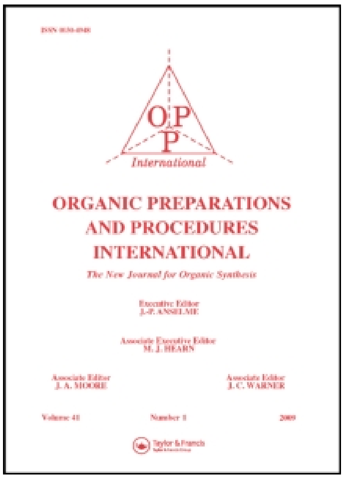

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REACTION OF 4-HOMOADAMANTENE WITH DICHLOROCARBENE[1]

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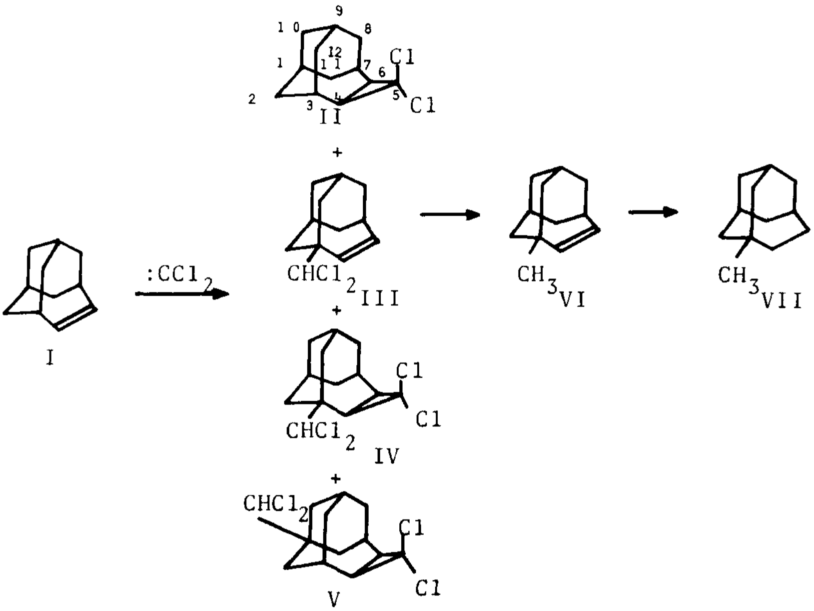
In an extension of our studies on homoadamantane derivatives,[2] we have investigated the reaction of 4-homoadamantene (I)[3] with dichlorocarbene under several conditions. The results are summarized in Scheme 1 and Table 1. Dichloro-



Scheme 1

carbene generated from the conventional system (e.g., NaOMe-CCl_3CO_2Et) was very unreactive toward the olefin I. However, by application of Seyferth's reagent[4] or especially of the phase-transfer technique,[5] I was converted to an adduct II and an insertion product III accompanied by small amounts of addition-insertion products IV and V. These products were isolated by chromatography on a silica gel column followed by recrystallization.

The major product II, mp 89-92° was assigned as a 1:1 adduct, 5,5-dichlorotetracyclo$[5.3.1.1.^{3,9}0^{4,6}]$dodecane on the basis of characteristic mass spectral ion peaks at *m/e* 230, 232 and 234 in 100:67:13 ratio and nmr signals ($CDCl_3$) at δ 2.73 (broad s, 2H), 2.49 (d, *J* 13.8 Hz, 2H), and 2.1-1.2 (m, 12H).

Oily product III was assigned as 3-dichloromethyl-4-homoadamantene, an allylic insertion product: $C_{12}H_{16}Cl_2$; *m/e* 230, 232 and 234 (100:67:16); ir (neat) 3035 and 1658 cm^{-1}; nmr ($CDCl_3$) δ 6.2-5.8 (m, 2H), 5.37 (s, 1H), 2.7-2.1 (m, 3H), and 2.05-1.3 (m, 10H). III was converted to known 3-methylhomoadamantane VII[2,6] *via* 3-methyl-4-homoadamantene VI, mp 43-48° by reduction with sodium-liquid ammonia or with sodium-*tert*-BuOH-tetrahydrofuran, followed by catalitic hydrogenation (Pd-C).

Compound IV, mp 154-156°, and V, mp 134-136°, both had the same formula $C_{13}H_{16}Cl_4$ on the basis of mass spectral ion peaks at 312, 314, 316 and 318 in 100:125:64:15 and 100:130:-60:25 ratio respectively. IV had nmr signals ($CDCl_3$) at δ 5.35 (s, 1H), 2.90 (broad s, 1H), 2.53 (d, *J* 13.8 Hz, 2H), and 2.1-1.2 (m, 12H) which permitted assignment of IV as 3-dichloromethyl-5,5-dichlorotetracyclo[$5.3.1.1.^{3,9}0^{4,6}$]dodecane. V had nmr signals ($CDCl_3$) at δ 5.53 (s, 1H), 3.1-2.3 (m, 4H), 2.2-1.1 (m, 11H) and was assigned as <u>anti</u>-1-dichloromethyl-5,5-dichlorotetracyclo[$5.3.1.1.^{3,9}0^{4,6}$]dodecane. An <u>anti</u> stereochemistry of dichloromethyl group and dichlorocyclopropane ring was tentatively assigned by appearance of the dichloromethine proton signal at <u>ca</u>. 0.2 ppm lower field than those of 1-dichloromethyladamantane (5.34).[5d] 1,3-bisdichloromethyladamantane (6.38),[7] III (5.37) and IV (5.35). These structural assignments were also supported by conversion of II to IV and V in 24:76 ratio on further treatment with dichlorocarbene by the phase-transfer method, and of III to IV exclusively.

TABLE 1 REACTION OF I WITH DICHLOROCARBENE

Reagent	Molar ratio to I	Solvent	React. conditions	Conversion (%)	Product, %[a]			
					II	III	IV	V
$CHCl_3$-KOH	10:1	C_6H_6-H_2O[b]	10°, 10 min	5	72	28	0	0
			10°, 90 min	60	59	35	1	3
			10°, 240 min	95	59	36	2	3.5
$C_6H_5HgCCl_3$	10:1	C_6H_6	refl., 90 hr	60	54	46	0	0
CCl_3CO_2Et-NaOMe	30:1	<u>n</u>-hexane	20°, 15 hr	3	75	25	0	0

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[a] Glpc analysis. [b] Catalyzed with benzyltriethylammonium chloride.

EXPERIMENTAL

Reaction of 4-Homoadamantene (I) with Dichlorocarbene under Phase-Transfer Catalyzed Conditions.-In a 50 ml., three-necked flask fitted with a dropping funnel and a mechanical stirrer, a mixture of 60% (w/w) aqueous potassium hydroxide (20 ml), benzene (2.5 ml), benzyltriethylammonium chloride (60 mg), and I (1.4 g, 9.4 mmol) was vigorously stirred for 0.5 hr at 43°. With continued stirring, the mixture was cooled with ice-water bath and chloroform (7.6 ml, 94 mmol) was added slowly to the cooled mixture over 0.5 hr. After the addition was completed the stirring was continued for 3 hr under ice-water cooling. The mixture was diluted with water (300 ml) and extracted with ether (50 ml x 6). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude product which was purified by chromatography on a silica gel column eluting *n*-hexane. The first fraction gave a mixture of II and III, from which pure II was obtained as colorless crystals after recrystallization from *n*-hexane (869 mg, 40%), mp 89-92°; ir (KBr) 2970 and 2880 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}Cl_2$: C, 62.35; H, 6.98.
Found: C, 62.39; H, 6.94.

The second fraction gave III as a colorless oil (593 mg, 27.3%).

Anal. Calcd for $C_{12}H_{16}Cl_2$: C, 62.35; H, 6.98.
Found: C, 62.48; H, 6.85.

The third fraction gave IV (39 mg, 1.3%) after recrystallization from *n*-hexane, mp 154-156°; ir (KBr) 2960, 2895, 2850 and 1445 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}Cl_4$: C, 49.71; H, 5.13.
Found: C, 49.53; H, 5.31.

The fourth fraction gave V as colorless crystals (60 mg, 2.0%) after recrystallization from *n*-hexane, mp 134-136°; ir (KBr) 2960, 2905, 2855, and 1445 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}Cl_4$: C, 49.71; H, 5.13.
Found: C, 49.73; H, 5.11.

Reduction of 3-Dichloromethyl-4-homoadamantene (III) to 3-Methyl-4-homoadamantene (VI) and 3-Methylhomoadamantane (VII).- To a refluxing mixture of tetrahydrofuran (1.5 ml), metalic sodium (260 mg, 11.3 mg atom) and *tert*-butanol (0.38 ml) was added III (217 mg, 0.943 mmol) in tetrahydrofuran (1.5 ml) under nitrogen. After refluxing for 15 hr, *tert*-butanol (0.2 ml) was added to the mixture and the refluxing was continued for further 24 hr. The remaining sodium was dissolved by addition of methanol (1 ml) and the mixture diluted with water (50 ml) and extracted with petroleum ether (bp 40-50°, 10 ml x 4). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude VI which was purified by sublimation to give VI (25 mg, 16%), mp 43-48°; ir (KBr) 3050, 2895, 2835, 1650, 1459, 1445, 945, 753, and 718 cm^{-1}; nmr ($CDCl_3$) δ 6.6-6.0 (m, 2H), 3.0-2.15 (m, 3H), and 2.15-0.6 (m, 13H).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18.
Found: C, 88.97; H, 11.05.

The Birch reduction of III by using sodium-liquid ammonia-ethanol at -78° gave also VI in 28% yield.

Catalytic hydrogenation of VI in *n*-hexane-ethanol (1:3) with 10% Pd-C afforded the known 3-methylhomoadamantane (VII).[2,6]

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7. This compound was obtained in 9% yield, mp 111-112°, together with the known dichloromethyladamantane (74%) by the reaction of adamantane with dichlorocarbene (ref 5d); our unpublished data.

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