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DEHALOGENATION OF ORGANIC HALIDES BY MEANS OF COPPER (I) CHLORIDE IN DIMETHYL SULPHOXIDE

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Abstract—Copper (I) chloride dissolved in DMSO is effective for Wurtz-type condensation of benzal bromide or dichlorodiphenylmethane affording *trans*-stilbene and tetraphenylethylene in preparative yields. The reaction of cinnamylidene chloride gives *p*-terphenyl in addition to all *trans*-1,6-diphenyl-1,3,5-hexatriene. Olefin-dihalocarbene adducts are also sensitive to this reagent and produce allenes and coupling products. Dehalogenation of *vic*-dihalides as well as halogen-exchange on olefinic carbon are described.

WURTZ-TYPE condensation has been observed in the reaction of certain organic halides with iron powder suspended in hot water[1,2] or with metal carbonyls.[3] Analogous dehalogenation condensations also occur with a homogeneous aqueous dimethylformamide solution of chromous ion.[4,5] We now report that copper (I) chloride dissolved in DMSO is an active dehalogenation reagent furnishing Wurtz-type condensates of some reactive halides. Lavine *et al.*[6] has reported that this reagent reacts with carbon tetrachloride and produces carbon dioxide and carbon

TABLE 1. WURTZ-TYPE CONDENSATION INDUCED BY 1M CuCl/DMSO SOLUTION[a]

Substrate	Reaction time hr	Product yield in %[b]
$PhCHCl_2$	5	$PhCHClCHClPh$ (*meso* 60)
$PhCCl_3$		
(Cl–Cu = 1:1·5)	12	$PhCCl_2CCl_2Ph$ (80)
(Cl–Cu = 1:2·5)	12	$PhCCl{=}CClPh$ (*cis* 51 : *trans* 13)
$PhCHBr_2$	17	$PhCH{-}CHPh$ (*trans* 60)
Ph_2CCl_2	15	$Ph_2C{=}CPh_2$ (quantitative)
$PhCH{=}CHCHCl_2$[c]	16	$PhCH{=}CHCH{=}CHCH{=}CHPh$ (all *trans* 24) and PhC_6H_4Ph (*para* 36)
$PhCH{=}CHCH_2Cl$	24	$PhCH{=}CHCH_2CH_2CH{=}CHPh$ (all *trans* 27) and $PhCH{=}CHCH_2OH$ (*trans* 28)
$PhCHBrCH_2Br$	47	$PhCH{=}CH_2$ (87)
$PhCHBrCHBrPh$ (*meso*)	40	$PhCH{=}CHPh$ (*trans* 96)
$PhCHBrCHBrCOPh$	4	$PhCH{=}CHCOPh$ (90)

[a] Unless otherwise stated the organic halides and copper (I) chloride were in the atomic ratio of 1:2·5 and the reaction was carried out at room temp.

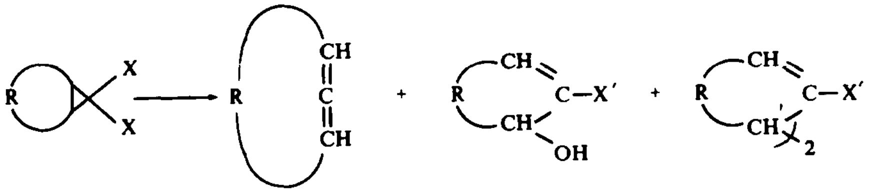
[b] Recovery was not considered in calculation of yields.

[c] The reaction was performed at 70°. At room temp an 8% yield of all *trans*-1,6-diphenyl-1,3,5-hexatriene was obtained.

monoxide. Copper (I) chloride in DMSO gives a colourless clear solution, which turns yellowish and cloudy upon stirring in a nitrogen atmosphere for several minutes.* The nature of this solution is still obscure. The reactions of benzylic and allylic halides with one mole of the copper salt in solution are summarized in Table 1.

Benzal chloride gives *meso*-α,α'-dichlorobibenzyl, whereas benzotrichloride gives a mixture of *cis* and *trans*-α,α'-dichlorostilbene. Such *vic*-dehalogenation also occurs with benzal bromide or dichlorodiphenylmethane, giving favourable yields or *trans*-stilbene and tetraphenylethylene, respectively. This is probably one of the simplest methods of preparing these hydrocarbons.† Benzyl chloride does not give even a trace of bibenzyl. This will be discussed later.

Cinnamylidene chloride gives a mixture of all *trans*-1,6-diphenyl-1,3,5-hexatriene and *p*-terphenyl—the all *trans* isomer being isolated as yellow plates by hand-sorting. Catalytic hydrogenation of the mixture followed by recrystallization furnishes *p*-terphenyl, the formation of which requires dehydrogenation, but the nature of oxidant(s) is not clear. In contrast to benzyl chloride, cinnamyl chloride gives the Wurtz-type condensate. The formation of hydrolysis products, observed in this case



I II III IV

TABLE 2. REACTION WITH OLEFIN-DIHALOCARBENE ADDUCTS

Substrate	Reaction			Recovery		Product[a]	
		Temp	Time	of I	II	III	IV
R	X	°C	hr	%	%	X' (%)	X' (%)
I_a $(CH_2)_4$	Br	45	40	nil	nil	Br (nil), Cl (17)	mixed (24)[b]
I_b $(CH_2)_6$	Br	85	24	nil	24	Br '12), Cl(20)	nil
I_c $(CH_2)_{19}$	Br[c]	55	120	nil	22	Br (23), Cl (22)	nil
I_d $(CH_2)_4$	Cl	r.t.	40	nil	nil	Cl (34)	Cl (35)
I_e $(CH_2)_{10}$	Cl						
cis		70	96	23	nil	Cl (63)	nil
I_f (*trans*[d]		85	400	92	nil	nil	nil
I_g $C_{10}H_{16}$	Br[e]	55	120	50	18	Br (42), Cl (16)	nil

[a] The yields of II, III and IV were all based on the amount of I consumed. The amounts of unchanged I were negligible with exception of Ie, If and Ig.

[b] The mixture was not separated into components.

[c] This is *cis*-cyclododecene-dibromocarbene adduct.

[d] The halide was totally unchanged (see text).

[e] Ig is *cis,trans,trans*-cyclododecatriene-dibromocarbene adduct. See Ref. 8.

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* For DMSO-metal salt complexes, see Ref. 6[c].

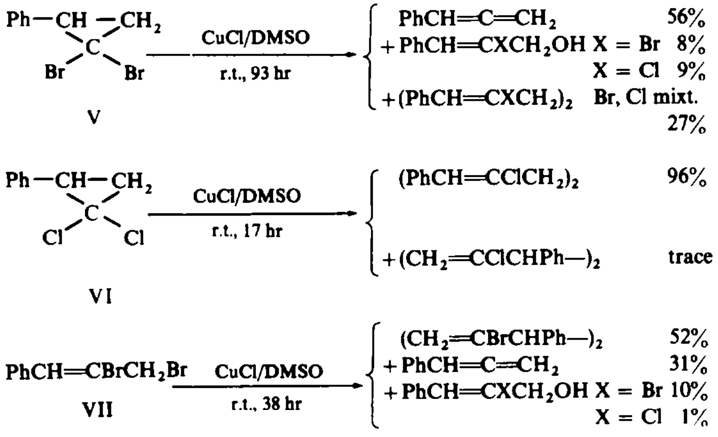
† Tetraphenylethylene has been synthesized by dehalogenation with metallic copper. See Ref. 7.

and others is summarized in Table 2. The source of the OH group is obscure.* Finally, *vic*-dibromides are more easily debrominated to olefins than the chlorides.

Table 2 records the action of the reagent on olefin-dihalocarbene adducts (I). *gem*-Dibromocyclopropanes give allenes (II). The reaction resembles that of chromous ion[4e] but the yields are considerably lower even with larger ring compounds. By-products III and IV were isolated and identified. Halogen-exchange occurs on the olefinic carbon and appears to be similar to the reaction of aryl halides with copper (I) chloride in DMSO.[9]

Parham and Sperley[10] have recorded the solvolysis of a mixture of Ie and If in water-dioxan in the presence of silver nitrate, in which the *cis*-cyclododecene adduct (Ie) gives *trans*-2-chloro-2-cyclotridecen-1-ol (IIIe) and the *trans* isomer If remains unchanged. Pure isomers of Ie and If have now been treated with copper (I) chloride in DMSO. The reaction of the *cis*-olefin adduct Ie is slow but gives a fair yield of IIIe, but the *trans*-olefin adduct If remains unchanged. This observation is explained by the account given[10] and indicates that both reagents are controlled by the common steric factor.

Dichlorocarbene adducts do not give allenic hydrocarbons (II) but allylic alcohols (III) and condensates (IV). The differences is clearly illustrated in the following reactions:



Styrene-dibromocarbene adduct V affords mainly phenylallene, whereas dichlorocarbene adduct VI gives quantitatively an allylic coupling product. β-Bromocinnamyl bromide[11] (VII) as an open chain isomer of V reacts with copper (I) chloride to give mainly an *isomerized* coupling product, which is a minor product in the reaction of VI. Comparison of these products from VII with those from V shows that part of the phenylallene may be produced by isomerization of V to VII followed by vicinal elimination. These organic halides do not react with copper (II) chloride in DMSO.

We are still not in a position to account for the observed reactions. In addition, when benzyl chloride reacts with the yellowish turbid solution of copper (I) chloride in DMSO, the solution becomes clear and colourless within 2–3 hr. The NMR

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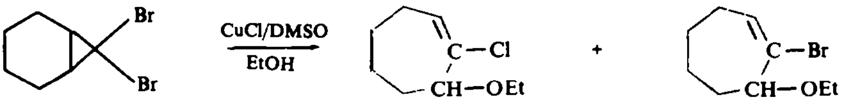
* Extra care was not directed to excluding the last trace of water in DMSO.

spectrum of this solution shows a novel CH_2 signal at δ 5·35 besides the CH_2 signal of unchanged chloride at δ 4·65 in an area-ratio of 0·4:1. Treatment of this clear solution with excess water affords benzyl alcohol in a 71% yield, whereas treatment with ethanol yields benzyl ethyl ether in a 40% yield. This observation may be formulated as follows:

$$PhCH_2Cl + Cu(I)L_n \rightleftarrows \underset{\text{VIII}}{PhCH_2\text{—}ClCu(I)L_{n-1}} \rightleftarrows$$

$$\underset{\text{IX}}{PhCH_2\text{-}\ ClCu(I)L_{n-m}(SH)_{m-1}} \rightarrow PhCH_2S \qquad L: \text{DMSO or } Cl^-;\ SH: \text{protic solvent}$$

The paramagnetic shift of the methylene signal is explained by assuming the adduct VIII. The addition of SH brings about ligand exchange followed by nucleophilic substitution on the benzylic carbon. Treatment of Ia in the presence of excess ethanol gives no dimers but solvolysis products:



Ia

The formation of a C—C bond possibly requires an intermediary organocopper compound or a copper carbenoid as postulated previously[4a, e, 12]. Work is progressing to prove these possible intermediates.

EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were obtained in $CDCl_3$ or CCl_4 soln on a 60 MHz instrument (JEOL C-60-H spectrometer) at 24°. The mass spectra were obtained on Hitachi RMU 6D spectrometer by the courtesy of Kao Soap Co. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University.

General procedure of reactions of organic halides by means of copper (I) chloride in DMSO. In a N_2 atmosphere Cu (I) Cl was dissolved in freshly distilled (over CaH_2) DMSO so to give ca. 1M soln (heating and stirring at 60–70° for 30 min), and then maintained at appropriate temp (20–80°). To this a soln (ca. 0·4M) of an organic halide in DMSO was added dropwise. The atomic ratio of halogen:Cu (I) was taken to be 1:2·5 unless otherwise stated. Heating and stirring were continued until the soln turned green and TLC indicated consumption of the halide. The mixture was treated with water and extracted with n-hexane, ether or benzene. The extract was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The products were separated and identified as usual. The following description is concerned with cases not covered by Tables 1 and 2.

Dechlorination of benzotrichloride. Benzotrichloride (4·0 g, 0·020 mole) was treated with a soln of Cu (I) Cl (10·0 g, 0·100 mole) in DMSO (70 ml) at room temp for 12 hr. Work up gave α,α,α′,α′-tetrachlorobibenzyl (2·6 g, 80%), m.p. and mixed m.p. 159–160° (EtOH) (lit.[13] 160–161°), which was identified by IR spectra. In another run benzotrichloride (1·96 g, 0·010 mole) was treated with a soln of Cu (I) Cl (7·5 g, 0·075 mole) in DMSO (60 ml) at room temp for 12 hr. Chromatography on a short alumina column, followed by recrystallization (EtOH) afforded a mixture (0·80 g, 64%) of *cis* and *trans*-α,α′-dichlorostilbene. Hand-sorting and recrystallizations gave pure constituents, the *cis* isomer (51%) as prisms, m.p. and mixed m.p. 60–62° (lit.[14] 62–63°), and the *trans* isomer (13%) as powdery microcrystals, m.p. and mixed m.p. 137–138° (lit.[14] 142°). The yields were calculated on the basis of product ratio determined by GLC (Apiezon L 30%).

Dechlorination of cinnamylidene chloride. Cinnamylidene chloride (3·8 g, 0·020 mole) was treated with a soln of Cu (I) Cl (10·0 g, 0·100 mole) in DMSO (70 ml) at 70–80° for 15 hr to give a mixture (1·60 g) of all *trans*-1,6-diphenyl-1,3,5-hexatriene (24%) and *p*-terphenyl (36%). The yields were calculated on the basis of product ratio determined by NMR. Recrystallization (EtOH) of the mixture gave all *trans*-1,6-diphenyl-1,3,5-hexatriene, m.p. 196–197° (lit.[15] 197–200°), which was further identified by IR, NMR and UV. Hydrogenation of the mixture in the presence of Raney Ni gave 1,6-diphenylhexane (oil) and unchanged *p*-terphenyl, m.p. 210–211° (EtOH) (lit.[16] 213–214°), both were identified by IR, UV and NMR.

Reaction of trans-*cinnamyl chloride. trans*-Cinnamyl chloride (10·0 g, 0·065 mole) was treated with a soln of Cu (I) Cl (16·2 g, 0·163 mole) in DMSO (100 ml) at room temp for 24 hr. The reaction products were chromatographed on a Silicagel column. Elution with n-hexane gave *trans,trans*-1,6-diphenyl-1,5-hexadiene (2·1 g, 27%), m.p. 79–81° (MeOH) (lit.[17] 82°), and elution with EtOH gave *trans*-cinnamyl alcohol (2·5 g, 28%), m.p. 32–33° (n-hexane) (lit. 33°).

Ring-cleavage of 9,9-dibromobicyclo[6.1.0]*nonane* (Ib). Dibromide Ib[18] (7·0 g, 0·025 mole) was treated with a soln of Cu (I) Cl (11·9 g, 0·120 mole) in DMSO (100 ml) at 85° for 24 hr. The reaction mixture was chromatographed on an alumina column. Elution with n-hexane gave 1,2-cyclononadiene (0·63 g, 24%), which was identified by IR and GLC retention time. Elution with EtOH followed by GLC separation (Apiezon L 30%) gave 2-chloro-2-cyclononen-1-ol (1·15 g, 20%) and 2-bromo-2-cyclononen-1-ol (0·87 g, 12%). The chloride formed an oil, b.p. 136–140°/3 mm (bath temp), IR (neat): 3380, 1645 cm^{-1}, NMR: δ (CCl_4, 8%): 5·78 (t, —CH=), 4·73 (t, methine), 2·15 (s, —OH) and 1·4–1·8 (m, methylenes). (Found: C, 62·0; H, 8·7. $C_9H_{15}OCl$ requires: C, 61·9; H, 8·7%). The bromide formed an oil, b.p. 140–145°/3 mm (bath temp), IR (neat): 3430, 1633 cm^{-1}; NMR: δ (CCl_4, 33%): 6·10 (t, —CH=), 4·68 (t, methine), 4·00 (s, —OH) and 1·4–1·8 (m, methylenes). (Found: C, 49·5; H, 7·2. $C_9H_{15}OBr$ requires: C, 49·3; H, 6·9%).

Ring-cleavage of 13,13-dibromo-cis-*bicyclo*[10.1.0]*tridecane* (Ic). Dibromide Ic[8] (7·0 g, 0·021 mole) was treated with a soln of Cu (I) Cl (10·2 g, 0·104 mole) in DMSO (100 ml) at 55° for 120 hr. Chromatography on an alumina column gave 1,2-cyclotridecadiene (0·81 g, 22%), IIIe (see below, 1·03 g, 22%) and 2-bromo-2-cyclotridecen-1-ol (1·29 g, 23%), m.p. 58–60°; IR (Nujol): 3210, 1648 cm^{-1}; NMR: δ (CCl_4, 30%): 5·98 (t, —CH=), 4·08 (t, $C\underline{H}OH$), 3·52 (s, —OH), 2·25 (m, $C\underline{H}_2CH$=) and 1·29 (complex s, methylenes). The analyses were unsatisfactory due to the presence of impurities. (Found: C, 57·9; H, 8·4. $C_{13}H_{23}OBr$ requires: C, 56·7; H, 8·4%).

Ring-cleavage of 7,7-dichlorobicyclo[4.1.0]*heptane* (Id). Dichloride Id[19] (7·0 g, 0·042 mole) was treated with a soln of Cu (I) Cl (21·0 g, 0·212 mole) in DMSO (130 ml) at room temp for 40 hr. Chromatography on an alumina column with n-hexane as an eluant gave 2,2′-dichloro-3,3′-dicycloheptenyl (1·90 g, 35%), m.p. 88–90° (n-hexane). IR (Nujol): 1645 cm^{-1}; NMR δ ($CDCl_3$, 5%): 6·00 (t, —CH=), 3·07 (m, methines) and 1·47–2·25 (m, methylenes). (Found: C, 64·6; H, 8·1. $C_{14}H_{20}Cl_2$ requires: C, 64·9; H, 7·9%). Elution with EtOH gave 2-chloro-2-cyclohepten-1-ol (2·1 g, 34%), 132–140°/15 mm (bath temp); IR (neat): 3370, 1645 cm^{-1}; NMR: δ (CCl_4, 5%): 5·98 (t, —CH=), 4·33 (m, methine), 2·28 (s, —OH), and 1·5–2·0 (m, methylenes). (Found: C, 57·2; H, 7·6. $C_7H_{11}OCl$ requires: C, 57·4; H, 7·6%).

Ring-cleavage of 13,13-dichloro-cis-*bicyclo*[10.1.0]*tridecane* (Ie). Dichloride Ie[8] (4·35 g, 0·0175 mole) was treated with a soln of Cu (I) Cl (8·7 g, 0·088 mole) in DMSO (100 ml) at 70° for 96 hr. Chromatography on a Silicagel column gave Ie (1·02 g) and *trans*-2-chloro-2-cyclotridecen-1-ol (IIIe) (1·95 g, 63%), m.p. and mixed m.p. 44–46° (*n*-hexane), which was identified by comparison with authentic sample[9e] (IR, NMR and elemental analyses).

Ring-cleavage of 13,13-dibromo-trans-*bicyclo*[10.1.0]*trideca*-cis-4-trans-8-*diene* (Ig). Dibromide Ig[8] (4·85 g, 0·0145 mole) was treated with a soln of Cu (I) Cl (8·9 g, 0·090 mole) in DMSO (90 ml) at 55° for 120 hr. Chromatography on an alumina column gave Ig (2·4 g), 1,2,6,10-cyclotridecatetraene[4e] (0·22 g, 18%), 2-bromo-2,6,10-cyclotridecatrien-1-ol (0·52 g, 43%) and 2-chloro-2,6,10-cyclotridecatrien-1-ol (0·26 g, 16%). The bromide formed an oil, 155–160°/0·08 mm (bath temp); IR (neat): 3370, 1652 cm^{-1}; NMR: δ (CCl_4, 5%): 5·78 (t, —CH=CBr—), 5·29 (m, vinylic H), 4·00 (t, methine), 2·20 (s, —OH) and 2·5–1·7 (m, methylenes). (Found: C, 57·3; H, 6·9. $C_{13}H_{19}OBr$ requires: C, 57·6; H, 7·1%). The chloride formed an oil, b.p. 143–146°/0·07 mm (bath temp); IR (neat): 3370, 1657 cm^{-1}; NMR: δ (CCl_4, 30%): 5·44 (t, —CH=CCl—), 5·20 (m, vinylic H), 4·13 (t, methine), 3·97 (s, —OH) and 2·5–1·7 (m, methylenes). (Found: C, 68·3; H, 8·5. $C_{13}H_{19}OCl$ requires: C, 68·9; H, 8·5%).

Ring-cleavage of 1,1-dibromo-2-phenylcyclopropane (V). Dibromide V[20] (7·0 g, 0·025 mole) was treated with a soln of Cu (I) Cl (12·6 g, 0·127 mole) in DMSO (100 ml) at room temp for 93 hr. Chromatography on an alumina column gave phenylallene[18] (1·70 g, 56%) and a crystalline mixture (1·38 g) of 2,5-dibromo-1,6-diphenyl-1,5-hexadiene, 2,5-dichloro-1,6-diphenyl-1,5-hexadiene and 2-bromo-5-chloro-1,6-diphenyl-

1,5-hexadiene, which was identified by mass spectra, IR and NMR. Further byproducts were β-bromocinnamyl alcohol (0·45 g, 8%) and β-chlorocinnamyl alcohol (0·38 g, 9%). β-Bromocinnamyl alcohol formed an oil, b.p. 140–145°/3 mm (bath temp); IR (neat): 3350, 1645 cm^{-1}; NMR: δ (CCl_4, 5%): 7·6–7·2 (m, phenyl), 7·00 (s, —CH═CBr—), 4·31 (s, —C$\underline{H}_2$OH) and 2·45 (s, —OH). (Found: C, 50·5; H, 4·5. C_9H_9OBr requires: C, 50·7; H, 4·3%). β-Chlorocinnamyl alcohol formed an oil, b.p. 143–153°/3 mm (bath temp); IR (neat): 3350, 1643 cm^{-1}; NMR: δ (CCl_4, 10%): 7·7–7·2 (m, phenyl), 6·75 (s, —CH═CBr—), 4·76 (s, —C$\underline{H}_2$OH) and 3·97 (m, —OH). (Found: C, 64·0; H, 5·5. C_9H_9OCl requires: C, 64·1; H, 5·4%).

Ring-cleavage and dechlorination of 1,1-*dichloro-2-phenylcyclopropane* (VI). Dichloride VI[21] (7·0 g, 0·038 mole) was treated with a soln of Cu (I) Cl (18·5 g, 0·187 mole) in DMSO (120 ml) at room temp for 17 hr. Recrystallization from EtOH gave 2,5-dichloro-1,6-diphenyl-1,5-hexadiene (5·5 g, 96%), m.p. 125–127°; IR (Nujol): 1640 cm^{-1}; NMR δ ($CDCl_3$, 4%): 7·5–7·2 (m, phenyl), 6·46 (s, PhCH═), 2·79 (s, ═CClCH$_2$—). (Found: C, 71·3; H, 5·3. $C_{18}H_{16}Cl_2$ requires: C, 71·3; H, 5·3%). The minor component of the crystalline mixture formed long hair-like needles, which were collected by hand-sorting and were identified to be 2,5-dichloro-3,4-diphenyl-1,5-hexadiene (trace), m.p. 173–175°; IR (Nujol): 1632, 890 cm^{-1}; NMR: δ ($CDCl_3$, 5%): 7·5–7·2 (m, phenyl), 5·11 and 5·01 (m, ═CH$_2$), and 4·31 (s, methines). (Found: C, 71·2; H, 5·5. $C_{18}H_{16}Cl_2$ requires: C, 71·3; H, 5·3%).

Preparation and reaction of β-bromocinnamyl bromide (VII). The preparation of VII has recently been reported.[11a] We have prepared the halide independently by a different route as follows. Styrene-dibromocarbene adduct[20] was treated with MeLi in ether at −60° to give phenylallene.[18] Br_2 (6·9 g, 0·043 mole) in $CHCl_3$ (30 ml) was added with stirring to a soln of phenylallene (5·0 g, 0·043 mole) in $CHCl_3$ (50 ml) at −20° (dry ice–MeOH) and the reaction mixture allowed to stand at room temp for 1 day. Distillation gave β-bromocinnamyl bromide, b.p. 103–104°/0·05 mm (5·2 g, 44%); IR (neat): 1635 cm^{-1}; NMR: δ (CCl_4, 20%): 7·27 (s, phenyl), 7·00 (s, —CH═) and 4·28 (s, —CH$_2$Br).

VII (4·0 g, 0·0145 mole) was treated with a soln of Cu (I) Cl (7·2 g, 0·073 mole) in DMSO (100 ml) at room temp for 38 hr. Chromatography on an alumina column with n-hexane as an eluant gave phenylallene (0·52 g, 31%) and 2,5-dibromo-3,4-diphenyl-1,5-hexadiene (1·48 g, 52%), m.p. 190–192° ($CHCl_3$); IR (Nujol): 1623, 899 cm^{-1}; NMR: δ ($CDCl_3$, 5%): 7·5–7·2 (m, phenyl), 5·60 and 5·25 (m, —CBr═CH$_2$), and 4·31 (s, PhC$\underline{H}$—). (Found: C, 54·9; H, 3·9. $C_{18}H_{16}Br_2$ requires: C, 55·1; H, 4·1%). Elution with EtOH followed by GLC separation on Apiezon L (30%) gave β-bromocinnamyl alcohol (0·30 g, 10%) and β-chlorocinnamyl alcohol (0·03 g, 1%), which were identical with the samples described above (IR spectra and GLC retention times).

Solvolysis of 7,7-*dibromobicyclo*[4.1.0]*heptane* (Ia). Dibromide Ia[19] (5·0 g, 0·020 mole) was treated with a soln of Cu (I) Cl (9·75 g, 0·098 mole) in DMSO (70 ml) and EtOH (5 ml) at 40° for 17 hr. GLC separation gave 2-chloro-3-ethoxycycloheptene (1·60 g, 47%) and 2-bromo-3-ethoxycycloheptene (0·80 g, 19%). The chloride formed an oil, b.p. 120–125°/15 mm (bath temp); IR (neat): 1643, 1100 cm^{-1}; NMR: δ (CCl_4, 5%): 6·08 (t, —CH═), 4·03 (m, methine), 3·55 (q, —OC$\underline{H}_2$CH$_3$), 2·4–1·5 (m, methylenes) and 1·18 (t, —OCH$_2$C$\underline{H}_3$). (Found: C, 61·7; H, 8·7. $C_9H_{15}OCl$ requires: C, 61·9; H, 8·7%). The bromide formed an oil, b.p. 130–134°/15 mm (bath temp); IR (neat): 1644, 1103 cm^{-1}; NMR: δ (CCl_4, 5%): 6·36 (t, —CH═), 4·13 (m, methine), 3·60 (q, —OC$\underline{H}_2$CH$_3$), 2·4–1·5 (m, methylenes) and 1·21 (t, —OCH$_2$C$\underline{H}_3$). (Found: C, 49·2; H, 6·8. $C_9H_{15}OBr$ requires- C, 49·3; H, 6·9%).

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