Synthesis and Reactions of the (1-Cyclobutenyl)triphenylphosphonium Salt

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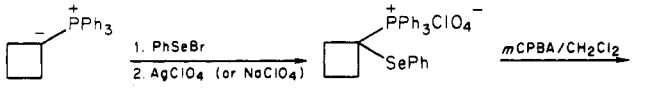
The (1-cyclobutenyl)triphenylphosphonium salt **2** was synthesized in high yield by phenylselenylation of cyclobutylidenetriphenylphosphorane with phenylselenyl bromide to a [1-(phenylseleno)cyclobutyl]phosphonium salt and subsequent oxidative elimination of the phenylseleno residue. Hydrolysis of **2** in aqueous alcohols containing sodium hydroxide gave (2-alkoxycyclobutyl)diphenylphosphine oxides **3a,b** in good yields, whereas similar treatment of **2** in tetrahydrofuran led to (1-cyclobutenyl)diphenylphosphine oxide (**4**) in 70% yield. The reaction of **2** with sodium salicylaldehyde in dimethylformamide at 130 °C for 15 h afforded 2*H*-cyclobuta[*b*]chromene (**7**) and a mixture of its two isomeric dimers in 47% and 31% yields, respectively. The phosphine oxide **4** underwent thermolysis, yielding the intermediate 2-(diphenylphosphinyl)-1,3-butadiene, which easily reacted with diethyl maleate, diethyl fumarate, and *N*-phenylmaleimide to produce *cis*- and *trans*-[4,5-bis(ethoxycarbonyl)-1-cyclohexeneyl]diphenylphosphine oxides [**11a** (71%) and **11b** (59%)] and *N*-phenyl-1,2,3,6-tetrahydro-4-(diphenylphosphinyl)phthalimide (**11c**, 76%). The ^{13}C NMR spectra of **2** and **4** were compared with those of the corresponding medium-ring 1-cycloalkenylphosphorus compounds.

Triphenylvinylphosphonium bromide and related alkenylphosphonium salts have been extensively used as useful intermediate reagents for the synthesis of a variety of carbocyclic[1] and heterocyclic compounds[2] and allyl amines.[3] Furthermore, the studies on the electronic structure of these salts by ^{13}C and ^{31}P nuclear magnetic resonance have been recently reported by Schweizer and co-workers.[4] However, these chemical and physical findings are limited to only alkenylphosphonium salts. On the other hand, we have previously reported the general synthesis and some reactions of 1-cycloalkenylphosphonium salts.[5] As a continuation of the studies on the 1-cycloalkenylphosphonium salts, we became interested in the influence of ring sizes of the salts on chemical and physical properties, since ring size effects are little understood. We report herein the synthesis and chemical and physical properties of a small-ring cycloalkenylphosphonium salt, (1-cyclobutenyl)triphenylphosphonium perchlorate.

Results and Discussion

Synthesis and Reaction of the 1-Cyclobutenylphosphonium Salt. As shown in eq 1, phenylselenylation



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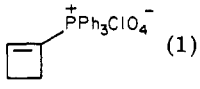
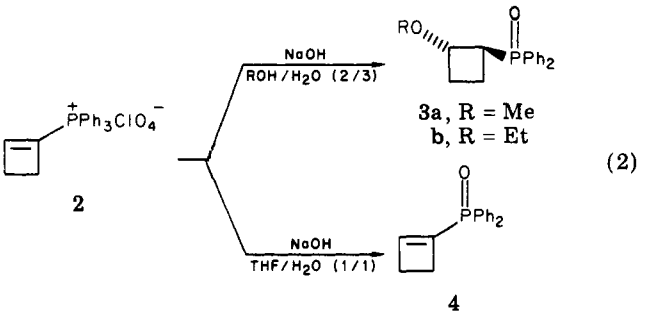


(1)

2

of cyclobutyltriphenylphosphonium ylide with phenylselenyl bromide to [1-(phenylseleno)cyclobutyl]triphenylphosphonium bromide, followed by an anion exchange to the corresponding perchlorate salt **1** with silver perchlorate (or sodium perchlorate) and oxidative elimination of the phenylseleno moiety in **1** as phenylselenic acid, led to the expected (1-cyclobutenyl)triphenylphosphonium perchlorate (**2**) in good yield (89.1% overall yield). The structure of **2** is supported by its spectra. Thus, the $\nu_{C=C}$ occurred characteristically for four-membered olefins (ca. 1565 cm^{-1})[6] at 1550 cm^{-1} in the IR spectrum. The ^1H NMR spectrum showed a methylene signal (s, 4 H) at δ 3.13 and olefinic and phenyl protons (m, 16 H) at δ 7.30–7.95.

For comparison of the reactivities of **2** with medium-ring 1-cycloalkenylphosphonium salts, hydrolysis of **2** was carried out in aqueous alcohols containing excess sodium hydroxide and gave only (2-alkoxycyclobutyl)diphenylphosphine oxides **3** (eq 2) in good yields, but none of expected (1-cyclobutenyl)diphenylphosphine oxide (**4**). Thus, the reactivity of **2** under such hydrolysis conditions is in contrast to those of medium-ring 1-cycloalkenylphosphonium salts which give the corresponding 1-cycloalkenylphosphine oxides.[5] On the other hand, similar treatment of **2** in aqueous tetrahydrofuran led to the anticipated **4** in 70% yield. Formation of **3** could be explained either by the Michael addition of alcohols to initially produced **4** under basic conditions or by hydrolysis of the intermediate Michael addition products of alcohols to **2**.



2 4

(2)

These results prompted us to utilize 2-substituted cyclobutyltriphenylphosphonium ylides in situ generated from **2** and various nucleophiles for the preparation of functionalized cyclobutanes. The 2-ethoxycyclobutylphosphonium ylide, generated via addition of an ethoxide anion to **2** in ethanol, reacted with benzaldehyde to provide 1-benzylidene-2-ethoxycyclobutane as a 7:2 mixture of *E*

(1) (a) Schweizer, E. E.; O'Neill, G. J. *J. Org. Chem.* **1965**, *30*, 2082. (b) Kawamoto, I.; Muramatsu, S.; Yura, Y. *Tetrahedron Lett.* **1974**, 4223 and references cited therein.

(2) (a) Schweizer, E. E.; Light, K. K. *J. Org. Chem.* **1966**, *31*, 870. (b) Schweizer, E. E.; Liehr, J.; Monako, D. J. *Ibid.* **1968**, *33*, 2416 and references cited therein. (c) For recent reviews, see: Zbiral, E. "Organophosphorus Reagents in Organic Synthesis"; Cadogan, J. I. G., Ed.; Academic Press: London, 1979; p 250. Becker, K. B. *Tetrahedron* **1980**, *36*, 1717.

(3) Meyers, A. I.; Lawson, J. P.; Carver, D. R. *J. Org. Chem.* **1981**, *46*, 3119.

(4) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 2946.

(5) Saleh, G.; Minami, T.; Ohshiro, Y.; Agawa, T. *Chem. Ber.* **1979**, *112*, 355.

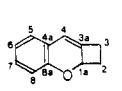
(6) Dolphin, D.; Wick, A. E. "Tabulation of Infrared Spectra Data"; Wiley-Interscience: New York, 1977; p 54.

0022-3263/83/1948-2569$01.50/0

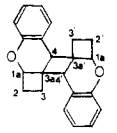
Table I. ^{13}C Chemical Shifts[a] of Compounds 7-9

	^{13}C chemical shifts, ppm										
compd	1a	2	3	3a	4	4a	5	6	7	8	8a
8a	71.0	22.8	19.1	50.5	45.5	126.4	128.4	121.5	128.1	118.7	151.2
8b	68.8	23.7	21.4	47.2	39.9	120.6	130.1	120.0	127.5	117.5	151.9
7	73.3	26.5	29.8	138.6	112.9	123.6	126.5	121.4	127.7	116.0	153.9
9	72.2	28.2	21.4	28.8	35.6	125.2	128.9	120.9	127.2	117.6	154.7

[a] Chemical shifts for $CDCl_3$ solutions with respect to Me_4Si. The numbering systems are as follows:



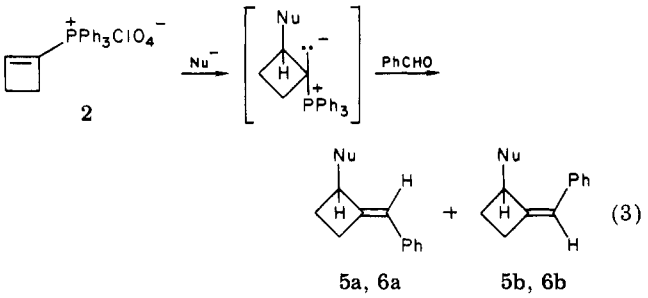
7



8

and *Z* isomers in 52% yield.

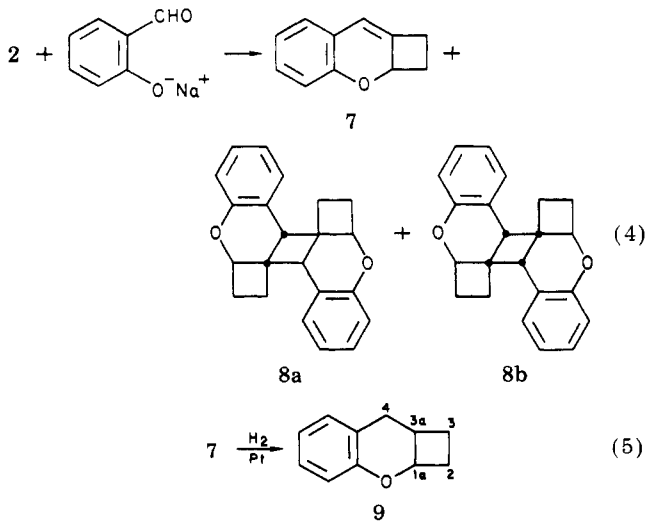
The phosphonium salt **2**, on similar treatment with *n*-butyllithium and benzaldehyde in THF, gave 1-benzylidene-2-*n*-butylcyclobutane (**6**, 52% yield; eq 3)



(3)

5, Nu = EtO; **6**, Nu = *n*-Bu

composed of a 1:1 mixture of E and Z isomers. The reaction of **2** with sodium salicylaldehyde in dimethylformamide at 130 °C for 15 h afforded 2*H*-cyclobuta[*b*]-chromene (**7**, 47%) and a mixture of its two stereoisomeric dimers (**8**, 31%) (eq 4). Although compound **7** was in-



(4)

capable of being isolated in pure form because of the ease of oxidation into an unidentified alcohol [ν_{OH} (neat) 3250 cm^{-1}], **7** was clearly characterized by its ^1H NMR spectrum ($CDCl_3$) [δ 2.0–2.90 (m, 4 H, CH_2), 4.85–5.17 (m, 1 H, OCH), 5.99 (d, J = 1.65 Hz, CH=C), 6.60–7.20 (m, 4 H)] and ^{13}C NMR spectrum (Table I). Furthermore, the structure of **7** was confirmed by its catalytic hydrogenation leading to cyclobuta[*b*]chroman (**9**, 94%) whose ^1H NMR spectrum shows signals at δ 1.25–3.00 (m, H-2,3,3a,4), 4.59 (t, J = 6.0 Hz, H-1a), and 6.65–7.30 (m, phenyl H) in the area ratio 7:1:4. On the other hand, each of pure dimeric products **8a** and **8b** was isolated by preparative TLC and tentatively identified as the trans head-to-tail and the cis head-to-tail dimers of **7** by their ^1H[7] and ^{13}C NMR spectra and mass spectral analysis.

(5)

Thus 2-substituted cyclobutylphosphonium ylides, derived from **2** and various nucleophiles, readily react with aldehydes to yield 2-substituted cyclobutylidene derivatives, whereas the corresponding cyclohexylphosphonium ylides from the 1-cyclohexenylphosphonium salt produce no product.[5] These results indicate that, in comparison with the latter phosphonium ylides, the former ones are sterically favored in the reactions with carbonyl reagents.

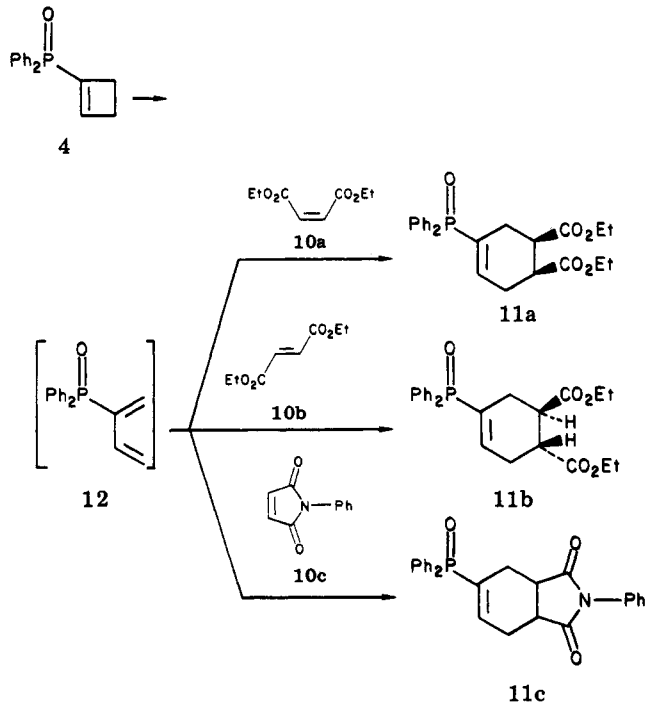
Synthetic Utilization of (1-Cyclobutenyl)diphenylphosphine Oxide (4) as a 2-(Diphenylphosphinyl)-1,3-butadiene Precursor. Since it is well-known that thermal ring opening of cyclobutenes has generated diene systems which have been widely used in organic syntheses,[8] the 1-cyclobutenylphosphine oxide **4** obtained above is also expected to undergo thermal ring opening, yielding 2-(diphenylphosphinyl)-1,3-butadiene (**12**). However, attempts to isolate the diene **12** on heating **4** were unsuccessful, and only the dimeric product of **12** was obtained. So, Diels–Alder reaction of the diene **12**, in situ generated, with dienophiles was studied. When a mixture of the phosphine oxide **4** and excess amounts of diethyl maleate (**10a**) and diethyl fumarate (**10b**) was heated at 155 °C for 10 h, desired *cis*- and *trans*-[4,5-bis(ethoxycarbonyl)-1-cyclohexenyl]diphenylphosphine oxides (**11a,b**) were obtained in 71% and 59% yields, respectively (Scheme I). The reaction of **4** with *N*-phenylmaleimide (**10c**) was carried out in benzene on heating at 150 °C for 6 h in a sealed tube to provide *N*-phenyl-1,2,3,6-tetrahydro-4-(diphenylphosphinyl)phthalimide (**11c**) in 76% yield.

Thus, the phosphine oxide **4** has been proved to be a versatile precursor for the phosphinylbutadiene **12**, which can be utilized for the synthesis of 1-phosphinylcyclohexenes which are convertible into various types of func-

(7) The ^1H NMR spectral data ($CDCl_3$) of **8a** and **8b** are as follows. **8a**: δ 1.40–2.25 (m, 8 H, CH_2), 2.91 (s, 2 H, CH), 4.65 (t, J = 7.05 Hz, 2 H, O–CH), 6.55–7.40 (m, 8 H, Ar H). **8b**: δ 1.40–2.25 (m, 8 H, CH_2), 3.71 (s, 2 H, CH), 4.57 (t, J = 7.10 Hz, 2 H, O–CH), 6.50–7.10 (m, 8 H, Ar H). Comparison of the ^1H NMR spectra of **8a** and **8b** indicates that the methine and the aromatic protons of the latter are shifted down- and upfield by 0.8 and ca. 0.2 ppm, respectively, due to the ring current of the adjacent two benzene rings. On this basis, the structures of **8a** and **8b** were assigned.

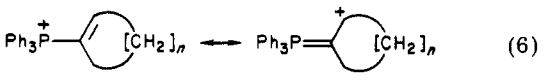
(8) See for examples: (a) Jefford, C. W.; Boschung, A. F.; Rimbault, C. G. *Tetrahedron Lett.* **1974**, 3387. (b) Trost, B. M.; Bridges, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5016. (c) Anderson, D. R.; Koch, T. H. *J. Org. Chem.* **1978**, *43*, 2726. (d) Wilson, S. R.; Phillips, L. R.; Natalie, K. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3340. (e) Halazy, S.; Krief, A. *Tetrahedron Lett.* **1980**, 1997. (f) Kametani, T.; Tsubuki, M.; Nemoto, H.; Suzuki, K. *J. Am. Chem. Soc.* **1981**, *103*, 1256. (g) For a review, see: Oppolzer, W. *Synthesis* **1978**, 793.

Scheme I



tionalized alicyclic and heterocyclic compounds.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy of 1-Cycloalkenylphosphonium Salts and 1-Cycloalkenylphosphine Oxides. The β carbons of **2** and (1-cyclopentenyl)- (**13**) and (1-cyclohexenyl)triphenylphosphonium perchlorate (**14**) resonate at δ 166.7, 162.2, and 156.0, respectively, in the ^{13}C NMR spectra, while the corresponding cycloalkenes exhibit the chemical shifts[9] of their olefinic carbons at δ 136.0, 129.6, and 126.2. Such substantial deshielding of the β carbons of the 1-cycloalkenylphosphonium salts, compared with the corresponding cycloalkenes, similarly points out significant contribution of d_π–p_π overlap between phosphorus and carbon (eq 6) for the 1-cycloalkenylphosphonium salts, as



(6)

2a, 13a, 14a 2b, 13b, 14b

2, n = 1; 13, n = 2; 14, n = 3

Schweizer and co-workers have discussed in the ^{13}C NMR of vinyltriphenylphosphonium bromide.[4] However, the differences in chemical shifts (29.8–32.6 ppm) between the β carbons of the 1-cycloalkenylphosphonium salts and the olefinic carbons of the corresponding cycloalkenes are approximately 8 ppm larger than that (22.4 ppm) between the corresponding carbon chemical shifts for the vinylphosphonium salt and ethylene. This fact suggests that the contribution of d_π–p_π overlap between phosphorus and α carbons in the 1-cycloalkenylphosphonium salts is more important than in the vinylphosphonium salt, since the ring strain of the 1-cycloalkenylphosphonium salts would be presumably reduced by overlap of a filled π orbital with an empty d orbital on phosphorus.

Similar low-field shifts of the β carbons of 1-cycloalkenylphosphine oxides **4** and **15** in the ^{13}C NMR spectra were found, although they are not so great as for the phosphonium homologues.

(9) Breitmaier, E.; Voelter, W. "^{13}C NMR Spectroscopy"; Verlag Chemie: Weinheim: New York, 1978; p 138.

Conclusion

The 1-cyclobutenylphosphonium salt and the 1-cyclobutenylphosphine oxide can be useful reagents for the synthesis of compounds containing the cyclobutyl moiety, which are not easily accessible, and for the preparation of the versatile 2-phosphinyl-1,3-butadiene. We have demonstrated that the 1-cyclobutenylphosphonium salt shows quite different reactivities from the medium-sized 1-cycloalkenylphosphonium salts, being due to both electronic and steric factors.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-FX-60 operating at 60 and 15.04 MHz with Me_4Si as an internal standard. IR spectra were recorded with a Shimazu IR-27c instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected. Distillations of products were carried out with a Kugelrohr apparatus, and bath temperatures are reported.

Preparation of [1-(Phenylseleno)cyclobutyl]triphenylphosphonium Perchlorate (1). The reaction of cyclobutyltriphenylphosphonium ylide (40 mmol) with phenylselenyl bromide (40 mmol) in dry tetrahydrofuran (100 mL) at −75 °C according to the established procedure[5] gave 19.7 g (36 mmol, 89%) yield of [1-(phenylseleno)cyclobutyl]triphenylphosphonium bromide: mp 202–203 °C ($CHCl_3$–ether); ^1H NMR ($CDCl_3$) δ 1.50–3.65 (br, 6 H, CH_2), 7.25–8.10 (m, 20 H, phenyl H). Treatment of the bromide salt (11.05 g, 20 mmol) with silver perchlorate (4.61 g, 20 mmol) (or sodium perchlorate) in CH_2Cl_2 (70 mL) (or aqueous ethanol) led to **[1-(phenylseleno)cyclobutyl]triphenylphosphonium perchlorate (1)**: 10.24 g (18 mmol, 90%); mp 185–186 °C (CH_2Cl_2–ether); IR (KBr) 1580, 1430, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–3.65 (br, 6 H, CH_2), 7.25–8.10 (m, 20 H, phenyl H).

Synthesis of (1-Cyclobutenyl)triphenylphosphonium Perchlorate (2). To a solution of **1** (10.21 g, 17.9 mmol) in CH_2Cl_2 (40 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (35.8 mmol) in ether/CH_2Cl_2 (1/1, 60 mL). After the solution was refluxed for 1 h, a large amount of ether was added to the reaction mixture. Filtration of the resulting precipitate afforded a 7.43 g (17.9 mmol, 99%) yield of **2**: mp 194–195 °C; IR (KBr) 1580, 1550, 1480, 1430, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.13 (br s, 4 H, CH_2), 7.30–7.95 (m, 16 H, Ph and CH=C). Anal. Calcd for $C_{22}H_{20}ClO_4P$: C, 63.72; H, 4.82. Found: C, 63.36; H, 4.86.

Alkaline Hydrolysis of 2. (A) Hydrolysis in Alcohols. A solution of **2** (1.66 g, 4 mmol) in methanol (or ethanol)/H_2O (2/3, 50 mL) containing NaOH (1.60 g, 40 mmol) was heated at reflux for 5 h. After the usual workup, distillation of the residue gave pure (2-alkoxycyclobutyl)diphenylphosphine oxides **3a,b**.

(2-Methoxycyclobutyl)diphenylphosphine oxide (3a): yield 0.92 g (3.22 mmol, 80%); bp 180 °C (3.5 mm); IR (neat) 1580, 1480, 1430, 1180, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–2.50 (m, 4 H, CH_2), 3.0 (s, 3 H, OMe), 2.90–3.45 (m, 1 H, CH—P=O), 3.85–4.50 (m, 1 H, CH–OMe), 7.10–8.0 (m, 10 H, phenyl H); MS, m/e 286 (M^+). Anal. Calcd for $C_{17}H_{19}O_2P$: C, 71.31; H, 6.69. Found: C, 71.41; H, 6.94.

(2-Ethoxycyclobutyl)diphenylphosphine oxide (3b): yield 0.88 g (2.93 mmol, 73%); bp 180 °C (2.0 mm); mp 53–55 °C; IR (neat) 1580, 1480, 1430, 1180, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 7.0 Hz, 3 H, CH_3), 1.60–2.60 (m, 4 H, CH_2), 2.85–3.50 (m, 3 H, OCH_2 and CH—P=O), 3.90–4.55 (m, 1 H, CH–OEt), 7.20–8.0 (m, 10 H, phenyl H); MS, m/e 300 (M^+). Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.99; H, 7.05. Found: C, 71.92; H, 7.05.

(B) Hydrolysis in Tetrahydrofuran. Similar treatment of **2** (1.24 g, 3 mmol) in THF/H_2O (1/1, 20 mL) gave 0.53 g (2.09 mmol, 70%) of (1-cyclobutenyl)diphenylphosphine oxide (**4**): mp 93–94 °C (hexane); IR (KBr) 1580, 1555, 1480, 1430, 1180, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.79 (br s, 4 H, CH_2), 6.72 (d, J = 4.2 Hz, 1 H, CH=C—P(O)), 7.31–7.94 (m, 10 H, phenyl H); MS, m/e 254 (M^+). Anal. Calcd for $C_{16}H_{15}OP$: C, 75.58; H, 5.95. Found: C, 75.64; H, 6.05.

1-Benzylidene-2-ethoxycyclobutane (5). To a solution of **2** (3.11 g, 7.5 mmol) in anhydrous ethanol (30 mL) was added

sodium metal (0.17 g, 7.5 mmol), and the solution was stirred at room temperature for 1 h. After benzaldehyde (0.80 g, 7.5 mmol) dissolved in 10 mL of ethanol was added to the solution, the reaction mixture was refluxed for 10 h. After the usual workup, distillation of the residue produced 0.74 g (3.94 mmol, 52%) of a 7:2 mixture of **(*E*)- and (*Z*)-1-benzylidene-2-ethoxycyclobutane [5a,b**; bp 109 °C (1.5 mm)] whose ratio was determined by gas chromatographic analysis and by ^{1}H NMR: IR (neat) 1680, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 and 1.24 (t, J = 7.14 Hz, 3 H, Me), 1.80–3.0 (m, 4 H, cyclobutyl CH_2), 3.25–3.75 (2 q, 2 H, OCH_2), 4.35–4.95 (m, 1 H, O–CH), 6.21 (q, J = 2.38 Hz, $^2/_9$ H, vinyl H), 6.41 (q, J = 2.20 Hz, $^7/_9$ H, vinyl H), 7.05–7.60 (m, 5 H, phenyl H); MS, m/e 188 (M^+). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found (for a mixture of **5a** and **5b**): C, 83.33; H, 8.40.

1-Benzylidene-2-butylcyclobutane (6). To a solution of the 2-butylcyclobutylphosphonium ylide, generated from **2** (2.07 g, 5 mmol) and *n*-butyllithium (5 mmol), in 40 mL of dry THF at room temperature was added a solution of benzaldehyde (0.53 g, 5 mmol) in 10 mL of dry THF. Then the solution was stirred for 1 h at this temperature and for 8 h at reflux. After the usual workup, distillation of the residue afforded 0.56 g (2.80 mmol, 56%) of a 1:1 mixture of **(*E*)- and (*Z*)-1-benzylidene-2-butylcyclobutane [6a,b**; bp 130 °C (2 mm)]. Pure samples of each were obtained by preparative GLC. The product **6a** had the following properties: IR (neat) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75–3.45 (m, 14 H, *n*-C_4H_9, cyclobutyl CH_2 and CH), 5.90–6.10 (m, 1 H, olefinic H), 7.05–7.35 (m, 5 H, phenyl H); MS, m/e 200 (M^+). The product **6b** had the following properties: IR (neat) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75–3.20 (m, 14 H, *n*-C_4H_9, cyclobutyl CH_2 and CH), 6.0–6.20 (m, 1 H, olefinic H), 7.05–7.40 (m, 5 H, phenyl H); MS, m/e 200 (M^+). Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found (for a mixture of **6a** and **6b**): C, 89.70; H, 9.70.

Reaction of 2 with Sodium Salicylaldehyde. The salt **2** (3.11 g, 7.5 mmol) and sodium salicylaldehyde (1.15 g, 8 mmol) were mixed in 35 mL of dry DMF, and this solution was stirred at 120 °C for 15 h. After evaporation of DMF in vacuo, the residue was extracted with ether, followed by washing with 5 % aqueous NaOH and with water. After removal of the ether, the remaining oil was distilled to give a 0.56 g (3.54 mmol, 47%) yield of **7**: bp 68 °C (1 mm); IR (neat) 1670, 1605, 1580, 1480, 1455, 1235, 1210, 1190, 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0–2.90 (m, 4 H, CH_2), 4.75–5.17 (m, 1 H, O–CH), 5.99 (d, J = 1.65 Hz, 1 H, CH=C), 6.60–7.20 (m, 4 H, aromatic H); MS, m/e 158 (M^+). The residue was chromatographed on preparative TLC with hexane–ether (4:1) as the eluent to give **8a** (0.23 g, 0.73 mmol, 19.4%) and **8b** (0.14 g, 0.44 mmol, 11.6 %). The product **8a** had the following properties: mp 142–143 °C; MS, calcd for $C_{22}H_{20}O_2$ m/e 316.1462 (M^+), found 316.1462. The product **8b** had the following properties: mp 96–101 °C; MS, calcd for $C_{22}H_{20}O_2$ m/e 316.1462 (M^+), found 316.1474.

Cyclobuta[*b*]chroman (9). The hydrogenation of **7** (0.38 g, 2.4 mmol) was accomplished in 5 h in ethanol over Pt to give **9** (0.36 g, 2.3 mmol, 94%) as a colorless oil: bp 75 °C (3 mm); IR (neat) 1600, 1575, 1480, 1450, 1220, 1115 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20–3.0 (m, 7 H, CH_2 and CH), 4.40–4.85 (m, 1 H, O–CH), 6.60–7.25 (m, 4 H, aromatic H); MS, m/e 160 (M^+). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46% H, 7.55. Found: C, 82.50; H, 7.27.

(*cis*-4,5-Bis(ethoxycarbonyl)-1-cyclohexenyl)diphenylphosphine Oxide (11a). A mixture of **4** (0.69 g, 2.7 mmol) and diethyl maleate (7 mL) was heated at 150 °C for 10 h. Removal of excess diethyl maleate under reduced pressure left 0.82 g (1.92 mmol, 71 %) of a white solid (mp 124–125 °C) whose structure was assigned as **11a** on the basis of its spectral properties: IR (KBr) 1720, 1640, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 and 1.22 (2 t, J = 7.14 Hz, 6 H, CH_3), 2.30–3.30 (br m, 6 H, CH_2 and CH), 3.80–4.35 (m, 4 H, OCH_2), 6.38 (br d, J = 19.0 Hz, 1 H, olefinic H), 7.20–7.95 (m, 10 H, phenyl H); MS, m/e 426 (M^+). Anal. Calcd for $C_{24}H_{27}O_5P$: C, 67.60; H, 6.38. Found: C, 67.21; H, 6.46.

(*trans*-4,5-Bis(ethoxycarbonyl)-1-cyclohexenyl)diphenylphosphine Oxide (11b). The adduct **11b** was similarly obtained from **4** (0.25 g, 1.0 mmol) and diethyl fumarate (4 mL) as a sticky oil: yield 0.25 g (0.59 mmol, 59%); IR (neat) 1725, 1635, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 and 1.24 (2 t, J = 7.08 Hz, 6 H, CH_3), 2.40–3.10 (m, 6 H, CH_2 and CH), 4.09 and 4.15 (2 q, 4 H, OCH_2), 6.32 (br d, J = 18 Hz, 1 H, olefinic H), 7.40–7.90 (m, 10 H, phenyl H); MS, calcd for $C_{24}H_{27}O_5P$ m/e 426.1595 (M^+), found 426.1591.

***N*-Phenyl-1,2,3,6-tetrahydro-4-(diphenylphosphinyl)phthalimide (11c).** Equimolar amounts of **4** (0.25 g, 1 mmol) and *N*-phenylmaleimide (**10c**) (0.17 g, 1 mmol) in benzene (5 mL) were reacted in a sealed tube at 150 °C for 6 h. After removal of the solvent in vacuo, the residue was crystallized from ether to give pure **11c**: 325 mg (0.76 mmol, 76%); mp 174.5–176 °C; IR (KBr) 1710, 1615, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40–3.40 (br m, 6 H, CH_2 and CH), 6.80–7.80 (br m, 16 H, phenyl H and olefinic H); MS, calcd for $C_{26}H_{22}NO_3P$ m/e 427.1336, found 427.1325.

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Registry No. $1^+ClO_4^-$, 86046-71-1; 1^+Br^-, 86046-87-9; **2**, 86046-73-3; **3a**, 86046-74-4; **3b**, 86046-75-5; **4**, 86046-76-6; **5a**, 86046-77-7; **5b**, 86046-78-8; **6a**, 86046-79-9; **6b**, 86046-80-2; **7**, 86046-81-3; **8**, 86046-82-4; **9**, 86046-83-5; **10c**, 941-69-5; **11a**, 86046-84-6; **11b**, 86046-85-7; **11c**, 86046-86-8; PhSeBr, 34837-55-3; PhCHO, 100-52-7; diethyl maleate, 141-05-9; diethyl fumarate, 623-91-6; cyclobutyltriphenylphosphonium ylide, 53213-06-2; sodium salicylaldehyde, 3116-83-4.

Supplementary Material Available: The ^{13}C NMR data (Table II) for compounds **2**, **4**, **13**, **14**, and **15** (1 page). Ordering information is given on any current masthead page.

Synthesis of 4,5,8-Eicosatrienoic Acids[1]

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The synthesis of (7-(*tert*-butyldimethylsiloxy)hepta-3,4-dien-1-yl)triphenylphosphonium iodide (**1**) is described. The ylide derived from **1** undergoes highly stereoselective Wittig reactions with aliphatic aldehydes to give a series of (7*Z*)-nonadeca-3,4,7-trien-1-ols (**4**) which were transformed into arachidonic acid analogues including (8*Z*,11*Z*,14*Z*)-eicosa-4,5,8,11,14-pentaenoic acid (**9**).

The recent determination of the structure of SRS-A and the discovery of leukotriene B_4 have opened a broad field to chemical investigation with the potential of unraveling the biochemical events in a variety of inflammatory and allergic diseases.[2] An early step in the biogenesis of these compounds was the oxygenation of arachidonic acid to 5-HPETE, catalyzed by a 5-lipoxygenase enzyme.[3] Nearly

(1) Contribution No. 641 from the Institute of Organic Chemistry, Syntex Research.

(2) For a recent survey see J. L. Marx, *Science (Washington, D.C.)*, **25**, 1380 (1982).

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