(2-CHLOROVINYL)CHLOROCARBENES: GENERATION AND REACTIONS WITH ALKENES*

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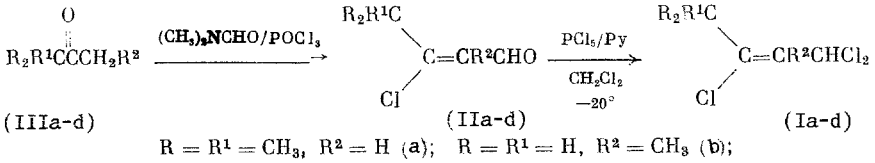
The treatment of Z-1,1,3-trichloro-4,4-dimethyl-2-pentene (Ia) with t-C_4H_9OK in boiling hexane or benzene gave rise to (Z-2-chloro-3,3-dimethyl-1-butenyl)chlorocarbene (IVa), which reacted with alkenes to give the cyclopropane derivatives (V) in 44-57% yields. Dichloro-(2-chloro-1-alkenyl)methanes (Ib-d), which have a hydrogen atom at the C_3 position of the alkenyl substituent, were also used as carbene precursors under these conditions. These compounds gave rise to mixtures of the cyclopropanes (VI)-(VIII) (obtained in up to 57% yields) and the dienes (IX)-(XI) (yields up to 54%). The reaction of cis-2-butene with (2-chloro-1-cyclopentenyl)chlorocarbene (IVd) was found to be completely stereospecific, indicating that this carbene exists in a singlet ground state.

1-Alkenyl-1-chlorocyclopropanes are versatile polyfunctional sythons [2, 3, 4]. The most general method for their preparation is the [1 + 2] cycloaddition of vinylchlorocarbenes to alkenes. The conversions of alkenes to vinylchlorocyclopropanes by reaction with perchlorovinylcarbene [3, 4], or by reaction with the carbenes formed upon treatment of 3,3-dichloro-, 1,1,3,3-tetrachloro-, and 1,2,3,3-tetrachloro-1-propene with lithium amide [2, 5], have been described. When the more easily accessible t-C_4H_9OK was used as a base, the latter two tetrachlorides gave rise to the corresponding dichlorovinylidenecyclopropanes instead of the expected gem-dichlorocyclopropanes. This is probably due to the intermediate formation of 1,3,3-trichloro-1-propyne and its subsequent conversion to dichlorovinylidenecarbene [6]. The ease of acetylene formation by base treatment of vinyl chlorides depends significantly on the structure of the latter and on the reaction conditions [7]. Previously, we have reported the first preparation of (2-chlorovinyl)chlorocarbenes by treatment of 1,1,3-trichloro-2-alkenes with t-C_4H_9OK and their ability to undergo intermolecular cyclopropanation of alkenes [1].

As an extension of these studies, we now report the reactions of a number of (2-chlorovinyl)chlorocarbenes with alkenes. These carbenes were generated from the dichloro-(2-chloro-1-alkenyl)methanes (I), which in turn were prepared by chlorination of the corresponding 3-chloro-2-alkenals (II) with PCl_5. The latter aldehydes are easily prepared by a Vilsmeier reaction from the accessible ketones (III) [8].



(IIIa-d) (IIa-d) (Ia-d)

R = R^1 = CH_3, R^2 = H (a); R = R^1 = H, R^2 = CH_3 (b);
R = H, $R^1 + R^2 = (CH_2)_3$ (c); R = H, $R^1 + R^2 = (CH_2)_2$ (d).

The vinylformylation of tert-butyl methyl ketone (IIIa) gave rise to Z-3-chloro-4,4-dimethyl-2-pentenal (IIa). The Z configuration of this compound was confirmed by the observed chemical shift of the vinyl hydrogen in its NMR spectrum and its comparison with the theoretically predicted chemical shifts for both the E and Z isomers as described in [9]. Similarly, methyl ethyl ketone (IIIb) gave a 3:7 mixture of the Z and E isomers of 3-chloro-

*For previous communication, see [1].

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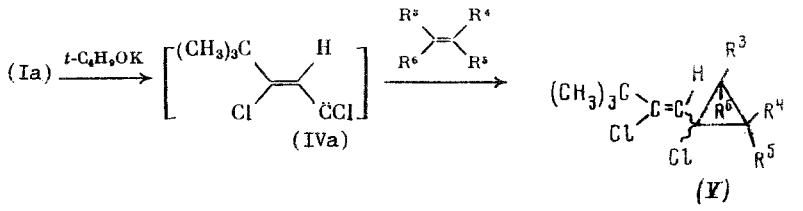
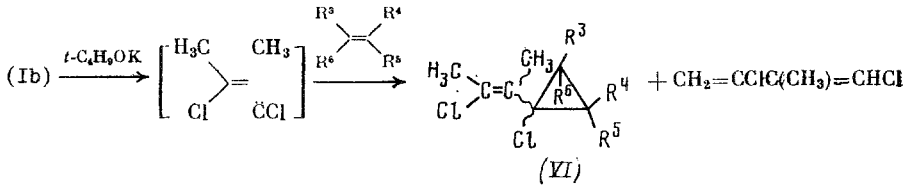
2-methyl-2-butenal (IIb) [10]. Chlorination of these aldehydes with PCl_5 produced Z-1,1,3-trichloro-4,4-dimethyl-2-pentene (Ia) and a 1:4 mixture of the Z and E isomers of 1,1,3-trichloro-2-methylbutene (Ib), respectively.

The formation of (Z-2-chloro-3,3-dimethyl-1-butenyl)chlorocarbene (IVa) by α elimination of HCl from (Ia) upon treatment with t-C_4H_9OK in boiling hexane or benzene was confirmed by its reaction with alkenes to give the corresponding cyclopropanes (V) in 44-57% yields.



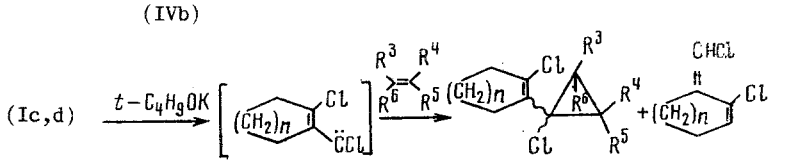
(IVa)

(V)



(VI)

(IVb)



(IVc,d) (VII), (VIII) (X), (XI)

$R^3 = R^6 = H$, $R^4 = R^5 = CH_3$ (a); $R^3 = R^4 = CH_3$, $R^5 = R^6 = H$ (b);
$R^3 = R^4 = R^5 = R^6 = CH_3$ (c); $R^3 + R^4 = (CH_2)_4$, $R^5 = R^6 = H$ (d).
$n = 1$ (IVd), (VIII), (XI), 2 (IVc), (VII), (X).

The dichloro-(2-chloro-1-alkenyl)methanes (Ib-d) have a hydrogen atom at the C_3 position. When these compounds were used for the generation of carbenes under similar conditions, the dienes (IX)-(XI) were formed in yields of up to 54% along with the cyclopropanes (VI)-(VIII) (obtained in up to 57% yields). The exact product composition depends on the structure of the starting chloride. Thus, using a tenfold molar excess of tetramethylethylene as the carbene scavenger the yield of 1,3-dichloro-2-methyl-1,3-butadiene (IX) from (Ib) was 54%, the yield of 2-chloro-3-(chloromethylene)cyclohexene (X) from (Ic) was 43%, and the yield of 2-chloro-3-(chloromethylene)cyclopentene (XI) from (Id) was 9%. The dienes (IX)-(XI) are probably formed from the carbenes (IV) by a 1,4-hydride shift [11].

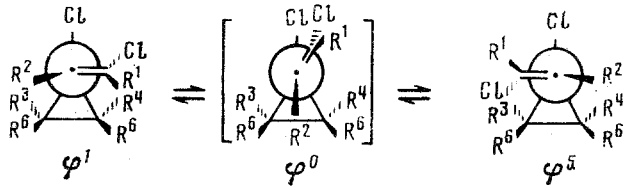
The structure of the cyclopropanes (V)-(VIII) was confirmed by IR, NMR, and mass spectroscopy (Table 1). Fairly strong molecular ion peaks with the characteristic isotopic triplets due to the presence of two chlorine atoms are seen in the mass spectra of these compounds. The IR spectra of compounds (V)-(VIII) show absorption bands at 1625-1654 cm^{-1} (C=C double bonds), whereas in their NMR spectra a group of singlets is present at δ 0.7-1.3 ppm, characteristic of methylated 1-substituted 1-chlorocyclopropanes (see [5, 12, 13]).

It should be noted that the four methyl groups of cyclopropanes (VIc) and (VIIc) have different chemical shifts in their NMR spectra. Also, in the spectrum of (VIIa) the CH_2 and $(CH_3)_2C$ fragments of the cyclopropane ring give rise to two groups of signals with an integral intensity ratio of 1.8:1 (δ, ppm, J, Hz): 0.76 d (3-H, J = 6.5), 0.8 d (6-H, J = 6.5), 1.08 s (4-CH_3), 1.42 s (5-CH_3), and 1.09 s (4-CH_3), 1.17 d (3-H, J = 7), 1.35 s (5-CH_3), 1.37 d (6-H, J = 7). These findings are in agreement with the existence of the cyclopropanes (V)-(VIII) as two stable conformers, φ^1 and φ^5 (see scheme on page 2231). Moreover, the rotational barrier around the C–C bond connecting the 2-chlorovinyl substituent with the cyclopropane ring in compounds (VIc), (VIIa), and (VIIc) is high enough to stabilize these conformations at ~20°C and to allow their observation by NMR (for a comparison with the similar gem-perchlorovinyl cyclopropanes see [4]).

TABLE 1. Spectral Data of Cyclopropanes (V)-(VIII)

Compound	R	R¹	R²	R³	R⁴	R⁵	R⁶	NMR spectrum: solvent	NMR spectrum: δ, ppm, J Hz	Mass spectrum m/z (M⁺ for Cl³⁵)	IR spectrum ν(C=C), cm⁻¹
(Va)	CH_3	CH_3^1	H^2	H^3	CH_3^4	CH_3^5	H^6	CCl_4	0,78 d (1H, H^3, $J_{3,6}$=6); 0,93 d (1H, H^6, J=6); 1,01 s (3H, CH_{3^4}); 1,12 s (9H, $C(CH_3)_2CH_3^1$); 1,28 s (3H, CH_3^5), 5,75 s (1H, H^2)	220	1634
(Vc)	CH_3	CH_3^1	H^2	CH_3^3	CH_3^4	CH_3^5	CH_3^6	C_6D_6	0,8 s (6H, CH_3^3, CH_3^4); 0,97 s (9H, $C(CH_3)_2CH_3^1$); 1,17 s (6H, CH_3^5, CH_3^6); 5,68 s (1H, H^2)	248	1632
anti-(Vd) *	CH_3	CH_3^1	H^2	$(CH_2)_4$		H^5	H^6	$CDCl_3$	1,23 s (9H, $C(CH_3)_2CH_3^1$); 1,16–2,04 m (10H, $(CH_2)_4$, H^5 & H^6); 5,84 s (1H, H^2)	246	1634
syn-(Vd) *	CH_3	CH_3^1	H^2	$(CH_2)_4$		H^5	H^6	$CDCl_3$	1,16 s (9H, $C(CH_3)_2CH_3^1$); 1,16–2,04 m (10H, $(CH_2)_4$, H^5 & H^6); 5,96 s (1H, H^2)	246	
(VIc)	H	H^1	CH_3^2	CH_3^3	CH_3^4	CH_3^5	CH_3^6	$CDCl_3$	1,05 s, 1,09 s, 120 s, 1,24 s (12H, CH_3^3, CH_3^4, CH_3^5, CH_3^6); 1,92 q (3H, CH_3^2, J=1,7); 2,16 q (3H, CH_2H^1, J=1,7)	220	1625
φ¹-(VIIa)	H	$(CH_2)_3$		H^3	CH_3^4	CH_3^5	H^6	$CDCl_3$	0,76 d (1H, H^3, $J_{3,6}$=6,5); 0,8 d (1H, H^6, J=6.5), 1,08 s (3H, CH_3^4); 1,42 s (3H, CH_3^5); 1,52–1,86 m (4H, CH_2); 2,30–2,53 m (4H, CH_2C=C)	218	1645
φ⁵-(VIIa)	H	$(CH_2)_3$		H^3	CH_3^4	CH_3^5	H^6	$CDCl_3$	1,09 s (3H, CH_3^4); 1,17 d (1H, H^3, $J_{3,6}$=7); 1,35 s (3H, CH_3^5); 1,37 d (1H, H^6, J=7); 1,52–1,86 m (4H, CH_2); 2,30–2,53 m (4H, CH_2C=C)	218	1645
(VIIc)	H	$(CH_2)_3$		CH_3^3	CH_3^4	CH_3^5	CH_3^6	$CDCl_3$	1,06 s, 1,12 s, 1,17 s, 1,25 s (12H, $CH_3^{3,4,5,6}$); 1,46–1,88 m (4H, CH_2); 2,18–2,46 m (4H, CH_2C=C)	246	1630
(VIIIa)	H	$(CH_2)_2$		H^3	CH_3^4	CH_3^5	H^6	CCl_4	090 d (1H, H^3, $J_{3,6}$=6); 0,98 s (3H, CH_3); 1,23 d (1H, H^6, J=6); 1,3 s (3H, CH_3^5); 1,6–2,2 m (2H, CH_2); 2,2–2,8 m (4H, CH_2C=C)	204	1654
Z-(VIIIb)	H	$(CH_2)_2$		CH_3^3	CH_3^4	H^5	H^6	$CDCl_3$	1,12 m (6H, CH_3^3 & CH_3^4); 1,16 m (2H, H^5 & H^6); 1,85–2,03 m (2H, CH_2); 2,43–2,65 m (4H, CH_2C=C)	204	1653
E-(VIIIb)	H	$(CH_2)_2$		CH_3^3	CH_3^4	H^5	H^6	$CDCl_3$	1,03 m (6H, CH_3^3 & CH_3^4); 1,54 m (2H, H^5 & H^6); 1,85–2,03 m (2H, CH_2); 2,43–2,65 m (4H, CH_2C=C)	204	
(VIIIc)	H	$(CH_2)_2$		CH_3^3	CH_3^4	CH_3^5	CH_3^6	CCl_4	1,05 s (6H, CH_3^3 & CH_3^4); 1,17 s (6H, CH_3^5 & CH_3^6); 1,70–2,17 m (2H, CH_2); 2,31–2,68 m (4H, CH_2C=C)	232	1650

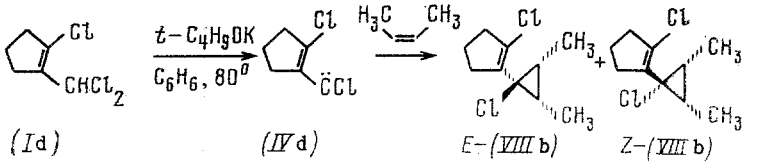
*Configurations were assigned as described in [5].



The methyl groups of compound (VIIIa) are present in its NMR spectrum at 20°C (90 MHz) as two singlets at δ 0.98 and 1.3 ppm, whereas at −50°C there are four individual singlets at δ 1.01, 1.11, 1.14, and 1.24 ppm. The temperature of coalescence is 0°C. The rotational barrier for the single C–C bond connecting the 2-chloro-1-cyclopentenyl substitutent with the cyclopropane ring can be calculated from Eq. (1) [4] as being 14.2 kcal/mole.

$$G^* = 4.57T_c\,(9.97 + \log T_c/\delta\nu) \qquad (1)$$

The addition of (2-chloro-1-cyclopentenyl)chlorocarbene (IVd) to cis-2-butene is completely stereospecific; thus this carbene must exist in the singlet state [14].



(Id) (IVd) E-(VIIIb) Z-(VIIIb)

Due to the presence of two different substituents in this carbene, the resulting cyclopropane (VIIIb) is actually a mixture of the Z and E isomers in a ratio of 4:1. Since in the Z configuration the interaction between the methyl groups and the bulky 2-chloro-1-cyclopentenyl substituent is eliminated, this configuration was assigned to the more abundant isomer [4].

It can be assumed that the structurally closely related carbenes (IVa-d) all exist in singlet ground state. This is in agreement with the singlet state of perchlorovinylcarbene, generated by thermolysis of perchlorocyclopropene [4], and also with nonempirical calculations carried out for carbenes with α-halogens [15].

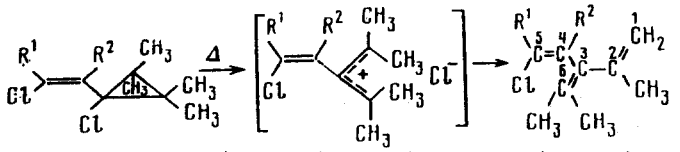
The selectivity of carbene (IVd) was determined by the method of Moss for singlet carbenes [16]. Thus, carbene (IVd) was generated by treatment of (Id) with t-C_4H_9OK in boiling benzene in the presence of a tenfold molar excesses of pairs of methyl substituted ethylenes, using isobutylene as a standard. The K/K_0 ratios were determined from the GC data (for the reaction with tetramethylethylene, the corresponding NMR data were also used). The values of K/K_0 and $\log K/K_0 + 1$ for (IVd) thus obtained, as well as the corresponding data for dichlorocarbene [17] shown for comparison, are summarized in Table 2. The selectivity index for this carbene was determined by the least squares method. The selectivity index is defined as the tangent of the slope of the line obtained by plotting $y = (\log K/K_0 + 1)_{IVd}$ against $x = (\log K/K_0 + 1)_{CCl_2}$. For the carbene under study, the selectivity index was found to be 0.62 ± 0.17. Thus, this carbene is electrophilic. The high value of standard deviation, S_m = ±0.17, is probably due to steric interactions coming into play during the reaction of (IVd) with its bulky 2-chloro-1-cyclopentenyl substituent with methyl-substituted ethylenes.

The cyclopropanes (Vc)-(VIIIc) are partially converted to the corresponding trienes (XII) during GC and GC-MS analysis. Compounds (XIIa) and (XIId) were isolated by prepara-

TABLE 2. Values of K/K_0 and $\log K/K_0 + 1$ for (2-Chloro-1-cyclopentenyl)chlorocarbene and Dichlorocarbene

Alkene	K_i/K_0		$\lg K_i/K_0+1$	
	CCl_2	(IVd)	CCl_2	(IVd)
Isobutylene	1	1	1	1
cis-2-Butene	0,23	0,16±0,03	0,36	0,20
2-Methyl-2-butene	3,05	1,70±0,08	1,48	1,23
2,3-Dimethyl-2-butene	7,41	1,26±0,05	1,86	1,10

tive gas chromatography. The triene (XIIa) could also be obtained in 81% yield by heating compound (Vc) in a sealed ampul for 6 h at 210°c.



(Vc), (VIc), (VIIc), (VIIIc) (XIIIa-d) (XIIa-d)

$R^1 = (CH_3)_3C$, $R^2 = H$ (Vc), (XIIIa), (XIIa); $R^1 = R^2 = CH_3$ (VIc), (XIIIb), (XIIb); $R^1 + R^2 = (CH_2)_3$ (VIIc), (XIIIc), (XIIc); $R^1 + R^2 = (CH_2)_2$ (VIIIc), (XIIId), (XIId).

The formation of trienes (XII) is most probably the result of a cyclopropyl–allyl rearrangement of cyclopropanes (Vc)-(VIIIc) [18]. The cations (XIII) formed as intermediates during this rearrangement are stabilized by the elimination of a proton from a methyl group.

EXPERIMENTAL

Starting materials and reaction mixtures were analyzed by gas chromatography (GC) using an LKhM-8MD chromatograph fitted with a flame ionization detector or a katharometer, and an I-02 integrator. The columns used were 0.3 × 200 cm, packed with either SP-2100 on inertone AW-HMDS or 5% Carbowax 6000 on chromatone N-AW-DMCS. The carrier gas was He, at 30 ml/min. Preparative separations were carried out using a LKhP-7I chromatograph, on a 1 × 100 cm column packed with 5% SE-30 on chromatone N-AW-DMCS, using N_2 at 400 ml/min as the carrier gas. NMR spectra were recorded on a Tesla BS-467, a Jeol FX-90Q, or a Bruker WM-250, using 3-10% solutions of the compounds in CCl_4, C_6D_6, or $CDCl_3$ with TMS as the internal standard. GC-MS analyses were carried out on a Finnigan MAT Incos-50, using a 30 m × 0.25 mm RSL-200 capillary column. IR spectra (neat or CCl_4 solutions) were taken on a Specord M-80.

3-Chloro-4,4-dimethyl-2-pentenal (IIa), 3-chloro-2-methyl-2-butenal (IIb), 2-chloro-1-formylcyclohexene (IIc), and 2-chloro-1-formylcyclopentene (IId) were prepared as described in [8].

Dichloro-(2-chloro-1-alkenyl)methanes (I), General Procedure. A solution of 0.048 mole of the aldehyde in 100 ml of CH_2Cl_2 was cooled to −35 to −30°C. To this solution was added 0.4 ml of pyridine, followed by 0.053 mole of PCl_5. The mixture was stirred at −20 to −10°C for 2 h, then 27 g of $NaHCO_3$ was added and the temperature was allowed to rise to 5°C. After 16 h at this temperature the precipitate was filtered off, the filtrate washed with a $NaHCO_3$ solution to pH 6, dried over $CaCl_2$, concentrated on a rotary evaporator, and the residue distilled in vacuum.

Compounds (Ia-d) were prepared according to this general procedure.

1,1,3-Trichloro-4,4-dimethyl-2-pentene (Ia). From 7 g (0.048 mole) of Z-(IIa) was obtained 4.35 g (45%) of (Ia), bp 76-80°C (15 mm). NMR spectrum (CCl_4, δ, ppm): 1.2 s [9H, $(CH_3)_3C$], 5.9 d (1H, CH=C, J = 9 Hz), 6.47 d (1H, $CHCl_2$, J = 9 Hz). IR spectrum (ν, cm^{-1}): 1640 (C=C). Mass spectrum, m/z: 200, 202, 204, and 206 [M^+]; 165, 167, and 169 [$M^+ - Cl$]; 119 and 121 [$M^+ - Cl, - HCl$]; 83 [$M^+ - Cl, - 2HCl$].

1,1,3-Trichloro-2-methyl-2-butene (Ib). From 5.9 g (0.05 mole) of (IIb) was obtained 4.5 g of (Ib) as a 1:4 mixture of Z and E isomers, bp 75-79°C (30 mm). NMR spectrum (CCl_4, δ, ppm, J, Hz): Z-(Ib): 1.91 q (3H, 2-CH_3, J = 1.2), 2.1 q (3H, CH_3, J = 1.2), 6.73 s (1H, $=CCHCl_2$); E-(Ib): 2.02 q (3H, 2-CH_3, J = 1.5), 2.17 q (3H, CH_3, J = 1.5), 6.53 s (1H, $=CCHCl_2$). IR spectrum (ν, cm^{-1}): 1625 (C=C). Mass spectrum, m/z: 172, 174, 176, and 178 [M^+]; 137, 139, and 141 [$M^+ - Cl$]; 101 and 103 [$M^+ - Cl, - HCl$]; 65 [$M^+ - Cl, - 2HCl$].

Dichloro-(2-chloro-1-cyclohexenyl)methane (Ic). From 7.53 g (0.052 mole) of (IIc) was obtained 6.82 g (66%) of (Ic), bp 76-79°C (5 mm). NMR spectrum (CCl_4, δ, ppm): 1.55-1.90 m (4H, CH_2CH_2), 2.23-2.65 m (4H, $CH_2C=CCH_2$), 6.87 s (1H, $CHCl_2$). IR spectrum (ν, cm^{-1}): 1645 (C=C). Mass spectrum, m/z: 198, 200, 202, and 204 [M^+]; 163, 165, and 167 [$M^+ - Cl$]; 127 and 129 [$M^+ - Cl, - HCl$]; 91 [$M^+ - Cl, - 2HCl$].

Dichloro-(2-chloro-1-cyclopentenyl)methane (Id). From 6.5 g (0.05 mole) of (IId) was obtained 5.68 g (61%) of (Id), bp 80-83°C (12 mm). NMR spectrum (CCl_4, δ, ppm): 1.77-2.28 m (2H, CH_2), 2.47-2.90 m (4H, $CH_2C=CCH_2$), 6.57 s (1H, $CHCl_2$). IR spectrum (ν, cm^{-1}): 1650

(C=C). Mass spectrum, m/z: 184, 186, 188, and 190 [M^+]; 149, 151, and 153 [M^+ – Cl]; 113 and 115 [M^+ – Cl, – HCl]; 77 (M^+ – Cl, – 2HCl].

Reaction of Dichloro-(2-chloro-1-alkenyl)methanes (I) with t-C_4H_9OK in the Presence of Alkenes. General Procedure. To a refluxing mixture of 0.1 mole of alkene and 0.02 mole of t-C_4H_9OK in 40 ml dry benzene (or hexane) was added 0.01 mole of (I). The mixture was refluxed until compound (I) was consumed (GC control). The precipitate was removed by filtration through silica gel, the filtrate concentrated on a rotary evaporator, and the colorless residue (free of tars at this stage) analyzed spectroscopically. Individual products were then obtained by vacuum distillation.

The following compounds were obtained according to the general procedure: (Va, c, and d), (VIc), (VIIa and c), and (VIIIa, b, and c).

1-Chloro-1-(2-chloro-3,3-dimethyl-1-butenyl)-2,2-dimethylcyclopropane (Va). From 2 g (0.01 mole) of (Ia) and isobutylene was obtained 1.05 g (47.5%) of (Va), bp 64°C (1 mm).

1-Chloro-1-(2-chloro-3,3-dimethyl-1-butenyl)-2,2,3,3-tetramethylcyclopropane (Vc). From 2 g (0.01 mole) of (Ia) and tetramethylethylene was obtained 1.1 g (44%) of (Vc), mp 42°C.

7-Chloro-7-(2-chloro-3,3-dimethyl-1-butenyl)norcarane (Vd). From 2 g (0.01 mole) of (Ia) and cyclohexene was obtained 1.4 g (57%) of (Vd) as a 2.3:1 mixture of syn- and anti-isomers, bp 106-110°C (2 mm).

1-Chloro-1-(2-chloro-1-methyl-1-propenyl)-2,2,3,3-tetramethylcyclopropane (VIc). From 0.87 g (5 mmoles) of (Ib) and tetramethylethylene was obtained 0.44 g of a residue containing 0.07 g (6%) of (VIc) and 0.37 g (54%) of (IX). NMR spectrum (CCl_4, δ, ppm, J, Hz): 1.95 d (3H, CH_3, J = 1.3), 5.28 br.d and 5.35 br.d (2H, $=CH_2$, J = 1.7), 6.67 m (1H, C=CHCl). Mass spectrum, m/z: 136, 138, and 140 [M^+]; 101 and 103 [M^+ – Cl]; 65 [M^+ – Cl, – HCl].

1-Chloro-1-(2-chloro-1-cyclohexenyl)-2,2-dimethylcyclopropane (VIIa). From 0.7 g (3.5 mmoles) of (Ic) and isobutylene was obtained 0.14 g (18%) of (VIIa) and 0.11 g (20%) of (X). NMR spectrum of (X) (CCl_4, δ, ppm): 1.53-1.92 m (2H, CH_2), 2.07-2.38 m (2H, CH_2C=CHCl), 2.39-2.68 m (2H, CH_2CH=CCl), 5.91 br.t (1H, CH_2CH=CCl), 6.44 br.s (1H, C=CHCl). Mass spectrum, m/z: 162, 164, and 166 [M^+]; 127 and 129 [M^+ – Cl]; 91 [M^+ – Cl, – HCl].

2-Chloro-1-(2-chloro-1-cyclohexenyl)-2,2,3,3-tetramethylcyclopropane (VIIc). From 2 g (0.01 mole) of (Ic) and tetramethylethylene was obtained 0.27 g (11%) of (VIIc), mp 48-50°C, and 0.71 g (43.5%) of (X), bp 74-77°C (7 mm).

1-Chloro-1-(2-chloro-1-cyclopentenyl)-2,2-dimethylcyclopropane (VIIIa). From 1 g (5.4 mmoles) of (Id) and isobutylene was obtained 0.73 g of a residue containing 0.66 g (57%) of (VIIIa) (isolated by distillation, bp 72-74°C at 1 mm), and 0.07 g (9%) of (XI). NMR spectrum of (XI) (CCl_4, δ, ppm): 2.28-2.68 m (4H, $2CH_2$ in cyclo-C_5H_5), 5.91-6.11 (2H, =CHCl and =CH). Mass spectrum, m/z: 148, 150 and 152 [M^+].

1-Chloro-1-(2-chloro-1-cyclopentenyl)-cis-2,3-dimethylcyclopropane (VIIIb). From 1 g (5.4 mmoles) of (Id) and cis-2-butene was obtained 0.44 g (40%) of (VIIIb), bp 53-55°C (1 mm).

1-Chloro-1-(2-chloro-1-cyclopentenyl)-2,2,3,3-tetramethylcyclopropane (VIIIc). From 0.92 g (5 mmoles) of (Id) and tetramethylethylene was obtained 0.55 g (48%) of (VIIIc), mp 46-48°C, and 0.09 g (12%) of (XI).

Thermal Isomerization of 1-Chloro-1-(2-chloro-3,3-dimethyl-1-butenyl)-2,2,3,3-tetramethylcyclopropane (Vc). A solution of 0.1 g of (Vc) in 2 ml of C_6D_6 was heated for 6 h in a sealed ampul at 210°C. GC analysis of the resulting mixture showed the presence of an unidentified, high-boiling product (9.5%) along with 5-chloro-2,6,6-trimethyl-3-(dimethylmethylene)-1,4-heptadiene (XIIa) (81%). NMR spectrum ($CDCl_3$, δ, ppm): 1.25 s [9H, 5-CC·$(CH_3)_3$], 1.66 s [3H, 6-C(CH_3)=], 1.78 m [6H, 6-C(CH_3)=, 2-C(CH_3)=], 4.73 m and 4.97 m (2H, 1-CH_2=), 5.97 br.s (1H, 4-CH=). Mass spectrum, m/z (I, %): 212 [M^+, Cl^{35}] (11), 177 (22), 161 (23), 155 (15), 135 (20), 133 (14), 121 (100), 120 (38), 119 (39), 103 (14), 93 (12), 91 (43), 81 (19), 79 (28), 78 (11), 77 (44), 65 (19), 57 (28), 53 (18), 41 (74), 39 (31), 29 (20), 28 (42).

2,4,4-Trimethyl-3-(2-chloro-1-cyclopentenyl)-1,3-pentadiene (XIId). This compound was isolated upon preparative chromatographic purification of compound (VIIIc) at 120°C. NMR

spectrum ($CDCl_3$, δ, ppm): 1.66 s [3H, 3-C(CH_3)=], 1.73 m [3H, 2-C(CH_3)=], 1.78 s [3H, 3-C(CH_3)=], 1.84-2.07 m (2H, CH_2); 2.44-2.68 m (4H, $CH_2C{=}C$), 4.7 m (1H, 1-CH=), 4.98 m (1H, 1-CH=). Mass spectrum, m/z (I, %): 196 [M^+, Cl^{35}] (17), 161 (58), 145 (59), 140 (16), 133 (27), 119 (18), 105 (40), 91 (25), 77 (22), 65 (16), 39 (12), 32 (22), 28 (100).

LITERATURE CITED

1. K. N. Shavrin, I. E. Dolgii, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1214 (1986).
2. R. A. Moss and R. C. Manjal, Synthesis, 425 (1979).
3. Th. Liese and A. de Meijere, Chem. Ber., 119, 2995 (1986).
4. W. Weber and A. de Meijere, Chem. Ber., 118, 2450 (1985).
5. Sch. Keyaniyan, W. Gothling, and A. de Meijere, Chem. Ber., 120, 395 (1987).
6. Sch. Keyaniyan, W. Gothling, and A. de Meijere, Tetrahedron Lett., 4105 (1984).
7. V. Jager, Methoden der Organischen Chemie (Houben-Weyl), E. Muller (ed.), Vol. V/2a, Georg Thieme Verlag, Stuttgart (1977), p. 53.
8. Z. Arnold and J. Zemljcka, Chem. Commun., No. 24, 2385 (1959).
9. C. Pascual, J. Meier, and W. Simon, Helv. Chim. Acta, 49, No. 1, 164 (1966).
10. J. M. F. Gagan, A. G. Lane, and D. Lloyd, J. Chem. Soc. C, No. 18, 2484 (1970).
11. G. L. Closs, L. E. Closs, and W. A. Boll, J. Am. Chem. Soc., 85, No. 23, 3796 (1963).
12. I. E. Dolgii, K. N. Shavrin, I. V. Krylova, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2380 (1986).
13. G. L. Closs and J. J. Coyle, J. Org. Chem., 31, No. 9, 2759 (1966).
14. P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc., 78, No. 17, 4496 (1956), P. S. Skell and A. V. Garner, J. Am. Chem. Soc., 78, No. 20, 5430 (1956).
15. J. F. Harrison, R. C. Liedtke, and J. F. Liebmann, J. Am. Chem. Soc., 101, No. 24, 7162 (1979).
16. R. A. Moss, Acc. Chem. Res., 13, No. 2, 58 (1980).
17. P. J. Stang and T. E. Fisk, J. Am. Chem. Soc., 102, No. 22, 6813 (1980).
18. G. S. Varakin and R. R. Kostikov, Current Problems of Organic Chemistry [in Russian], Leningrad University Publishing House, Leningrad (1986), p. 75.