rest upon both the similarity of magnitudes of phosphorus–carbon coupling to those reported for (2-methylpropenyl)triphenylphosphonium chloride[4] and comparison of chemical shifts with those for 1-cyclohexenyl-[2a] and cyclohexyltriphenylphosphonium salts.[5]

In an attempt to examine the reactivities of the salts **2**, hydrolysis of **2b** and **2c** was carried out at room temperature for 8 h in aqueous tetrahydrofuran (THF) containing excess sodium hydroxide to give a quantitative yield of triphenylphosphine oxide (**3**) in both cases by generation of 1-methylcycloalkenes, of which 1-methylcyclopentene was successfully characterized by comparison of GLPC with that of an authentic sample. On the other hand, similar treatment of **2d** led to a mixture of **3** (46%) and (cyclohexylidenemethyl)diphenylphosphine oxide (**4**) (38%) (eq 2).[6] These results could be explained by pos-



(2)

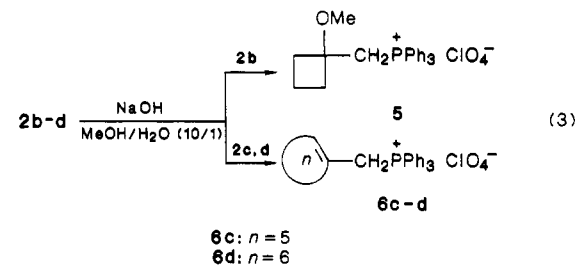
(4) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 2946.
(5) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 2942.
(6) No attempt to detect 1-methylcyclohexene by a GLPC analysis was done.

Table II. Synthesis of 1-Alkenylcycloalkenes 10 and Allenes 11 from the (Cycloalkylidenemethyl)phosphonium Salts 2 and Aldehydes 9

entry	starting materials: salt 2	starting materials: 9 (R)	conditions[a] ratio of 2:*n*-BuLi	products (% yield)[b]: 10	11	16
1	2c	9a (Ph)	1:1.1	10a (71)		
2[c]	2c	9a (Ph)	1:1.5	10a (60)		16a (86)[d]
3	2c	9b (PhCH=CH)	1:1.1	10b (66)		
4	2c	9b (PhCH=CH)	1:1.5	10b (56)		*e*
5[c]	2c	9b (PhCH=CH)	1:1.5	10b (80)		16b (63)[d]
6	2c	9c (Me_2C=CH)	1:1.1	10c (68)		
7	2c	9c (Me_2C=CH)	1:1.5	10c (68)		*e*
8	2d	9a (Ph)	1:1.1	10d (56)		
9	2d	9a (Ph)	1:1.5	10d (17)	11d (52)	
10	2d	9a (Ph)	1:2.0	10d (35)	11d (52)	
11	2d	9b (PhCH=CH)	1:1.1	10e (81)		
12	2d	9b (PhCH=CH)	1:1.5	10e (7)	11e (65)	
13	2d	9b (PhCH=CH)	1:2.0	10e (12)	11e (57)	
14	2d	9c (Me_2C=CH)	1:1.1	10f (65)		
15	2d	9c (Me_2C=CH)	1:1.5		11f (68)	

[a] Unless otherwise stated all reactions were carried out using 2 (1 mmol) and 9 (1.2 mmol) in THF (5 mL). [b] Isolated yields. [c] 2 equiv (2 mmol) of 9 was used. [d] The yield is based on an excess (0.5 mmol) of *n*-BuLi. [e] No attempt to isolate 16 was made.

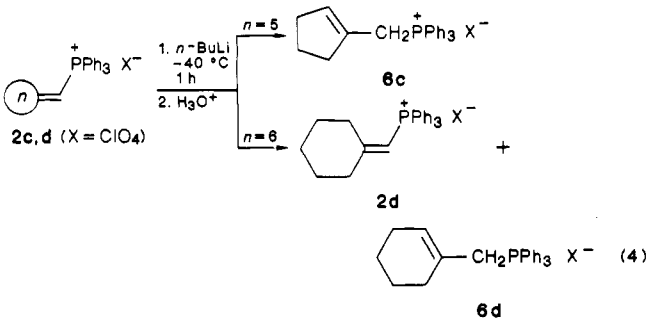
tulating that, compared with **2d**, the salts **2b,c** underwent an easier isomerization into the corresponding (1-cycloalkenylmethyl)triphenylphosphonium salts, followed by hydrolysis to yield **3** and 1-methylcycloalkenes. Furthermore, treatment of **2b** in aqueous methanol under similar conditions gave [(1-methoxycyclobutyl)methyl]triphenylphosphonium perchlorate (**5**), which was formed by the Michael addition of methanol to **2b**, in quantitative yield. In contrast to **2b**, similar treatment of **2c** and **2d** exclusively led to (1-cyclopentenylmethyl)- (**6c**) and (1-cyclohexenylmethyl)triphenylphosphonium perchlorates (**6d**) (eq 3). Thus, toward a methoxide anion, the salt **2b**



(3)

exhibited a similar reactivity to that of the 1-cyclobutenylphosphonium salt reported previously.[2a]

In order to utilize the phosphonium salts **2b–d**, we have studied the reactions of **2b–d** and butyllithium (*n*-BuLi) with aldehydes **9**. The ylide **8d**, prepared from **2d** and 1.1 molar equiv of *n*-BuLi at −40 °C for 0.5 h in THF, was allowed to react with benzaldehyde (**9a**) at −75 °C for 1 h and at room temperature for 8 h to afford 1-(phenylethenyl)cyclohexene (**10d**) in 56% yield. With a view of improving the product yield, we have examined the effect of the molar ratio of *n*-BuLi to **2d**. Interestingly, the reaction using 1.5 equiv of *n*-BuLi to **2d** resulted in the formation of a mixture of **10d** (17%) and (2-phenylvinylidene)cyclohexane (**11d**) (52%), while the use of 2 equiv of *n*-BuLi led to a mixture of **10d** (35%) and **11d** (52%). Thus, even in the cases using more than 1 molar equiv of *n*-BuLi to **2d**, the addition product of *n*-BuLi to **9a** was not observed. Similar results were obtained under the same conditions using **2d**, cinnamaldehyde (**9b**), and 3-methylbutenal (**9c**) (Table II, entries 11–15). Thus, the reaction products and their yields were strongly dependent upon the molar ratio of *n*-BuLi to **2d**. In contrast, respective treatment of the (cyclopentylidenemethyl)-phosphonium salt **2c** with 1.1 equiv and 1.5 equiv of *n*-BuLi, followed by the reaction with **9**, led to 1-alkenylcyclopentenes **10a–c** (66–71%) (Table II, entries 1, 3, and 6) and mixtures of **10a–c** and carbinols **16**, of which 1-phenyl-1-pentanol (**16a**) and 1-phenyl-1-hepten-3-ol (**16b**) were isolated in pure forms (Table II, entries 2, 4, 5, and 7). However, no corresponding allene derivative to **11d–f** was formed. These results indicate that, in the case using **2c**, an excess of *n*-BuLi was consumed to react with aldehydes **9** to provide **16** but not to yield allenes. Based on these observations, the formation of the 1-alkenyl-cycloalkenes **10** and the allenes **11** could be explained as follows. That is, (cycloalkylidenemethylene)triphenylphosphoranes **7c,d**, generated by abstraction of the acidic α-hydrogen to the phosphorus atom in **2c,d** with *n*-BuLi,[7] are stable toward aldehydes **9** under these conditions and therefore undergo rearrangement into thermodynamically favorable (1-cycloalkenylmethylene)triphenylphosphoranes **8c,d** and the subsequent Wittig condensation with **9** to give **10** (Scheme I, path C). The presence of the ylides **8c,d** as interemediate reagents was clearly supported from the results that, after keeping a THF solution of the initially generated ylide **7c** at −40 °C for 1 h, quenching the solution with an aqueous NH_4Cl solution exclusively produced the (1-cyclopentenylmethyl)phosphonium salt **6c** in quantitative yield and treatment of the ylid **7d** under the same conditions led to a ca. 1:1 mixture of the starting phosphonium salt **2d** and its isomeric salt **6d** (eq 4). Moreover,

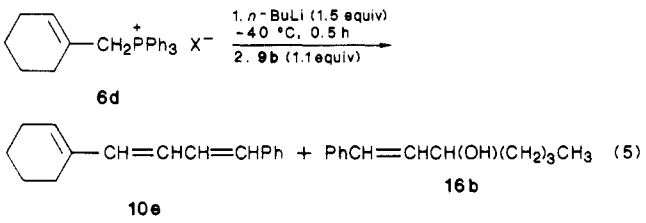


(4)

these experimental results indicate that isomerization of **7c** to **8c** occurred much faster than that of **7d** to **8d**. In the case where an excess of *n*-BuLi was used, further abstraction of the γ-hydrogen (allylic hydrogen) of **7d** with

(7) α-Lithiation of vinyl compounds containing organohetero groups such as PhS, PhSe, and PhTe at the α-position has been well-known. See, for examples: (a) Vlattas, I.; Della Vecchia, L.; Lee, A. O. *J. Am. Chem. Soc.* **1976**, *98*, 2008. (b) Kauffmann, T. *Angew. Chem.* **1982**, *94*, 401. (c) Servin, M.; Denis, J. N.; Krief, A. *Angew. Chem.* **1978**, *90*, 550; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 526.

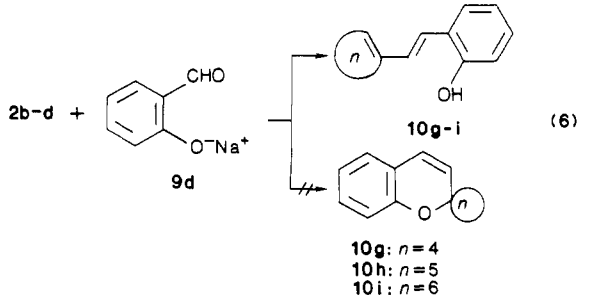
excess *n*-BuLi took place to form a new reactive ylide, [(2-lithiocyclohexylidene)methylene]triphenylphosphorane (**12**) which readily reacts with aldehydes **9** to produce lithiated allenes **14** and lithiated alkenylcyclohexenes **15**, followed by protonation with **7d** and/or with an aqueous NH_4Cl solution on workup to **11** and **10** (Scheme I, path D). Corey and co-workers[8] have recently reported a new reactive reagent, α-lithiomethylenetriphenylphosphorane analogous to our γ-lithio ylide **12**. In order to make the formation mechanism of **11** clear, independent treatment of **6d**[9] with 1.5 equiv of *n*-BuLi, followed by the reaction with 1.1 equiv of **9b**, did not lead to **11e** but to only a mixture of **10e** (71%) and **16b** (37%)[10] (eq 5). Thus, the



(5)

Wittig reaction product was not influenced by the molar ratios of *n*-BuLi to **6d**. Accordingly, this experiment demonstrates that, in the presence of excess *n*-BuLi, the γ-lithio ylide **12** was generated via the ylide **7d**, but not via the ylide **8d**. Other groups have already reported that the Wittig reaction of **6d** and phenyllithium (or *n*-BuLi) with α,β-unsaturated aldehydes gave same simple Wittig condensation products as our above results.[11] The reaction of the (cyclobutylidenemethyl)phosphonium salt **2b** with **9a** under the same conditions, on the other hand, gave no assignable product.[12]

Since the salt **2b** was proved a good Michael acceptor toward an alkoxide, we anticipated that the Michael addition of sodium salicylaldehyde (**9d**) would generate an ylide, followed by the intramolecular Wittig reaction to produce benzopyran-2-spirocyclobutane.[2a,13] However, the only product obtained was 1-[(*o*-hydroxyphenyl)ethenyl]cyclobutene (**10g**) (64% yield). Similar treatment of **2c,d** with **9d** led to similar Wittig olefination products **10h,i** in 54–70% yields (eq 6).[14]



(6)

(8) (a) Corey, E. J.; Kang, J. *J. Am. Chem. Soc.* **1982**, *104*, 4724. (b) Corey, E. J.; Kang, J.; Kyler, K. *Tetrahedron Lett.* **1985**, *26*, 555.

(9) The bromide salt **6d** (X = Br)[11a] was used.

(10) The yield is based on the molar ratio of **9b**.

(11) (a) Inhoffen, H. H.; Irmscher, K. *Chem. Ber.* **1956**, *89*, 1833. (b) Gedye, R. N.; Arora, P.; Khalil, A. H. *Can. J. Chem.* **1975**, *53*, 1943.

(12) Although a mixture of products showing several spots on TLC analysis was obtained, their purification was difficult.

(13) (a) Schweizer, E. E.; Light, K. K. *J. Am. Chem. Soc.* **1964**, *86*, 2963. (b) Becker, K. B. *Tetrahedron* **1980**, *36*, 1717 and references cited therein.

(14) All products **10g–i** were obtained as single stereoisomers. Since the product **10d** was assigned the trans isomer on the basis of its ^1H NMR data, we tentatively assigned the products **10g–i** as the trans structures **10g–i** although the vicinal H–H coupling constant in the vinyl group of **10g–i** was obscured by phenyl peaks.

In summary, we note the following points from this investigation: (1) a new family of phosphonium salts, (cycloalkylidenemethyl)triphenylphosphonium perchlorates **2b–d**, was synthesized; (2) a new type of γ-lithiated ylide **12** was proposed; (3) the (cyclohexylidenemethyl)phosphonium salt **2d** provided an efficient method to prepare allenes **11**; (4) the salts **2b–d** are versatile reagents for the synthesis of 1-alkenylcycloalkenes.

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-FX-60 spectrometer in $CDCl_3$ operating at 60 and 15.04 MHz with Me_4Si as an internal standard. IR spectra were recorded with a Shimazu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Analytical gas chromatography (GLPC) was performed on a Shimazu GC-8A capillary gas chromatograph with a flame ionization detector using a 25 m × 0.25 mm, Silicone OV-1 column; helium was used as the carrier gas. Melting points were measured in open capillary tubes and are uncorrected.

Materials. (Cyclopropylmethyl)-, (cyclobutylmethyl)-, (cyclopentylmethyl)-, and (cyclohexylmethyl)triphenylphosphonium bromides were prepared from the reaction of triphenylphosphine with the corresponding cycloalkylmethyl bromides. Solutions of the phosphonium bromides (0.05 mol) in ethanol were treated with an ethanolic solution of $NaClO_4$ (0.1 mol) at room temperature for 8 h to give the corresponding (cycloalkylmethyl)triphenylphosphonium perchlorates in 85–95% yields. (1-Cyclohexenylmethyl)triphenylphosphonium bromide (**6d**, X = Br instead of ClO_4) was synthesized in 84% yield by the reaction of 1-cyclohexenylmethyl bromide with triphenylphosphine: mp 229–230 °C (lit.[11a] mp 246 °C); ^1H NMR δ 1.10–2.20 (br, 8 H, CH_2), 4.50 (d, J = 14.65 Hz, 2 H, $CH_2^+PPh_3$), 5.40–5.70 (br s, 1 H, olefinic H), 7.40–8.00 (m, 15 H, phenyl H).

General Procedure for the Synthesis of 1a–d. According to the established procedure,[1a,2a] the phosphonium salts **1a–d** were prepared by the reaction of (cycloalkylmethylene)triphenylphosphoranes, generated in situ from the (cycloalkylmethyl)triphenylphosphonium perchlorates and equimolar amount of *n*-BuLi with 1 equiv of benzeneselenenyl bromide.

[Cyclopropyl(phenylseleno)methyl]triphenylphosphonium perchlorate (1a): yield 72%; mp 166–168 °C; ^1H NMR δ 0.4–1.4 (m, 5 H, cyclopropyl H), 4.72 (dd, J = 8.57 Hz, 8.57 Hz, 1 H, methine H), 7.23 (s, 5 H, PhSe), 7.40–8.10 (m, 15 H, phenyl H).

Anal. Calcd for $C_{28}H_{26}ClO_4PSe$: C, 58.80; H, 4.58. Found: C, 58.58; H, 4.63.

[Cyclobutyl(phenylseleno)methyl]triphenylphosphonium perchlorate (1b): yield 62%; mp 167–169 °C; ^1H NMR δ 1.40–2.20 (br, 7 H, cyclobutyl H), 5.04 (dd, J = 6.74 Hz, 7.04 Hz, 1 H, methine H), 7.26 (s, 5 H, PhSe), 7.40–8.0 (m, 15 H, phenyl H).

Anal. Calcd for $C_{29}H_{28}ClO_4PSe$: C, 59.44; H, 4.81. Found: C, 59.41; H, 4.83.

[Cyclopentyl(phenylseleno)methyl]triphenylphosphonium perchlorate (1c): yield 90%; mp 192–194 °C; ^1H NMR δ 0.90–2.34 (m, 9 H, cyclopentyl H), 5.09 (br d, J = 7.91 Hz, 1 H, methine H), 7.24 (s, 5 H, PhSe), 7.40–8.0 (m, 15 H, phenyl H).

Anal. Calcd for $C_{30}H_{30}ClO_4PSe$: C, 60.06; H, 5.04. Found: C, 60.06; H, 5.21.

[Cyclohexyl(phenylseleno)methyl]triphenylphosphonium perchlorate (1d): yield 82%; mp 192 °C; ^1H NMR δ 0.60–2.40 (br, 11 H, cyclohexyl H), 4.65 (d, J = 10.40 Hz, 1 H, methine H), 7.21 (s, 5 H, PhSe), 7.40–7.96 (m, 15 H, phenyl H).

Anal. Calcd for $C_{31}H_{32}ClO_4PSe$: C, 60.64; H, 5.25. Found: C, 60.50; H, 5.35.

General Procedure for the Synthesis of 2b–d. According to the established procedure,[1a,2a] a mixture of the salt **1** and 1.2 equiv of *m*-chloroperbenzoic acid in CH_2Cl_2 was heated at reflux for 1 h to give the salt **2**. The ^{13}C NMR data of **2b–d** are summarized in Table I.

(Cyclobutylidenemethyl)triphenylphosphonium perchlorate (2b): yield 91%; mp 210–212 °C; IR (KBr) 1625, 1440, 1090 cm^{-1}; ^1H NMR δ 1.80–2.40 (br, 4 H, CH_2), 2.90–3.44 (br, 2

H, CH_2), 6.37 (d, J = 20.66 Hz, 1 H, CH=C<), 7.40–7.96 (m, 15 H, phenyl H).

Anal. Calcd for $C_{23}H_{22}ClO_4P$: C, 64.45; H, 5.17. Found: C, 64.43; H, 5.32.

(Cyclopentylidenemethyl)triphenylphosphonium perchlorate (2c): yield 97%; mp 180–182 °C; IR (KBr) 1620, 1440, 1090 cm^{-1}; ^1H NMR δ 1.60–2.0 (br, 6 H, CH_2), 2.60–3.12 (br, 2 H, CH_2), 6.43 (d, J = 22.11 Hz, 1 H, CH=C<), 7.40–7.90 (m, 15 H, phenyl H).

Anal. Calcd for $C_{24}H_{24}ClO_4P$: C, 65.09; H, 5.46. Found: C, 65.01; H, 5.58.

(Cyclohexylidenemethyl)triphenylphosphonium perchlorate (2d): yield 87%; mp 206–208 °C; IR (KBr) 1605, 1440, 1090 cm^{-1}; ^1H NMR δ 1.0–2.28 (br, 8 H, CH_2), 2.40–2.88 (br, 2 H, CH_2), 6.15 (d, J = 23.73 Hz, 1 H, CH=C<), 7.24–7.96 (m, 15 H, phenyl H).

Anal. Calcd for $C_{25}H_{26}ClO_4P$: C, 65.72; H, 5.74. Found: C, 65.82; H, 5.83.

Alkaline Hydrolysis of the Salts 2b–d in THF. General Procedure. A solution of **2c** (0.44 g, 1 mmol) in THF/H_2O (1/1, 10 mL) containing NaOH (0.20 g, 5 mmol) was stirred at room temperature for 8 h. The mixture was distilled under atmospheric pressure to give a THF solution containing a collected volatile product, which was identified as 1-methylcyclopentene by GLPC analysis. The residue was extracted with CH_2Cl_2, washed with H_2O, and dried over Na_2SO_4. After removal of the CH_2Cl_2, the residue was chromatographed by preparative TLC (silica gel, ethyl acetate) to give **3** (0.28 g, 1 mmol, 100%).

Similar reaction using **2b** gave **3** in quantitative yield. Similar treatment of **2d** led to a difficulty separable mixture of **3** and **4**, whose ratio was 55/45 by the ^1H NMR data, in 0.24-g (84%) yield. The mixture had the following properties: IR (KBr) 1620 (C=C), 1440, 1190, 1120 cm^{-1}; ^1H NMR δ 1.28–1.88 (br, 6 H, CH_2), 2.08–3.10 (br, 4 H, CH_2), 5.82 (d, J = 26.37 Hz, 1 H, CH=C<), 7.24–7.96 (m, 28.4 H, phenyl H of the **3** + **4** mixture); MS, m/e 296 (M^+) and 278 (M^+).

Methanolysis of 2b–d. General Procedure. A solution of **2** (0.1 g) in MeOH/H_2O (10/1, 5 mL) containing 2 equiv of NaOH was treated as described above. After evaporation of the solvent in vacuo, the residue was extracted with CH_2Cl_2, washed with H_2O, dried over Na_2SO_4, and evaporated. The residue was crystallized from ether to give samples **5** or **6c,d**. The products had the following properties.

[(1-Methoxycyclobutyl)methyl]triphenylphosphonium perchlorate (5): yield 106 mg (100%); mp 202–204 °C; IR (KBr) 1440, 1090 cm^{-1}; ^1H NMR δ 1.40–2.60 (br, 6 H, cyclobutyl CH_2), 2.94 (s, 3 H, OCH_3), 3.92 (d, J = 11.72 Hz, 2 H, $CH_2{}^+PPh_3$), 7.50–8.0 (m, 15 H, phenyl H).

Anal. Calcd for $C_{24}H_{26}ClO_5P$: C, 62.54; H, 5.69. Found: C, 62.76; H, 5.66.

(1-Cyclopentenylmethyl)triphenylphosphonium perchlorate (6c): yield 0.73 g (73%); mp 172–174 °C; IR (KBr) 1610, 1590, 1090 cm^{-1}; ^1H NMR δ 1.32–2.60 (br, 6 H, CH_2), 4.25 (d, J = 14.65 Hz, 2 H, $CH_2{}^+PPh_3$), 5.40–5.76 (br, 1 H, olefinic H), 7.32–8.04 (m, 15 H, phenyl H).

Anal. Calcd for $C_{24}H_{24}ClO_4P$: C, 65.09; H, 5.46. Found: C, 65.15; H, 5.52.

(1-Cyclohexenylmethyl)triphenylphosphonium perchlorate (6d): yield 0.82 g (82%); mp 225–227 °C; IR (KBr) 1600, 1580, 1090 cm^{-1}; ^1H NMR δ 1.16–2.20 (br, 8 H, CH_2), 4.01 (d, J = 14.65 Hz, 2 H, $CH_2{}^+PPh_3$), 5.36–5.68 (br, 1 H, olefinic H), 7.40–7.90 (m, 15 H, phenyl H).

Anal. Calcd for $C_{25}H_{26}ClO_4P$: C, 65.72; H, 5.74. Found: C, 66.00; H, 5.85.

General Procedure for the Synthesis of Alkenylcycloalkenes 10 and Allenes 11 from the Salts 2c,d and Aldehydes 9. After the phosphonium ylides, generated in situ from the phosphonium salts **2c,d** (1 mmol) and n-BuLi (1.1, 1.5, and 2.0 mmol) in dry THF (5 mL) at −40 °C for 0.5 h, were cooled to −75 °C, aldehydes **9** (1.2 mmol) were added to the solution while the mixture was stirred at this temperature for 1 h. The mixture was then allowed to warm to room temperature and to stir for 8 h. After similar workup, the residue was chromatographed on preparative TLC (silica gel, Wakogel B-5F, hexane) to give samples **10** and/or **11**. The yields of the products are summarized in Table II.

(*E*)-1-(Phenylethenyl)cyclopentene (10a): oil; IR (neat) 1625, 960 cm^{-1}; ^1H NMR δ 1.18–2.70 (m, 6 H, CH_2), 5.78 (br s, 1 H, cyclopentenyl olefinic H), 6.31 (d, J = 16.0 Hz, 1 H, trans *H*C=CPhH), 6.95 (d, J = 16.0 Hz, 1 H, trans HC=CPh*H*), 7.10–7.48 (m, 5 H, phenyl H); MS, m/z 170 (M^+).

1-(4-Phenyl-1,3-butadienyl)cyclopentene (10b): oil; IR (neat) 1605, 990 cm^{-1}; ^1H NMR δ 1.40–2.90 (m, 6 H, CH_2), 5.77 (br, 1 H, cyclopentenyl olefinic H), 6.04–6.96 (m, 4 H, olefinic H), 7.0–7.50 (m, 5 H, phenyl H); HRMS, m/z calcd for $C_{15}H_{16}$ 196.1252, found 196.1253.

1-(4-Methyl-1,3-pentadienyl)cyclopentene (10c):[15] oil; IR (neat) 1625, 965 cm^{-1}; ^1H NMR δ 1.44–2.90 (m, 6 H, CH_2), 1.78 (s, 6 H, Me), 5.50–6.50 (m, 4 H, olefinic H).

(*E*)-1-(Phenylethenyl)cyclohexene (10d): oil; IR (neat) 1630, 960 cm^{-1}; ^1H NMR δ 1.30–1.92 (m, 4 H, CH_2), 1.92–2.40 (m, 4 H, CH_2), 5.87 (br, 1 H, cyclohexenyl olefinic H), 6.36 (d, J = 16.0 Hz, 1 H, trans *H*C=C*P*hH), 6.79 (d, J = 16.0 Hz, 1 H, trans HC=CPh*H*), 7.0–7.50 (m, 5 H, phenyl H); HRMS, m/z calcd for $C_{14}H_{16}$ 184.1251, found 184.1239.

1-(4-Phenyl-1,3-butadienyl)cyclohexene (10e): oil; IR (neat) 1610, 990 cm^{-1}; ^1H NMR δ 1.40–1.88 (br, 4 H, CH_2), 1.92–2.40 (br, 4 H, CH_2), 5.64–5.96 (br, 1 H, cyclohexenyl olefinic H), 6.16–6.84 (m, 4 H, olefinic H), 7.08–7.50 (m, 5 H, phenyl H); HRMS, m/z calcd for $C_{16}H_{18}$ 210.1408, found 210.1428.

1-(4-Methyl-1,3-pentadienyl)cyclohexene (10f): oil; IR (neat) 1640, 1610, 950 cm^{-1}; ^1H NMR δ 1.40–1.82 (br, 4 H, CH_2), 1.78 (s, 6 H, Me), 1.82–2.40 (br, 4 H, CH_2), 5.50–6.48 (m, 4 H, olefinic H); HRMS, m/z calcd for $C_{12}H_{18}$ 162.1408, found 162.1410.

(2-Phenylvinylidene)cyclohexane (11d): oil; IR (neat) 1950 cm^{-1}; ^1H NMR δ 1.40–2.0 (br, 6 H, CH_2), 2.0–2.48 (br, 4 H, CH_2), 5.99 (br s, 1 H, allenic H), 7.26 (s, 5 H, phenyl H); ^{13}C NMR δ 26.2, 27.8, 31.4, 92.4, 106.5, 126.3, 126.5, 127.7, 136.2, 199.7; HRMS, m/z calcd for $C_{14}H_{16}$ 184.1251, found 184.1257.

(5-Phenyl-1,2,4-pentatrienylidene)cyclohexane (11e): oil; IR (neat) 1946 cm^{-1}; ^1H NMR δ 1.30–1.90 (br, 6 H, CH_2), 1.90–2.40 (br, 4 H, CH_2), 5.68–6.60 (m, 3 H, allenic and olefinic H), 7.10–7.48 (m, 5 H, phenyl H); ^{13}C NMR δ 26.2, 27.4, 31.6, 92.7, 103.9, 126.1, 126.9, 128.5, 129.2, 137.0, 137.7, 202.8; HRMS, m/z calcd for $C_{16}H_{18}$ 210.1408, found 210.1398.

(5-Methyl-1,2,4-hexatrienylidene)cyclohexane (11f): oil; IR (neat) 1945 cm^{-1}; ^1H NMR δ 1.10–1.86 (br, 6 H, CH_2), 1.73 (s, 6 H, Me), 1.86–2.36 (br, 4 H, CH_2), 5.32–6.40 (m, 2 H, allenic and olefinic H); ^{13}C NMR δ 18.0, 26.0, 26.2, 27.6, 31.8, 88.5, 103.0, 121.2, 132.7, 201.2; HRMS, m/z calcd for $C_{12}H_{18}$ 162.1408, found 162.1403.

1-Phenyl-1-pentanol (16a): oil; IR (neat) 3350 cm^{-1}; ^1H NMR δ 0.84–1.87 (m, 9 H, Me and CH_2), 3.51 (s, 1 H, OH), 4.37–4.49 (m, 1 H, >CHO-), 7.21 (s, 5 H, phenyl H); MS, m/z 164 (M^+).

1-Phenyl-1-hepten-3-ol (16b): oil; IR (neat) 3300 cm^{-1}; ^1H NMR δ 0.60–1.90 (m, 9 H, Me and CH_2), 2.67 (br s, 1 H, OH), 3.96–4.36 (m, 1 H, >C*H*OH), 6.0–6.68 (m, 2 H, -C*H*=C*H*-), 7.26 (s, 5 H, phenyl H); HRMS, m/z calcd for $C_{13}H_{18}O$ 190.1357, found 190.1388.

Isomerization of the (Cycloalkylidenemethyl)phosphonium Salts 2c,d. General Procedure. To a cooled solution of the salts **2c,d** (1.0 mmol) in dry THF (5 mL) at −40 °C was added a n-BuLi hexane solution (1.1 mmol), and the mixture was allowed to stir for 1 h at this temperature. After an aqueous NH_4Cl solution was added to the reaction mixture, the mixture was concentrated in vacuo, extracted with CH_2Cl_2, washed with H_2O, and dried over Na_2SO_4. After evaporation of CH_2Cl_2, the residue was triturated with dry ether to produce **6c** (0.44 g, 1 mmol, 100%) or a 1:1 mixture (0.46 g, 1 mmol, 100%) of **2d** and **6d**.

Reaction of 6d (X = Br) with n-BuLi and 9b. The reaction of the phosphonium ylide, generated in situ from **6d** (0.44 g, 1.0 mmol) and n-BuLi (1.5 mmol) in dry THF (5 mL), with **9b** (0.15 g, 1.1 mmol) was carried out under the same conditions as above to provide **10e** (0.15 g, 0.71 mmol, 71%) and 1-phenyl-1-hepten-3-ol (**16b**) (0.08 g, 0.4 mmol, 37%).

Reaction of 2b–d with Sodium Salicylaldehyde (9d). A suspension of the salt **2** (1 mmol) and **9d** (0.22 g, 1.5 mmol) in THF/DMF (5/1, 12 mL) was heated at reflux for 8 h. After similar workup, the residue was chromatographed by preparative TLC (silica gel, hexane/ethyl acetate = 7/1) to give the pure samples **10g–i**.

1-[2-(*o*-Hydroxyphenyl)ethenyl]cyclobutene (10g): yield 0.11 g (0.64 mmol, 64%); IR (neat) 3300, 960 cm^{-1}; ^1H NMR δ 2.30–2.80 (m, 4 H, CH_2), 4.70–5.70 (br, 1 H, OH), 6.0 (t, J = 1.1 Hz, 1 H, -C*H*=C<), 6.60–7.60 (m, 6 H, olefinic and aromatic H); HRMS, m/z calcd for $C_{12}H_{12}O$ 172.0888, found 172.0858.

1-[2-(*o*-Hydroxyphenyl)ethenyl]cyclopentene (10h): yield 0.10 g (0.54 mmol, 54%); IR (neat) 3250, 1620, 960 cm^{-1}; ^1H NMR δ 1.50–2.20 (m, 2 H, CH_2), 2.20–2.80 (m, 4 H, CH_2), 4.60–5.60 (br, 1 H, OH), 5.82 (br s, 1 H, -C*H*=C<), 6.40–7.48 (m, 6 H, olefinic and aromatic H); HRMS, m/z calcd for $C_{13}H_{14}O$ 186.1044, found 186.1042.

1-[2-(*o*-Hydroxyphenyl)ethenyl]cyclohexene (10i): yield 0.14 g (0.72 mmol, 72%); IR (neat) 3350, 1630, 965 cm^{-1}; ^1H NMR δ 1.32–1.88 (m, 4 H, CH_2), 1.88–2.40 (m, 4 H, CH_2), 5.36 (s, 1 H, OH), 5.86 (br, 1 H, -C*H*=C<), 6.48–7.50 (m, 6 H, olefinic and aromatic H); HRMS, m/z calcd for $C_{14}H_{16}O$ 200.1200, found 200.1170.

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1-Phenylisobenzofuran, 1-Phenylnaphtho[2,3-*c*]furan, 1-Phenylnaphtho[1,2-*c*]furan, and 3-Phenylnaphtho[1,2-*c*]furan via Cyclic Hemiaminal, Hemiacetal, and Acetal Precursors

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The title compounds have been generated via cyclic hemiaminal, hemiacetal, and acetal precursors and trapped in Diels–Alder reactions with several dienophiles. The precursors are easily prepared from *o*-bromobenzyl alcohol, 2-bromo-3-naphthalenemethanol, or 1-bromo-2-naphthalenemethanol. Metalation of the bromo alcohols followed by reaction with benzonitrile gave cyclic hemiaminals. In the presence of acid, the hemiaminals eliminate NH_3, generating 1-phenylisobenzofuran, 1-phenylnaphtho[2,3-*c*]furan, and 1-phenylnaphtho[1,2-*c*]furan. Metalation of 1-bromo-2-(phenylhydroxymethyl)naphthalene (prepared by reaction of PhMgBr with 1-bromo-2-naphthaldehyde) followed by reaction with dimethylformamide gives a cyclic hemiacetal precursor to 3-phenylnaphtho[1,2-*c*]furan. Cyclic acetal precursors to 1-phenyl- and 1-(2-naphthyl)naphtho[1,2-*c*]furan were prepared by the metalation of 1-bromo-2-(dimethoxymethyl)naphthalene, reaction with benzaldehyde and 2-naphthaldehyde, respectively, and cyclization in methanol/Dowex 50W-X8. The various transient furanoid species were trapped with dimethyl acetylenedicarboxylate, forming oxabicyclo adducts which aromatized in situ. With methyl acrylate, all of the furans reacted to give ortho adducts almost exclusively. The Diels–Alder reaction of 3-phenylnaphtho[1,2-*c*]furan with methyl acrylate is reversible. Ortho or meta adducts predominated, depending on the reaction conditions. Oxabicyclo adducts formed in these Diels–Alder reactions could usually be aromatized, giving phenyl-substituted naphthalenes, anthracenes, and phenanthrenes. Other polycyclic aromatic systems are also accessible: annelated fluorenones, phenylnaphthacene- and phenylpentacenequinones, and annelated pyrenes. The hemiaminals were hydrolyzed in water/THF/Dowex, giving a series of compounds that exhibited ring–chain tautomerism between hemiketal and ketone forms.

Isobenzofuran (IBF, **1**) and its derivatives are very reactive dienes[1] and readily undergo Diels–Alder reactions with a wide variety of dienophiles to give oxabicyclo adducts. These adducts have proven to be extremely versatile intermediates in the preparation of arylnaphthalene[2-5] and aryl tetralin lignans,[6-9] anthracyclinones,[10,11] and polycyclic aromatic hydrocarbons (PAHs).[12-15] Isonaphthofurans (INFs) naphtho[2,3-*c*]furan (**2**) and naphtho[1,2-*c*]furan (**3**), homologues of IBF, have also been useful intermediates in PAH synthesis.[16,17] 1-Benzyl derivatives of **1** and **2** have recently been employed in the preparation of a variety of PAH ring systems.[18] Despite the substantial interest in IBF, its 1-phenyl derivative **4** has received very little attention[19-21]

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