Registry No.—**1a**, 19765-82-3; **2a**, 19765-81-2; **7**, 19765-84-5; **9**, 19766-22-4; **12**, 19766-24-6; **13a**, 59034-37-6; **14a**, 59034-38-7; **15**, 33495-51-1; **17**, 59034-39-8; **18**, 59034-40-1; **19**, 59034-41-2; **20**, 59034-42-3; **21**, 59034-43-4; **22**, 59034-44-5; **23**, 59034-45-6; **24**, 59034-46-7; **25**, 59091-69-9; **28**, 59034-47-8; **29**, 59034-48-9; **30**, 81-84-5; **31a**, 518-05-8; **31b**, 10060-33-0; **32a**, 59034-49-0; **32b**, 59034-50-3; **33a**, 59034-51-4; **33b**, 59034-52-5; **34**, 59034-53-6; **36**, 3400-35-9; **37a**, 622-29-7; **38**, 579-75-9; **39b**, 59034-54-7; **40b**, 21173-69-3.

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Crown Ether Catalyzed Synthesis of Dialkylvinylidenecyclopropane Derivatives[1]

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In the phase-transfer catalyzed synthesis of dimethylvinylidenecyclopropanes from 3-chloro-3-methyl-1-butyne (**1a**) and olefins in the presence of 51% aqueous potassium hydroxide, the effect of crown ethers as the catalyst was examined in comparison with quaternary ammonium salts such as benzyltriethylammonium chloride. Crown ethers such as dibenzo-18-crown-6, dicyclohexyl-18-crown-6, and 18-crown-6 were found to be more effective catalysts than quaternary ammonium salts. Application of this method to the synthesis of some new dimethyl- and pentamethylenevinylidenecyclopropane derivatives has been described.

Recently it has been reported that the phase-transfer catalyzed generation of dimethylvinylidenecarbene can be carried out effectively by using appropriate quaternary ammonium salts such as benzyltriethylammonium chloride (BTAC)[2,3] and tricaprylylmethylammonium chloride (Aliquat-336)[4,5] as the catalyst. This method provides a facile synthesis of dimethylvinylidenecyclopropanes from 3-chloro-3-methyl-1-butyne (**1a**)[2–4] or 1-bromo-3-methyl-1,2-butadiene[5] and appropriate olefins compared to the noncatalyzed method.[6] However, quaternary ammonium salts are not always satisfactory catalysts. For example, the yields of dimethylvinylidenecyclopropanes are much lower for olefinic substrates having hydrophilic or potentially hydrophilic functions such as hydroxyl, ester, and pyridyl groups.[2a] As shown in this paper, certain crown ethers, which are powerful complexing agents for alkali metal cations, and provide highly reactive and unsolvated anions,[7,8] may be more effective or at least as effective catalysts as quaternary ammonium salts in the phase-transfer catalyzed synthesis of dialkylvinylidenecyclopropanes.[9,10]

Results and Discussion

The Catalytic Effect of Crown Ethers on Dimethylvinylidenecyclopropanation of Styrene. In order to compare the catalytic effect of crown ethers with quaternary ammonium salts, dimethylvinylidenecyclopropanation of styrene was investigated under two-phase reaction conditions by using 18-crown-6 and BTAC as the catalyst. The reaction was carried out by slow addition of **1a** (10 mmol) in benzene (5 ml) to a vigorously stirred mixture of 51% aqueous potassium hydroxide (30 ml), benzene (5 ml), and styrene (30 mmol) in the presence of the catalyst (0.7 mmol). The product **2**[6] was analyzed on GLC at appropriate times.[11] The results are shown in Figure 1. From these data it is clear that 18-crown-6 is a more effective catalyst than BTAC at all temperatures examined. Even at 45 °C, 18-crown-6 was effective, in contrast to BTAC,[2a] although the product **2** decomposed rapidly at this temperature. Hence, it seems most convenient to carry out the reaction at 25 °C (i.e., around room temperature), at which temperature the optimum yield of **2** was obtained after 5–7 h.

The catalytic effect of several other crown ethers was examined at 20–25 °C as summarized in Table I. Except for 15-crown-5 and dibenzo-24-crown-8, the three 18-crown-6 ethers gave better results than BTAC. Such ring-size effect of crown ethers as the catalyst may be attributable to the stability difference of metal–polyether complexes.[7b]

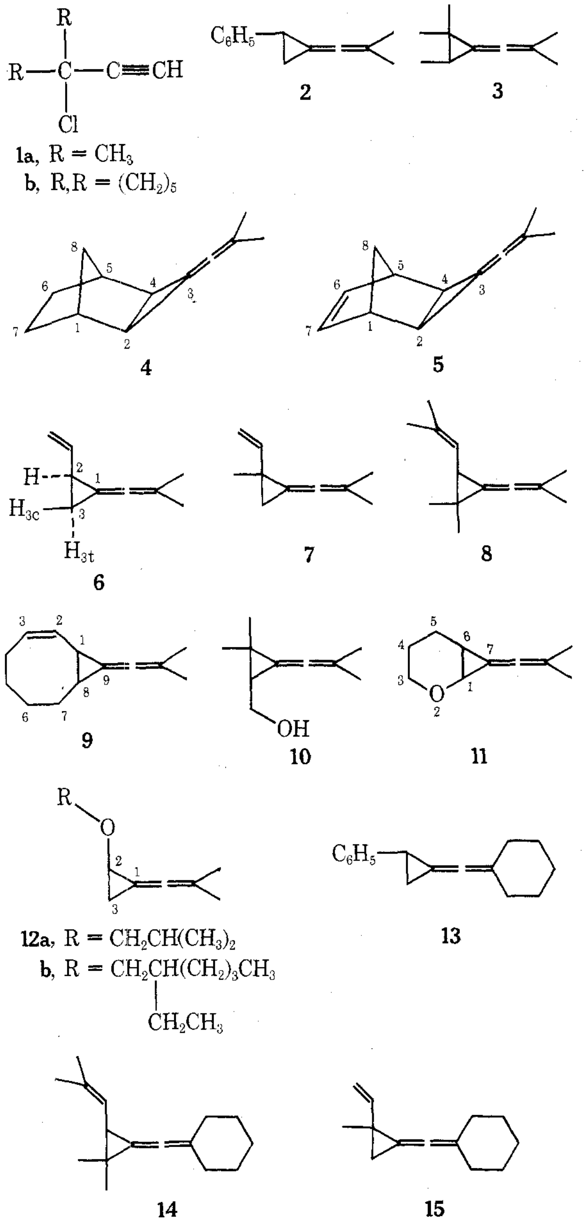
Table I. Dimethylvinylidenecyclopropanation of Styrene with Various Crown Ethers[a]

Catalyst	Yield of 2, %[b]
15-Crown-5	56.4
18-Crown-6	63.5
Dibenzo-18-crown-6	63.0
Dicyclohexyl-18-crown-6	69.0
Dibenzo-24-crown-8	10.3
BTAC	61.0[c]

[a] Reactions were carried out by method A (see Experimental Section) at 20–25 °C for 9 h. [b] Isolated yield. [c] See ref 2a.

Application of Crown Ether Catalyzed Dialkylvinylidenecyclopropanation to Various Olefins. The above dimethylvinylidenecyclopropanation with crown ethers as the catalyst was applied to various olefinic substrates and the results are summarized in Table II and Chart I.

Chart I



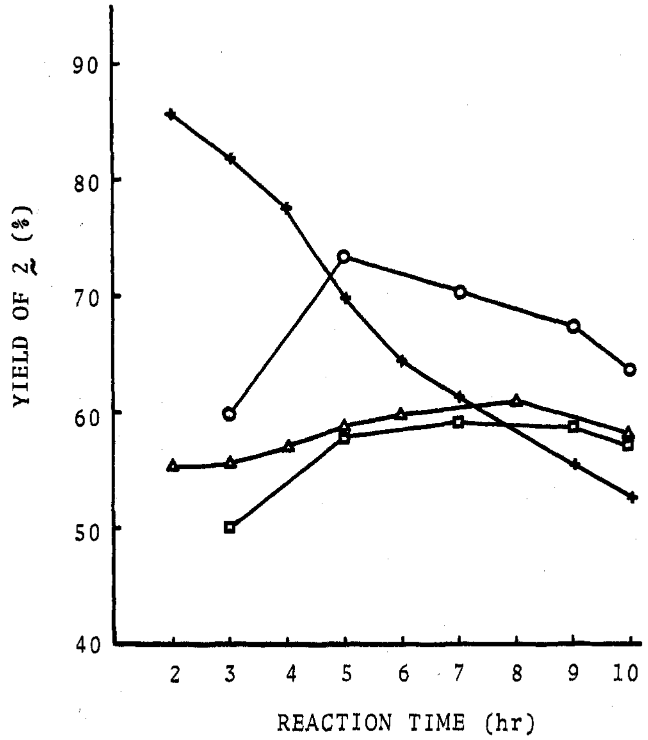


Figure 1. The yield of 2 as a function of reaction time (addition time of 1a, 2 h was involved) under the phase-transfer catalyzed conditions, in which the catalyst and reaction temperature are -×-, 18-crown-6 (45 °C); -○-, 18-crown-6 (25 °C); -△-, 18-crown-6 (5 °C); -□-, BTAC (20–25 °C).

The products 3, 7, 8, and 10 were identified by comparison of spectral (ir and NMR) data, GLC retention times, and nD values with those of authentic samples.[2a,6] The yields of these adducts were all improved considerably (10–30%) compared to those of BTAC-catalyzed reactions (see the yields in parentheses in Table II) under similar conditions.

The reaction of **1a** with norbornene and norbornadiene afforded adducts **4** and **5**, respectively, in only modest yields. The structural assignments were based on spectral and analytical data (Table III) as well as analogy to the mode of unsaturated carbene addition to those substrates.[12] In NMR spectra, appearance of the characteristic AB quartet signals at δ 0.96 (**4**) and 1.26 (**5**) supported the assigned exo configuration.

Butadiene afforded adduct **6** at −78 °C by using powdered KOH (method B in Table II) instead of aqueous KOH (method A). It should be noted that method B is obviously useful for low-boiling substrates such as butadiene, and also for hydrophilic or potentially hydrophilic substrates such as prenol or prenol acetate (Table II). However, application of method B to 4-vinylpyridine resulted in a rapid polymerization of the substrate.

Reaction of 1,3-cyclooctadiene as a cyclic conjugated olefin gave adduct **9** but in a lower yield than obtained with acyclic dienes.

Vinyl ethers such as dihydropyran, isobutyl and 2-ethylhexyl vinyl ethers as electron-rich olefins afforded the corresponding adducts **11**, **12a**, and **12b**, respectively, in better yields than cyclohexene (26%) and 1-hexene (12%).[6]

Pentamethylenevinylidenecarbene from **1b** was also successfully trapped by styrene, 2,5-dimethyl-2,4-hexadiene, and isoprene (method A) affording adducts **13**, **14**, and **15**, respectively, in moderate yields.[13] All of these adducts were characterized by analysis and spectral data (Table III).

The above results indicate that crown ethers, especially dicyclohexyl-18-crown-6, are useful catalysts for dialkylvinylidenecyclopropanation of olefins with **1a** or **1b** in the presence of potassium hydroxide.

Table II. Crown Ether Catalyzed Dialkylvinylidenecyclopropanation of Various Olefins

Olefin[g]	Precursor	Method[a] (cat.)[b]	Reaction temp, °C	Product[h]	Yield, %[c]	Bp, °C (mm)	nD (temp, °C)
2-Methyl-2-butene	**1a**	A (DC-18)	20–25	**3**[d]	37.0 (23.0)[d]		
Norbornene	**1a**	A (DC-18)	20–25	**4**	18.8	75–77 (30)	1.5280 (21)
Norbornadiene	**1a**	A (DC-18)	20–25	**5**	17.7	60–62 (10)	1.5534 (22)
Butadiene	**1a**	B (DC-18)	−78	**6**	58.0	60–62 (25)	1.5199 (19)
Isoprene	**1a**	A (DC-18)	8–10	**7**[e]	38.5 (26.0)[e]		
2,5-Dimethyl-2,4-hexadiene	**1a**	A (DC-18)	20–25	**8**[e]	59.0 (28.5)[e]		
1,3-Cyclooctadiene	**1a**	A (18-C)	20–25	**9**	11.7	46–47 (0.23)	1.5482 (19)
Prenol	**1a**	B (DB-18)	20–25	**10**[f]	48.0 (45.0)[f]		
Prenol acetate	**1a**	B (DC-18)	20–25	**10**[f]	46.0 (14.5)[e]		
Dihydropyran	**1a**	A (DB-18)	20–25	**11**	37.8	65–66 (11)	1.5312 (19)
Isobutyl vinyl ether	**1a**	A	20–25	**12a**	35.2	62–63 (10)	1.4842 (19)
2-Ethyl-1-hexyl vinyl ether	**1a**	A (DC-18)	20–25	**12b**	64.9	70–74 (0.15)	1.4690 (16)
Styrene	**1b**	A (DC-18)	20–25	**13**	39.5	93–95 (0.23)	1.5921 (18)
2,5-Dimethyl-2,4-hexadiene	**1b**	A (DC-18)	20–25	**14**	36.5	84–87 (0.30)	1.5350 (17)
Isoprene	**1b**	A (18-C)	20–25	**15**	31.5	60–62 (0.25)	1.5430 (20)

[a] For detailed procedure of method A and B, see Experimental Section. [b] DC-18 = dicyclohexyl-18-crown-6; 18-C = 18-crown-6; DB-18 = dibenzo-18-crown-6. [c] Isolated yield. [d] See ref 6. [e] See ref 2a. [f] See R. W. Mills, R. D. H. Murray, and R. A. Raphael, *J. Chem. Soc., Perkin Trans. 1,* 133 (1973). [g] Registry no. are, respectively, 513-35-9, 498-66-8, 121-46-0, 106-99-0, 78-79-5, 927-97-9, 1700-10-3, 556-82-1, 1191-16-8, 110-87-2, 109-53-5, 103-44-6, 100-42-5, 1111-97-3. [h] Registry no. are, respectively, 6209-75-2, 59055-13-9, 59055-14-0, 59055-15-1, 59055-16-2, 59055-17-3, 54492-86-3, 59055-18-4, 59055-19-5, 59055-20-8, 59055-21-9, 16069-36-6, 17455-13-9, 14187-32-7.

Table III. Spectral and Analytical Data of Dialkylvinylidenecyclopropane Derivatives

Compd	Ir, cm^{-1} (neat)	NMR chemical shift, δ (CCl_4, 60 MHz)	Formula	Anal.	% C	% H
4	2020, 1450, 1005, 820	2.44 (bs,[a] 2 H, H_1 and H_5), 0.96 (AB q,[b] 2 H, $H_8 \times 2$), 2.0–1.2 (m, 12 H, other H)	$C_{12}H_{16}$	Calcd Found	89.94 90.06	10.06 9.94
5	3060, 2010, 1450, 1105, 700	6.24 (t, J = 1.5 Hz, 2 H, H_6 and H_7), 2.98 (m, 2 H, H_1 and H_5), 1.73 (m, 8 H, H_2, H_4, and vMe_2[c]), 1.20 (AB q,[d] 2 H, $H_8 \times 2$)	$C_{12}H_{14}$	Calcd Found	91.08 90.97	8.92 9.03
6	3080, 2015, 1630 1445, 980, 900	5.85–4.7 (m, 3 H, $CH{=}CH_2$), 2.29 (d,d,d[e] 1 H, H_2), 1.75 (s, 6 H, vMe_2[c]), 1.88–1.55 (m, 1 H, H_{3t}), 1.29 (d,d,[f] 1 H, H_{3c})	C_9H_{12}	Calcd Found	89.94 89.93	10.06 10.07
9	3020, 2018, 1641, 1455, 670	5.8–5.1 (m, 2 H, $CH{=}CH$), 1.72 (s, 6 H, vMe_2[c]), 2.7–1.05 (m, 10 H, other H)	$C_{13}H_{18}$	Calcd Found	89.59 89.66	10.41 10.34
11	2008, 1435, 1100 770	3.95 (d, J = 7.0 Hz, 1 H, H_1), 3.46 (m, 2 H, $H_3 \times 2$), 1.79 and 1.73 (each s, each 3 H, vMe_2[c]), 2.2–1.1 (m, 5 H, other H)	$C_{10}H_{14}O$	Calcd Found	79.95 80.01	9.39 9.34
12a	3050, 2020, 1450 1180, 1080	3.73 (t, J = 4.5 Hz, 1 H, H_2), 3.22 (d, J = 6.0 Hz, 2 H, OCH_2), 2.1–1.65 (m, 7 H, vMe_2[c] and C**H**Me_2), 1.55 (d, J = 4.5 Hz, 2 H, $H_3 \times 2$), 0.88 (d, J = 6.0 Hz, 6 H, CH**Me_2**)	$C_{11}H_{18}O$	Calcd Found	79.46 79.59	10.92 10.79
12b	3050, 2010, 1445, 1170, 1070	4.2–3.6 (m, 1 H, H_2), 3.6–3.1 (m, 2 H, OCH_2), 2.1–1.7 (m, 7 H, vMe_2[c] and CH), 1.65–0.6 (m, 16 H, other H)	$C_{15}H_{26}O$	Calcd Found	81.02 80.84	11.79 11.97
13	3060, 3035, 2020 1603, 755, 690	7.08 (m, 5 H, C_6H_5), 2.81 (d,d, J = 8.0 and 5.0 Hz, 1 H, H_2), 2.55–2.0 (m, 4 H, $C{=}CCH_2 \times 2$), 2.0–1.3 (m, 8 H, other H)	$C_{16}H_{18}$	Calcd Found	91.37 91.47	8.63 8.53
14	2015, 1660, 1455, 850, 770	4.88 (bd,[g] J = 7.5 Hz, 1 H, $C{=}CH$), 1.28 and 1.15 (each s, each 3 H, $C{=}CMe_2$), 2.5–1.4 (m, 17 H, other H)	$C_{16}H_{24}$	Calcd Found	88.82 88.65	11.18 11.35
15	3085, 3045, 2020, 1635, 990, 895	5.85–4.63 (ABX m, 3 H, $CH{=}CH_2$), 2.30 (bs,[a] 4 H, $C{=}CCH_2 \times 2$), 1.32 (s, 3 H, Me), 1.9–1.4 (m, 7 H, other H)	$C_{13}H_{18}$	Calcd Found	89.59 89.67	10.41 10.33

[a] bs = broad s. [b] J = 9.8 Hz, $\Delta\delta/J$ = 2.308. [c] $vMe_2 = C{=}C{=}CMe_2$. [d] J = 9.8 Hz, $\Delta\delta/J$ = 2.231. [e] $J_{H_2,H_{3c}} = 5.0$, $J_{H_2,H_{3t}} = 7.0$, $J_{H_2,HC{=}C} = 8.0$ Hz, [f] $J_{H_2,H_{3c}} = 5.0$, $J_{H_{3c},H_{3t}} = 6.8$ Hz. [g] bd = broad d.

Experimental Section[14]

General Procedure for Crown Ether Catalyzed Synthesis of Dialkylvinylidenecyclopropane Derivatives. Method A. In a 100-ml three-necked flask fitted with a dropping funnel and a mechanical stirrer, a mixture of 51% (w/w) aqueous potassium hydroxide (30 ml), benzene (5 ml), appropriate crown ether (0.5–0.7 mmol), and an olefinic substrate (30 mmol) was vigorously stirred under nitrogen. While stirring was continued, 3-chloro-3-methyl-1-butyne[15] (**1a,** 1.03 g, 10.0 mmol) or 1-chloro-1-ethynylcyclohexane[15] (**1b,** 1.43 g, 10.0 mmol) in benzene (5 ml) was added slowly to the mixture over 2 h. After the addition was completed, the mixture was stirred for a further

5–7 h. The diluted mixture with water (120 ml) was extracted with *n*-hexane or ether (4 × 30 ml). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude product which was purified by distillation under reduced pressure (Table II).

Method B. Instead of aqueous KOH in method A, powdered solid KOH was used. As an example, the reaction of butadiene is described. To a magnetically stirred and cooled (−78 °C) mixture of powdered KOH (85% purity, 4.20 g, 63.6 mmol), dicyclohexyl-18-crown-6 (0.27 g, 0.72 mmol), and butadiene (6.50 g, 120 mmol) was added **1a** (2.06 g, 20.0 mmol) slowly over 2 h under nitrogen. After stirring was continued for a further 15 h at the same temperature, the mixture was allowed to warm to room temperature in order to remove the excess butadiene and an oily residue was purified by distillation to afford **6** (1.40 g, 58.0%). Analytical and physical data of all new compounds are summarized in Tables II and III.

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Phosphonic Acid Chemistry. 1. Synthesis and Dienophilic Properties of Diethyl 2-Formylvinylphosphonate and Diethyl 2-Formylethynylphosphonate[1a,b]

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The synthesis of the title compounds, **5** and **11**, was accomplished from diethyl 3,3-diethoxy-1-propyn-1-ylphosphonate (**6**). A reported synthesis of diethyl 3,3-diethoxy-1-propen-1-ylphosphonate (**4**) from PCl_5 and ethyl allyl ether was investigated and found not to give **4** as claimed. The isomeric phosphonyl dichloride (**17**) and the isomeric vinylphosphonates, **18** and **19**, were obtained instead. The dienophiles, **5**, **11**, dimethyl acetylenedicarboxylate (**7**), and propiolaldehyde (**8**), were treated with isoprene and the order of reactivity for these dienophiles was found to be **5** > **7** > **11** > **8**. The resultant cycloadducts **21** and **23** were obtained in good yield and the structure of **23** was established unambiguously by conversion to the known xylenylphosphonic acid (**28**). This latter compound and its isomer (**30**) were prepared using photochemical Arbuzov reaction methods. The increased dienophilic reactivity of **5** and **11** as compared to **7** and **8**, respectively, was in accord with published data that the diethyl phosphonyl group exerts an activating effect on the dienophilic character of an olefin.

A number of phosphorus-containing dienes[2] and dienophiles[3–5] have been synthesized and investigated for their ability to undergo Diels–Alder reactions. The dienophilic character of **1**[6] was reported to be less than that of α,β-unsaturated carbonyl and nitrile compounds. More recently, Diels–Alder reactions have been reportedly carried out with **2**, generated in situ, from **4**[7,8] and with **3**.[9] The compound **3** was reported to react exothermically with cyclopentadiene.

The present communication describes further Diels–Alder studies, involving the dienophiles **5** and **11** (the pure cis isomer of **2**) and their synthesis from **6**. The dienophile **5** is shown to be more reactive toward isoprene than **11**, **7**, and **8**. The communication also presents evidence that the reported synthesis of **4**, which was used to generate **2**, in situ, for Diels–Alder reactions was in error. Compounds **11** and **5** were of interest because of their potential usefulness in the preparation of new and novel alicyclic analogues of pyridoxal phosphate.[1a]

$R{-}CH{=}CHPO(OC_2H_5)_2$

1, R = H
2, R = CHO
3, R = CN
4, R = $CH(OC_2H_5)_2$

$R{-}C{\equiv}CPO(OC_2H_5)_2$

5, R = CHO
6, R = $CH(OC_2H_5)_2$

$CH_3OOCC{\equiv}CCOOCH_3$
7

$HC{\equiv}CCHO$
8

Synthesis. The synthesis of **5** was done from **6**, whose preparation has been described.[1a] The acetal **6** was hydrolyzed with 97% HCOOH to give **5** in quantitative yield. The compound was isolated by fractional distillation and proved to be a stable, colorless liquid which when stored for several months at 0 °C under N_2 showed no decomposition.

The synthesis of **11** was done from **6** also. Catalytic hydrogenation of **6** using 5% $Pd/CaCO_3$, poisoned with quinoline, gave a mixture of acetals **9** and **10**, from which the cis isomer