Work-up for Measuring the Absolute Yield of Products from 1. The reaction mixture was filtered and to the filtrate was added 0.124 mmol of bibenzyl[24] as an nmr standard. The solvent was com-carefully removed on a rotary evaporator.[25] The residue was completely dissolved in $CDCl_3$ and analyzed by nmr.

Work-up for Uncomplexed Materials. After filtration, a routine ether extraction was carried out and the residue was analyzed by mass spectroscopy and nmr.

Acknowledgment. We wish to thank Professor M. D. Rausch and Dr. G. A. Moser for making their results available to us prior to publication.

Registry No.—**1**, 51286-77-2; **2**, 2734-13-6; **3**, 51286-78-3; **3**-d_2, 51349-37-2; **4**, 5675-64-9; $Cr(CO)_3(NCCH_3)_3$, 22736-49-8.

Supplementary Material Available. The 100-MHz pmr spectra in $CDCl_3$ of **1**, **3**, and the tricarbonylchromium complexed products from the deuteration of **1** (mainly **3**-d_2 with the deuteriums on the ethano bridge anti to the tricarbonylchromium group) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-1920.

References and Notes

(1) (a) Part VI: W. S. Trahanovsky, D. J. Kowalski, and M. J. Avery, *J. Amer. Chem. Soc.*, **96**, 1502 (1974). (b) Based on work by C. R. B. in partial fulfillment of the requirements for the M.S. degree at I. S. U. (c) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) See paragraph at end of paper regarding supplementary material.

(3) D. E. F. Gracey, W. B. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. B*, 1210 (1969).

(4) (a) D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 7461 (1970); (b) D. K. Wells, Ph.D. Thesis, Iowa State University of Science and Technology, 1969.

(5) H. Simon and O. Berngruber, *Tetrahedron*, **26**, 161 (1970).

(6) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969), and references cited therein.

(7) B. B. Jarvis, J. P. Govoni, and P. J. Zell, *J. Amer. Chem. Soc.*, **93**, 913 (1971).

(8) This lack of rearrangement during the catalytic reduction of the uncomplexed olefin **2** has been observed previously.[9]

(9) (a) S. J. Cristol and N. H. Hause, *J. Amer. Chem. Soc.*, **74**, 2193 (1952); (b) A. Streitwieser, Jr., M. J. Maskornick, and G. R. Ziegler, *Tetrahedron Lett.*, 3927 (1971).

(10) I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(11) G. C. Bond and P. B. Wells, *Advan. Catal.*, **15**, 91 (1964).

(12) (a) K. Schrage and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **88**, 4555 (1966); (b) R. L. Burwell, Jr., *Chem. Eng. News*, **44**, 56 (Aug 22, 1966); (c) R. L. Burwell, Jr., *Accounts Chem. Res.*, **2**, 289 (1969), and references cited therein.

(13) J. J. Philipson and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **92**, 6125 (1970).

(14) W. C. Baird, B. Franzus, and J. H. Surridge, *J. Org. Chem.*, **34**, 2944 (1969).

(15) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1298, 1314 (1965).

(16) O. S. Mills, *Pure Appl. Chem.*, **20**, 117 (1970).

(17) S. J. Cristol and W. Y. Lim, *J. Org. Chem.*, **34**, 1 (1969).

(18) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

(19) R. B. King, *J. Organometal. Chem.*, **8**, 139 (1967).

(20) W. Strohmeier, *Chem. Ber.*, **94**, 2490 (1961).

(21) Complex **1** has also been prepared by G. A. Moser and M. D. Rausch, *Syn. Reactiv. Inorg. Metal-Org. Chem.*. **4**, 37 (1974).

(22) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 333 and 1022.

(23) W. S. Trahanovsky and D. H. Bohlen, *J. Org. Chem.*. **37**, 2192 (1972).

(24) When 1,1,2,2-tetrachloroethane was used as the standard, it caused decomposition of the complex.

(25) When the dioxane was removed by washing an ether solution of the complex several times with water followed by drying with $MgSO_4$, the complex unexplainably decomposed upon removal of the ether on the rotary evaporator.

Phase-Transfer Catalyzed Synthesis of Dimethylvinylidenecyclopropane Derivatives in Aqueous Medium[1]

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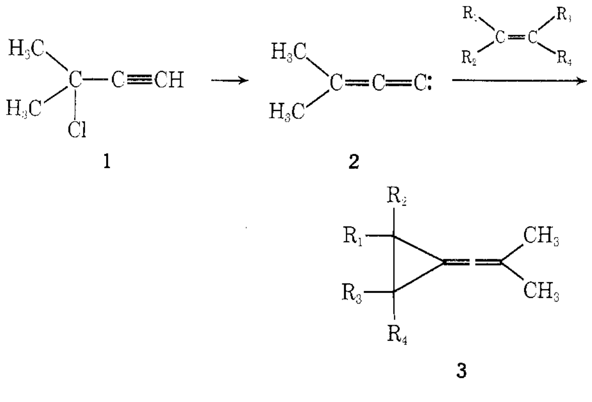
Phase-transfer catalyzed synthesis of dimethylvinylidenecyclopropane derivatives in aqueous medium from 3-chloro-3-methyl-1-butyne (**1**) and various olefins are described. Slow addition of **1** to a stirred mixture of 51% aqueous potassium hydroxide, benzene, and an appropriate substrate olefin (3-molar excess to **1**) in the presence of benzyltriethylammonium chloride as a catalyst afforded the corresponding dimethylvinylidenecyclopropane in moderate yields.

Since Hartzler's report on the generation of dimethylvinylidenecarbene (**2**) from 3-chloro-3-methyl-1-butyne (**1**) or 1-chloro-3-methyl-1,2-butadiene *via* base-catalyzed γ- or α-eliminations of hydrogen chloride, and on its reaction with some simple olefins (eq 1),[2-4] his procedure has been used widely for preparation of alkenylidenecyclopropane derivatives.[5] However, cyclopropanation of olefins with this carbene generally proceeds in low yield owing to the relatively low electrophilic reactivity of the carbene.[2,6] Furthermore, Hartzler's procedure requires rigorously anhydrous conditions for generation of the carbene **2**. This paper describes a convenient method for the generation of **2** in aqueous medium by the phase-transfer technique, and its wide applicability to the synthesis of various dimethylvinylidenecyclopropane derivatives.[7,8]



(1)

Results and Discussion

Reaction with Styrene under Various Conditions. In order to find the optimum conditions for the cyclopropanation of olefins with **2**, **1** was added to a stirred mixture of 51% aqueous potassium hydroxide[9] and styrene under several conditions (eq 2). The results are given in Table I. The best yield of the adduct 1-dimethylvinylidene [or -(2-methylpropenylidene)] -2-phenylcyclopropane (**4**)[2a] was

Table I
Yield Data of 4 under Various Conditions[a]

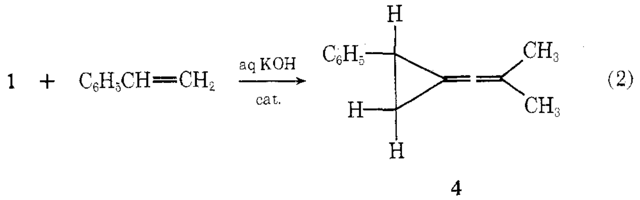
Run no.	Base	Catalyst	Solvent	Reaction temp, °C	Time,[b] hr	Stirring method	Yield, %[c]
1	51% aq KOH	$Me(CH_2)_{15}\overset{+}{N}Me_3Br^-$	*n*-Hexane	20–25	15	Magnetic	27.3
2	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	*n*-Hexane	20–25	15	Magnetic	30.0
3	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	20–25	15	Magnetic	38.6
4	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	20–25	15	Mechanical	60.1
5	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	7–10	15	Mechanical	60.7
6	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	3	Mechanical	50.0
7	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	8	Mechanical	61.0
8	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	23	Mechanical	60.0
9	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl$	Benzene	45	3	Mechanical	38.0
10	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	45	15	Mechanical	8.3
11	51% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	45	20	Mechanical	8.5
12	34% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	7	Mechanical	12.0
13	34% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	23	Mechanical	18.0
14	34% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	32	Mechanical	12.0
15	17% aq KOH	$C_6H_5CH_2\overset{+}{N}Et_3Cl^-$	Benzene	15–18	23	Mechanical	0
16	*t*-BuOK	None	*t*-BuOH	−10 to 0	3	Magnetic	35.0

[a] A 3.8-molar excess amount of styrene was used (see Experimental Section). [b] Addition time (*ca.* 2.5 hr) was involved. [c] Isolated yield. [d] A 48% yield was reported by Hartzler (ref 2a).

Table II
Dimethylvinylidenecyclopropane Derivatives from Various Olefins[a]

Olefin	Registry no.	Reaction temp, °C	Product	Yield, %[b]	Bp, °C (mm)	n_D (temp, °C)
α-Pinene	80-56-8	20–25	**3a**	20.0	62–65 (0.20)	1.5236 (25)
β-Pinene	127-91-3	20–25	**3b**	31.1	55–57 (0.20)	1.5247 (24)
Δ^3-Carene	13466-78-9	20–25	**3c**	20.0	58–60 (0.20)	1.5151 (23)
Camphene	79-92-5	20–25	**3d**	6.0	60–65 (0.27)	1.5227 (24)
1,5-Cyclooctadiene	111-78-4	20–25	**3e**	18.9	62–65 (0.26)	1.5424 (27)
Methallyl alcohol	513-42-8	20–25	**3f**	13.7	37–39 (0.20)	1.5096 (24)
Prenol acetate	1191-16-8	20–25	**3g**	14.5	54–56 (0.25)[c]	
Cinnamyl alcohol	104-54-1	20–25	**3h**	21.0	109–111 (0.23)	1.5805 (24)
2,5-Dimethyl-2,4-hexadiene	764-13-6	20–25	**3i**	28.5	40–44 (0.20)	1.5069 (22)
Isoprene	78-79-5	8–10	**3j** (+ **3j′**)[d]	26.0	68–72 (29)	1.5074 (24)
2,5-Dimethylhexa-1,5-dien-3-yne	3725-01-5	8–10	**3k**	38.1	55–57 (0.25)	1.5285 (23)
α-Methylstyrene	98-83-9	20–25	**3l**	51.5	61–65 (0.27)	1.5568 (30)
β-Methylstyrene	637-50-3	20–25	**3m**	35.7	60–64 (0.25)	1.5609 (24)
Indene	95-13-6	20–25	**3n**	15.9	75–77 (0.22),[e] mp 72–74°	

[a] The reaction was carried out under the conditions in run 4 in Table I. [b] Isolated yield. [c] Lit.[5a] bp 40° (0.02 mm). [d] 9:1 ratio. [e] Solidified distillate was recrystallized from ethanol.



4

obtained by slow addition of 1 (10 mmol) to a vigorously stirred mixture of 51% aqueous potassium hydroxide (50 ml), benzene (10 ml), and styrene (38.4 mmol) in the presence of a catalytic amount (150 mg) of benzyltriethylammonium chloride (BTA). The data in Table I shows that, as a phase-transfer catalyst, BTA was more effective than cetyltrimethylammonium bromide, and, as an organic solvent, benzene gave somewhat better results than *n*-hexane. Mechanical stirring was more effective than magnetic stirring. The reactions at 8-10 and at 20-25° gave similarly good results, but that at 45° gave a very low yield of **4**. This is due to some decompositions of the product **4** and to occurrence of some side reactions because several unidentified products were detectable on glc analysis. The decomposition of **4** was not serious at below 25° under the reaction conditions. Higher concentration of the base gave better results than lower ones.

Reaction of 2 with Various Olefins. Reactions of **2** with various olefinic substrates, including mono- and bicyclic olefins, olefins having alcoholic or ester functions, and conjugated olefins, were carried out under the conditions given at run 4 or 5 in Table I. These results are summarized in Table II and Chart I.

Chart I

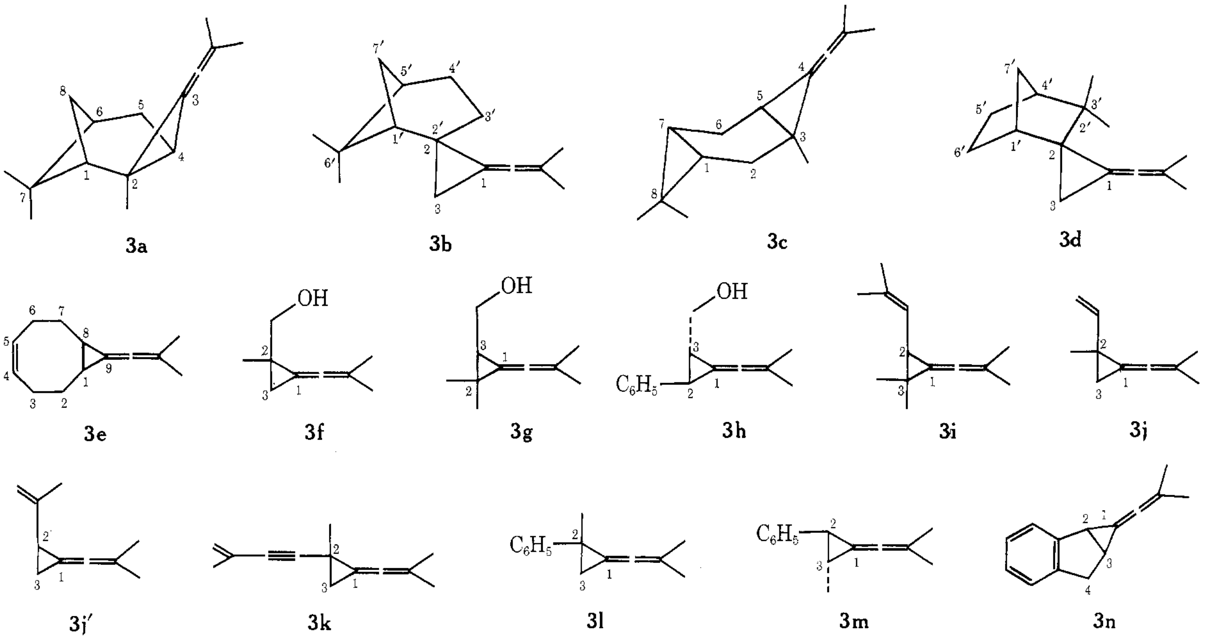


Table III
Spectral Data for Dimethylvinylidenecyclopropane Derivatives 3a–n[a,h]

Compd	Ir, cm^{-1} (neat)	Nmr chemical shift, δ (CCl_4)
3a	2010, 1450, 1370, 1030	1.75 (s, 6 H, vMe$_2$[b]), 1.30 (s, 6 H, C_7Me_2), 1.10 (s, 3 H, C_2Me), 1.07 (d, 1 H, J = 7 Hz, C_8H syn to C=C=C), 2.5–1.4 (m, 6 H, other H)
3b	2010, 1445, 1365, 1017	1.66 (s, 6 H, vMe$_2$), 1.30 (s, 2 H, C_3H_2), 1.8–1.4 (m, 2 H, $C_{1'}H$, $C_{3'\text{-endo}}H$), 1.17 (s, 3 H, $C_{6'\text{-endo}}Me$), 0.97 (s, 3 H, $C_{6'\text{-exo}}Me$), 2.4–1.7 (m, 6 H, other H)
3c	2000, 1442, 1372, 1020	1.65 (s, 6 H, vMe$_2$), 1.12 (s, 3 H, $C_{8\text{-endo}}$-Me), 0.97 (s, 3 H, $C_{8\text{-exo}}Me$), 0.77 (s, 3 H, C_3Me), 0.40 (d, d, 1 H, J = 9.2 and 4.6 Hz, C_5H), 2.5–1.2 (m, 6 H, other H)
3d	2012, 1445, 1362, 1295, 1020	1.72 (s, 6 H, vMe$_2$), 0.87 (s, 6 H, C_3Me), 2.3–1.2 (m, 10 H, other H)
3e	2005, 1445	5.63–5.38 (m, 2 H, CH=CH), 1.68 (s, 6 H, vMe$_2$), 2.5–1.7 (m, 10 H, other H)
3f	3400, 2030, 1445, 1380, 1030	3.45 (s, 2 H, CH_2OH), 2.09 (bs,[c] 1 H, OH),[d] 1.71 (s, 6 H, vMe$_2$), 2.30 (s, 3 H, C_2Me), 1.5–1.12 (m, 2 H, C_3H_2)
3h	3320, 3060, 3030, 2010, 1600, 1500, 1450, 1100, 1035, 970, 750, 690	7.6–6.9 (m, 5 H, C_6H_5), 4.29 and 3.75 (each d, 2 H, J = 4.8 and 6.7 Hz, CH_2OH), 2.73 (d, 1 H, J = 4.5 Hz, C_2H) 2.4 (bs, 1 H, OH),[d] 2.35–1.9 (m, 1 H, C_3H), 1.79 (s, 6 H, vMe$_2$)[g]
3i	2003, 1658, 1448, 1376, 1145, 1065	4.85 (bd,[e] 1 H, J = 8.0 Hz, C=CH), 2.05 (d, 1 H, J = 8.0 Hz, C_2H),1.64 (s, 12 H, vMe$_2$), C=CMe$_2$), 1.26 and 1.15 (each s, 6 H, C_3Me_2)
3j[f]	2020, 1635, 1450, 995, 895	3.9–4.8 (AB pattern, m, 3 H, CH=CH$_2$), 1.70 (s, 6 H, vMe$_2$), 1.45 (s, 2 H, C_3H_2), 1.31 (s, 3 H, C_2Me)
3k	3090, 2200, 2010, 1790, 1610, 1020, 890	5.07 (bs, 2 H, C=CH$_2$), 1.85–1.72 (m, 9 H, vMe$_2$, C=CMe), 1.66–1.37 (m, 2 H, C_3H_2), 1.40 (s, 3 H, C_2Me)
3l	3060, 3040, 2010, 1600, 1500, 1445, 1060, 1025, 760, 690	7.12 (s, 5 H, C_6H_5), 1.79 (s, 6 H, vMe$_2$), 1.65 (s, 3 H, C_2Me), 1.60 (s, 2 H, C_2H_2)
3m	3060, 3030, 2005, 1600, 1495, 1445, 1012, 750, 692	7.25–6.8 (m, 5 H, C_6H_5), 2.39 (d, 1 H, J = 4.5 Hz, C_2H), 1.75 (s, 6 H, vMe$_2$), 1.7–1.4 (m, 1 H, C_3H), 1.34 (d, 3 H, J = 6.0 Hz, C_3Me)
3n	3060, 3010, 2001, 1600, 1440, 1100, 775, 712	7.3–6.8 (m, 4 H, phenyl), 3.3–3.0 (m, 3 H, C_1H, C_4H_2), 2.7–2.4 (m, 1 H, C_3H), 1.68 and 1.55 (each s, 6 H, vMe$_2$)

[a] For **3g,** see ref 5a. [b] vMe$_2$ = C=C=CMe$_3$. [c] bs = broad s. [d] Disappeared on shaking with D_2O. [e] bd = broad d. [f] The signals due to isomeric **3j′** overlapped at δ 4.47 and 1.7–1.4. Glc analysis showed a 9:1 ratio of **3j**:**3j′**. [g] In $CDCl_3$. [h] Satisfactory elemental analytical data were reported for all compounds in the table.

Bicyclic monoterpene olefins such as α-pinene, β-pinene, and Δ^3-carene afforded the corresponding adducts 3a, 3b, and 3c, respectively, in modest yields, but camphene gave only a very low yield of the adduct 3d.[10] The structures of these adducts were characterized by analytical and spectral data (Table III).[11]

1,5-Cyclooctadiene afforded the adduct 3e but norbornene as a strained olefin did not afford any isolable amount of the corresponding adduct.[12]

Olefinic alcohols such as methallyl alcohol and cinnamyl alcohol, and esters like prenol acetate, afforded the adducts **3f, 3h,** and **3g,**[5a] respectively; the acetate group of prenol acetate was hydrolyzed simultaneously to afford **3g,** which is known to be obtained from **1** and prenol with *tert*-butoxide.[5a]

The reactions with conjugated olefins, especially those having phenyl substituents, afforded better yields of the adducts. Symmetrically substituted 2,6-dimethyl-2,4-hexadiene afforded the adduct **3i.** In the reaction with unsymmetrically substituted isoprene, a 9:1 mixture of isomeric adducts **3j** and **3j′** was obtained as demonstrated by glc and nmr analyses. Such a higher reactivity of the methyl-substituted double bond of isoprene is well known for dihalocarbenes and acyl- and carbethoxycarbenes.[13]

2,5-Dimethylhexa-1,5-dien-3-yne as an olefinic substrate conjugated with a triple bond afforded an adduct **3k** to the end methylene group exclusively.[14] Diphenylacetylene as an acetylenic substrate did not afford any adduct, indicating considerably lower reactivity of **2** to the triple bond.

Styrene derivatives such as α-methyl- and β-methylstyrenes afforded the adducts **3l** and **3m** in moderate yields but indene as a cyclic substrate gave only a low yield of **3n**.[15]

Reactions with some other conjugated olefins such as cycloheptatriene and 4-vinylpyridine were also examined; however, no isolable amounts of the corresponding adducts were obtained.

Experimental Section[16]

Materials. 3-Chloro-3-methyl-1-butyne (**1**) was prepared by the reported method.[17] Prenol acetate (3-methylbut-2-enyl acetate) was prepared by the method of Halsall and Hands,[18] bp 55-56° (40 mm). All other olefinic substrates were commercially available and used after distillation.

General Procedure for Phase-Transfer Catalyzed Synthesis of Dimethylvinylidenecyclopropane Derivatives. 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[9] (50 ml), benzene (4 ml), BTA (150 mg, 0.66 mmol), and an appropriate olefin (30 mmol) was vigorously stirred for 0.5 hr at *ca.* 25° under nitrogen. While stirring was continued, 3-chloro-3-methyl-1-butyne (**1**, 1.03 g, 10.0 mmol) in benzene (6 ml) was added slowly to the mixture over 2.5 hr. After the addition was completed, the mixture was stirred for a further 10–13 hr at 20–25°. The mixture was diluted with water (200 ml) and extracted with *n*-hexane or ether (4 × 30 ml). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude adduct, which was purified by distillation under reduced pressure. The yields, boiling points, and n_D of the products **3a–n** are summarized in Table II. Spectral and analytical data are given in Table III.

Acknowledgment. The authors wish to thank Mr. Yoshihiko Tanaka, Nissin Chemical Industries, Ltd., for providing samples of **1** and some olefinic substrates and valuable suggestions.

Registry No.—**1**, 1111-97-3; **3a**, 51269-93-3; **3b**, 51269-94-4; **3c**, 51269-95-5; **3d**, 51269-96-6; **3e**, 51269-97-7; **3f**, 51269-98-8; **3g**, 32916-63-5; **3h**, 51269-99-9; **3i**, 51270-00-9; **3j**, 51270-01-0; **3j′**, 51270-02-1; **3k**, 51270-03-2; **3l**, 40922-91-6; **3m**, 33530-27-7; **3n**, 31462-23-4; **4**, 4544-23-4.

References and Notes

(1) Studies on Reactions of Isoprenoids. XIX. Part XVIII: T. Sasaki, S. Eguchi, and H. Yamada, *J. Org. Chem.*, **38**, 679 (1973).

(2) (a) H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4990 (1961); (b) *ibid.*, **83**, 4997 (1961); (c) *J. Org. Chem.*, **29**, 1311 (1964).

(3) For the possibility of a chloride anion–carbene pair of the intermediate **2**, see W. J. le Noble, Y. Tatsukami, and H. F. Morris, *J. Amer. Chem. Soc.*, **92**, 5681 (1970). See also W. J. le Noble, *ibid.*, **85**, 2434 (1965).

(4) (a) For di-*tert*-butylvinylidenecarbene, see H. D. Hartzler, *J. Amer. Chem. Soc.*, **93**, 4527 (1971); (b) for diphenylvinylidenecarbene, see D. J. Northington and W. M. Jones, *Tetrahedron Lett.*, 317 (1971); (c) for monoalkylvinylidenecarbene, see J. C. Craig and C. D. Beard, *Chem. Commun.*, 691 (1971); J. C. Craig and C. D. Beard, *ibid.*, 692 (1971); (d) for vinylallenic carbene, see J. Gore and A. Doutheau, *Tetrahedron Lett.*, 253 (1973).

(5) (a) For application to the synthesis of *trans*-chrysanthemic acid, see R. W. Mills, R. D. H. Murray, and R. A. Raphael, *J. Chem. Soc., Perkin Trans. 1*, 133 (1973); (b) for use as substrates in cycloaddition reactions, see D. J. Pasto, A. F.-T. Chen, and G. Binsch, *J. Amer. Chem. Soc.*, **95**, 1553 (1973); D. J. Pasto, A. F.-T. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, **38**, 1015 (1973).

(6) For example, in the reaction with styrene derivatives, a *ca.* 30% yield of the adduct is reported: T. B. Patrick, E. C. Haynie, and W. J. Probst, *J. Org. Chem.*, **37**, 1553 (1972).

(7) (a) For a recent review on the use of quaternary ammonium compounds in organic synthesis, see J. Dockx, *Synthesis*, 441 (1973); (b) for application of the phase-transfer catalyst to the synthesis of cyclohexylidenecyclopropane derivatives, see M. S. Newman and Z. ud Din, *J. Org. Chem.*, **38**, 547 (1973).

(8) For the mechanism of the phase-transfer catalyzed reactions, see (a) A. W. Herriot and D. Picker, *Tetrahedron Lett.*, 4521 (1972); (b) C. M. Starks, *J. Amer. Chem. Soc.*, **95**, 3613 (1973).

(9) This was prepared by dissolving commercially available potassium hydroxide (85% purity) in water.

(10) (a) For dihalocarbene addition to α-pinene, see J. Hatem and B. Waegell, *Tetrahedron Lett.*, 2069 (1971); J. Graefe, Q. T. Lam, and M. Muehlstaedt, *Z. Chem.*, **11**, 252 (1971); A. N. Vereshchagin, S. G. Vul'fson, N. I. Gubkina, and B. A. Arbuzov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2467 (1970); *Chem. Abstr.*, **75**, 20650p (1971); M. K. Saxena and M. M. Bokadia, *Indian J. Chem.*, **5**, 396 (1967); (b) for dihalocarbene addition to Δ^3-carene, see Y. P. Volkov, *Tr. Tsent Nauch.-Issled. Dezinfek. Inst.*, 387 (1969); *Chem. Abstr.*, **76**, 14725w (1972); A. N. Vereshchagin, S. G. Vul'fson, and B. A. Arbuzov, *Dokl. Akad. Nauk SSSR*, **177**, 1081 (1967); *Chem. Abstr.*, **68**, 11476h (1968); H. Frishleder, J. Graefe, H. Van Phiet, and M. Muehlstaedt, *Tetrahedron*, **25**, 2081 (1969); (c) for dihaloacarbene addition to camphene and β-pinene, see J. Graefe, Q. T. Lam, and M. Muehlstaedt, *Z. Chem.*, **11**, 304 (1971).

(11) The stereochemical assignment should be considered tentative.

(12) Dichloro- and dibromocarbene are known to afford ring-opened products of the corresponding adducts in 74–88 and 25–40% yields, respectively: (a) C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. Le Gras, and B. Waegell, *Org. Syn.*, **51**, 60 (1971); (b) C. W. Jefford, S. Mahajan, J. Waslyn, and S. Waegell, *J. Amer. Chem. Soc.*, **87**, 2183 (1965).

(13) For a recent excellent review, see "Carbenes," Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N. Y., 1973, p 291.

(14) For dichlorocarbene addition to conjugated enynes, see E. V. Dehmlow, *Chem. Ber.*, **101**, 427 (1968); see also ref 13, pp 294–295.

(15) For this compound, *cf.* I. H. Sadler and J. A. G. Stewart, *Chem. Commun.*, 1588 (1970), but no physical and spectral data are described.

(16) Boiling points are uncorrected. Nmr spectra were recorded on a JEOL-C-60HL spectrometer at 60 MHz, and ir spectra with a JASCO IRA-1 spectrometer. Glc analyses were performed with a JEOL JGC-20K gas chromatograph on a 1-m silicone SE-30 and/or Apiezon grease L column. Microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

(17) G. F. Hennion and K. W. Nelson, *J. Amer. Chem. Soc.*, **79**, 2142 (1957).

(18) T. G. Halsall and A. R. Hands, *J. Chem. Soc.*, 3251 (1961).