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Mild Dehalogenative Reduction of Tri- and Di-halogenomethyl Compounds to Lower Halides by Nickel Tetracarbonyl[1]

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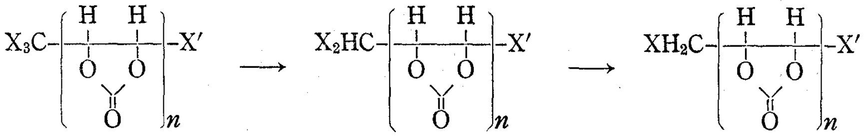
Nickel carbonyl in tetrahydrofuran reductively converts polyhalomethyl groups into di- (or mono-) halomethyls in high to moderate yields under quite mild conditions. Polyhalides studied here include type **1** telomers, arising from the radical reaction of vinylene carbonate and polyhalomethanes, whose successful reduction to *gem*-dihalides opens up a new route to aldo-sugars. Tetrahydrofuran is the most effective for the reduction among the solvents examined such as isopropanol, dioxane, tetrahydrothiophene, cyclohexene (-hexane) and benzene, while dimethylformamide gives the entirely different products like the olefines (**9**, **10**) and the carboxylic acids (**11**, **12**). The plausible mechanisms involving radical and carbene intermediates are discussed for the reactions in both solvents.

Keywords——nickel carbonyl; 1,1,1-trihalides; dehalogenative reduction; tetrahydrofuran; vinylene carbonate telomers; radicals

The need for a mild reduction of polyhalomethyl compounds to *gem*-di- and mono-halides became apparent in connection with the stereoselective synthesis of aldo-sugars[3] by free radical telomerization of vinylene carbonate with polyhalomethanes.[4] Among the reducing agents (methods)[5] which have been employed to effect such a change, only few including photolysis in tetrahydrofuran[6] appear to be mild and selective enough to permit the reductive conversion of such labile compounds as the type **1** telomers of vinylene carbonate into the lower halides, **2** and **3**, in which the carbonate rings and the substituents (X′) are retained completely unaffected. And the products have been shown to be highly potential as synthetic intermediates for aldo-sugars.[3]



1 (n=1, 2, 3…) **2** **3**

(X=Br, Cl. X′=Br, Cl, H, OCH_3, CN, $COOCH_3$)

This paper describes a promising procedure for such a selective reduction of polyhalides by nickel carbonyl under neutral conditions (at room temperature or 40° under nitrogen

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[1] A portion of this work has appeared in preliminary form: T. Kunieda, T. Tamura, and T. Takizawa, *Chem. Commun.*, **1972**, 885.

[2] Location: *Hongo, Bunkyo-ku, Tokyo, 113, Japan.*

[3] *a*) T. Takahata, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 3019 (1975); *b*) Y. Nii, T. Kunieda, and T. Takizawa, *Tetrahedron Lett.*, **1976**, 2323; *c*) T. Matsuura, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 239 (1977).

[4] T. Tamura, T. Kunieda, and T. Takizawa, *Tetrahedron Lett.*, **1972**, 2219; *idem*, *J. Org. Chem.*, **39**, 38 (1974).

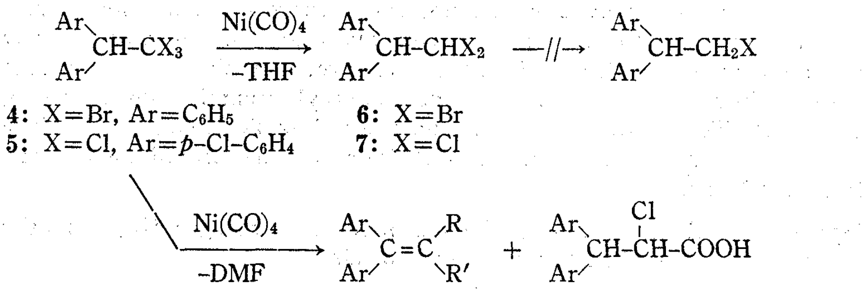
[5] *a*) C.A. Buchler and D.E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, 1970, p. 408; *b*) H.G. Kuivila, *Accounts of Chem. Research*, **1**, 299 (1968); *c*) I.M. Downie and J.B. Lee, *Tetrahedron Lett.*, **1968**, 4951; *d*) R.G. Petrova and R.K. Freidlina, *Izv. Akad. Nauk SSSR, Ser., Khim.*, **1970**, 1574; E.T. Chukovskaya, N.A. Kuzmina, and R.K. Freidlina, *ibid.*, **1970**, 2343; *e*) C.F. Lane, *Synthesis*, **1975**, 135; E.R.H. Walker, *Chem. Soc. Rev.*, **5**, 23 (1976) *etc.*

[6] N. Mitsuo, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **38**, 2255 (1973).

atmosphere) and the stepwise substitution of hydrogen for halogen may be important for the preparation of lower halides, particularly *gem*-dihalides which may serve as a protected carbonyl function.(3a,b),7)

Tribromo- and trichloro-diarylethanes **4** and **5** (DDT) chosen as model compounds were selectively reduced with an excess nickel carbonyl in tetrahydrofuran at 40° into the dihalomethyl derivatives **6** and **7** (DDD), respectively, in high yields. Generality of this reaction was further provided by similar conversion of non-activated halide, 1,1,1,3-tetrabromo-5-phenylpentane (**8**) to the *gem*-dibromide, 1,1,3-tribromo-5-phenylpentane. As might be expected, the tribromo compounds were much more rapidly converted (within several hours) than the trichloride which required more than 48 hr (Table I).

On the other hand, benzylic trihalide, *i.e.*, benzotrichloride, underwent a smooth dehalogenative dimerization on the similar treatment to give 1,1,2,2-tetrachloro-1,2-diphenylethane

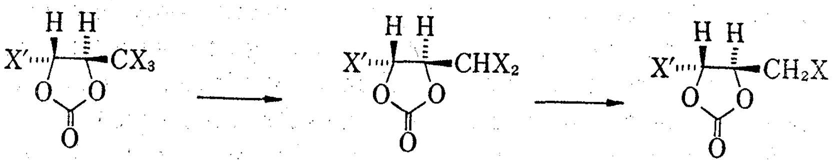


4: X=Br, Ar=C_6H_5
5: X=Cl, Ar=*p*-Cl-C_6H_4
6: X=Br
7: X=Cl

9: R=R'=Cl
10: R=H, R'=Cl
11: R=H, R'=COOH

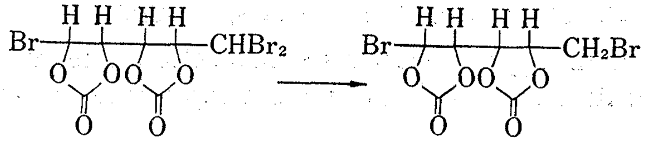
12

THF=tetrahydrofuran
DMF=dimethylformamide



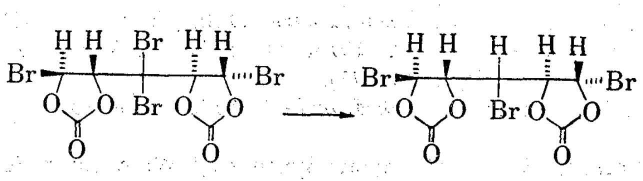
13a–**h** **14a**–**h** **15a**

	a	b	c	d	e	f	g	h
X :	Br	Br	Cl	Cl	Cl	Cl	Cl	Cl
X' :	Br	COOMe	Cl	Br	H	OMe	CN	COOMe



16a : "*syn*"-form[4)]
16b : "*anti*"-form[4)]

17a : "*syn*"-form
17b : "*anti*"-form



18 ("*anti*")8)

19 ("*anti*")

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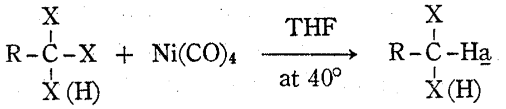
7) B.M. Trost and M.J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 2038 (1973).

8) K. Hosoda, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **24**, 2927 (1976).

Table I. Reductive Conversion of Polyhalomethyl Compounds to Lower Halides



$$\mathrm{R{-}\overset{X}{\underset{X\,(H)}{C}}{-}X + Ni(CO)_4 \xrightarrow[\text{at }40^\circ]{\text{THF}} R{-}\overset{X}{\underset{X\,(H)}{C}}{-}\underline{Ha}}$$

Compound	X	Mole ratio $Ni(CO)_4$/Halide	Reaction time (hr)	Product	Isolated yield (%)	mp [bp/mmHg] (°)	Chemical shfit(*Ha*)[a] (δ)
4	Br	2	5	**6**	86	85—86[b]	6.28
5	Cl	2	48	**7**	86	108—110[b]	6.24
8	Br	2.2	20	*c*)	60	[122/0.1]	5.83
13a	Br	3	5	**14a**(**15a**)	69(3)	[105/0.03]	5.75
13b	Br	2.5	2.5	**14b**[d]	63	oil	5.84
13c	Cl	2[e]	48	**14c**	53	31—33[b]	5.95
13d	Cl	2[e]	48	**14d**	62	[99/1]	5.80
13e	Cl	2	24	**14e**	38[f]	61—63[b]	6.00
13f	Cl	2[e]	48	**14f**	59	[102/1.5]	6.00
13g	Cl	5	28	**14g**[g]	49	oil	6.01
13h	Cl	3.3	64	**14h**[d]	70	[124/0.4]	5.96
16a	Br	*ca.* 30	18	**17a**	35	169—171[h]	3.65[i]
16b	Br	*ca.* 50	16	**17b**	42	126—128[h]	3.73[i]
18	Br	6	3	**19**	71	122—124.5[h]	4.61[i]

a) Measured in $CDCl_3$ at 60 MHz.
b) Recrystallized from *n*-hexane.
c) 1,1,3-Tribromo-5-phenylpentane.
d) Taken from ref (3a).
e) Initial molar ratio, After 24 hr, another amount (2 fold mol) of $Ni(CO_4)$ was added.
f) Recovery of **13e** was 55%.
g) Characterized by conversion to **14h**.
h) Recrystallized from $CHCl_3$.
i) In CH_3CN.

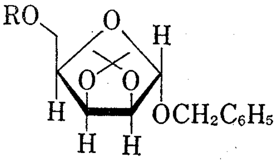
in 73% yield and no benzal chloride was detectable in analogy with the case of photolysis[6] previously described.

Tetrahydrofuran is the most effective solvent examined so far in the reduction and solvents such as dioxane, isopropanol, cyclohexene (-hexane) and benzene were practically ineffective, although a reaction carried out in tetrahydrothiophene afforded **7** in 35% yield together with unidentified products. In strong contrast, the reaction of **5** in dimethylformamide (or hexamethylphosphoramide) gave the olefinic halides **9** and **10**, and the carboxylated derivatives **11** and **12** as the major products in addition to only a trace of **7**.

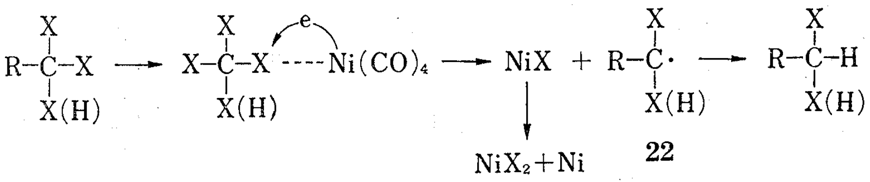
This dehalogenative reaction which proceeds smoothly in tetrahydrofuran under very mild conditions, has been successfully applied for the reductive conversion of the ethylene-carbonate derivatives[3a,4] **13a**—**h**. possessing tribromo- and trichloro-methyl groups, into *gem*-dihalides, **14a**—**h**, with the carbonate rings unaffected and the satisfactory results are summarized in Table I, comparable to the photo-induced reduction.[6] Subjecting of compound **13c** to the reducing systems of tris(diethylamino)phosphine-ethanol,[5c] iron pentacarbonyl[5d]-tetrahydrofuran and sodium cyanoborohydride[5e]-hexamethylphosphoramide gave only poor yields of **14c** (9%, 3%, and 31%, respectively).

Treatment of **13a** at 40° for 5 hr gave 69% of **14a** in addition to a small amount of monobromide **15a**, while the reaction of longer duration (overnight) resulted in a formation of 1 : 1 mixture of **14a** and **15a** (27%). This type of bromo derivative was found to be exceptionally reduced stepwise to monobromomethyl compound, in contrast to the trichlorides and the tribromides such as **4** and **8** which could not be converted to monohalides under the conditions described here. Thus, the isomeric $n=2$ telomers[4] of vinylene carbonate and methylene bromide, **16a**, **b**, were reductively converted with large excess of nickel carbonyl in moderate yields into the monobromomethyl telomers **17a**, **b**, whose hydrolysis gave 5-bromo-5-deoxypentoses.[4] Conversion of telomerization product **18** (*trans-"anti"-trans* form[8]) to **19** provides another example of reduction of *gem*-dibromo group, while 1,1-dibromocyclohexane was nearly unreactive. Under similar conditions, 7,7-dibromonorcarane gave a mixture of *exo*- and *endo*-7-bromo derivatives (in a ratio of 1: 3.5) in less than 5% yield, although the use of bis(1,5-cyclooctadiene) nickel in place of nickel carbonyl raised the yield to 20% or higher.[9]

On the other hand, treatment of **13a,c,f** with nickel carbonyl in dimethylformamide at 0° resulted in an immediate gas evolution to give a dark mixture and the reductive cleavage to 3,3-dichloroacrolein is presumably involved as a part of the reaction, since 3,3-dichloro- allylalcohol was isolated in the case of **13e**. Such conditions may be used for the removal of *β,β,β*-trihaloethoxy groups and thus, treatment of the trichloroethyl carbonate **20** with nickel carbonyl in dimethylformamide-methanol at 40° gave high yield of the alcohol **21**, though the cleavage proceeded slower than with zinc-acetic acid agents.[10]



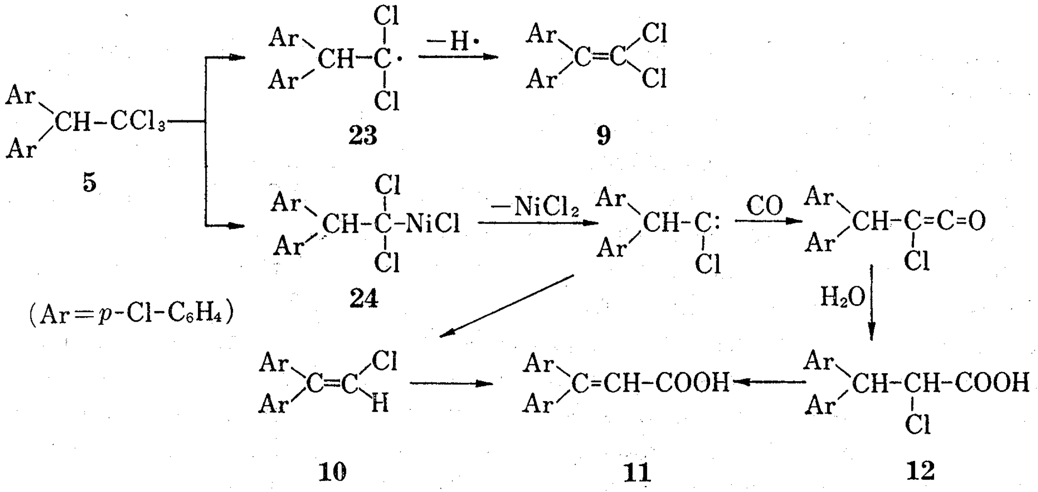
20 : R=Cl_3CCH_2OCO
21 : R=H



$$R-\underset{X(H)}{\overset{X}{C}}-X \longrightarrow X-\underset{X(H)}{\overset{X}{C}}-X\cdots Ni(CO)_4 \longrightarrow NiX + R-\underset{X(H)}{\overset{X}{C}}\cdot \longrightarrow R-\underset{X(H)}{\overset{X}{C}}-H$$

$NiX \longrightarrow NiX_2+Ni$ **22**

A plausible mechanism for the reduction of polyhalides in tetrahydrofuran may involve the initial one-electron transfer from nickel(0) complex to give di- (or mono-) halomethyl radicals **22** which then abstract hydrogen from the solvent.[11] Nickel(I) halide initially formed would undergo spontaneous disproportionation to nickel(II) salt and a nascent metallic nickel



(Ar=*p*-Cl-C_6H_4)

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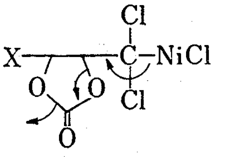
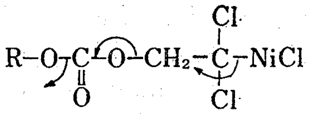
9) T. Kunieda and T. Takizawa, unpublished results.

10) T.B. Windholz and D.B.R. Johnston, *Tetrahedron Lett.*, **1967**, 2555. The reactions probably involve to a certain extent *β*-elimination of the oxidative addition complexes (**i** and **ii**) postulated as plausible intermediates to effect the cleavage of the C–O bond in a fashion as indicated below.



i



ii

11) No attempts were made to isolate the compounds derived from the resulting tetrahydrofuran radicals. *a*) E.J. Corey and L.S. Hegedus, *J. Am. Chem. Soc.*, **91**, 1233 (1969).

which could be reactive enough to operate in the reduction as well. This pathway may be consistent with no incorporation of deuterium to the products in the reduction using tetrahydrofuran containing deuterium oxide.

The following scheme may account for the reaction of DDT (**5**) in more polar, coordinating media, dimethylformamide (or hexamethylphosphoramide), which would stabilize better the oxidative addition complexes like **24** anticipated as a common intermediate for the products **10**, **11** and **12**. Compound **11** may be derived from dehydrochlorination of **12** with the nickel reagents and possibly from carboxylation[11a)] of the olefinic halide **10** as well. The dichloromethyl radicals **23** are reasonably plausible as a precursor of **9**, since the formation of olefinic compounds was also observed in tetrahydrofuran, though to much less extent.

For the reduction of acid-sensitive compounds, the present method will take advantage over the photo-induced procedure[6)] which accompanies the formation of acids in substantial amounts.

Experimental[12)]

Chemicals——Nickel carbonyl is highly toxic and should be handled in an efficient hood with great care. Commercially available nickel carbonyl, DDT (**5**) and benzotrichloride were used without further purification. Literature procedures were followed in the preparation of compound **4**,[13)] 7,7-dibromonorcarane,[14)] vinylene carbonate telomers, **13a**,[4)] **13c**,[4)] **13d**,[4)] **13e**,[4)] **16a**,**b**[4)] and **18**,[4,8)] and their derivatives **13f**[3c)] and **13g**.[3a)] **13e** was also prepared by a new synthetic procedure described below.

1,1,1,3-Tetrabromo-5-phenylpentane (8)——A solution of 4-phenyl-1-butene (5.0 g, 0.038 mol) and carbon tetrabromide (25 g, 0.075 mol) was refluxed in the presence of catalytic amount of benzoyl peroxide (0.3 g) under nitrogen gas for 2 hr. After removal of the solvent, the residue was chromatographed on silica gel using *n*-hexane as an eluting solvent to give the 1: 1 adduct **8** (12.8 g, 73%) as a pale yellow oil. Vacuum distillation gave an analytical sample as a slightly yellow liquid, bp 155—160° (0.1 mmHg). NMR δ 2.30 (2H, m), 2.80 (2H, m), 3.50 (1H, d.d, $J=16$ Hz, $J'=6.0$ Hz), 3.84 (1H, d.d, $J=16.0$ Hz, $J'=4.0$ Hz), 4.14 (1H, m), 7.16 (5H, s). *Anal.* Calcd. for $C_{11}H_{12}Br_4$: C, 28.45; H, 2.59. Found: C, 28.34; H, 2.84.

4-Trichloromethyl-1,3-dioxolan-2-one (13e)——The mixture of vinylene carbonate (25 g, 0.29 mol) and sodium trichloroacetate[15)] (25 g, 0.135 mol) in dimethoxyethane (150 ml, dried over potassium) was refluxed for 5 hr, while another amount (15 g) of sodium salt was portionwise added at hourly intervals. Dark precipitates were removed by filtration and the filtrate was evaporated *in vacuo* to give an oily residue, from which vinylene carbonate (16 g, bp 75—85°/40 mm) was recovered by distillation under diminished pressure. Residual product solidified at room temperature was purified by chromatography on silica gel using benzene. **13e** was obtained as colorless crystals, mp 96—97° weighing 5.5 g (25.5% based on unrecovered vinylene carbonate). This was identical with the authentic $n=1$ telomer previously obtained.[4)]

General Procedure for Reduction with Nickel Carbonyl——Excess nickel carbonyl was added to a solution of polyhalides (*ca.* 1 mmol) in dry tetrahydrofuran (30 ml) which was stirred in the slow stream of nitrogen and the mixture was maintained at 40° for 2.5 hr to 64 hr depending on the halides. In certain cases of polychloro compounds, another same amount of nickel carbonyl was added after *ca.* 24 hr in order to compensate loss of the agent. After removal of the precipitates by filtration, the filtrate was evaporated *in vacuo*.. Chromatography of the oily residue on silica gel gave dihalo- (or monohalo-) methyl compounds which were further purified by recrystallization or vacuum distillation to give the analytical samples. Results are summarized in Table I.

Among the products thus obtained, the known compounds **14a**,[4)] **15a**,[4)] **14c**,[6)] **17a**, **b**[4)] and **19**[8)] which we synthesized previously and **7** (DDD) were identified by direct comparison with the authentic specimens, and new compounds and **6** were characterized by the following spectral data as well as elemental analysis.

1,1-Dibromo-2,2-diphenylethane (**6**)[16)]: NMR δ 4.68 (1H, d, $J=8.0$ Hz), 6.28 (1H, d, $J=8.0$ Hz), 7.30 (10H, b.s). *Anal.* Calcd. for $C_{14}H_{12}Br_2$: C, 49.41; H, 3.53. Found: C, 49.11; H, 3.55.

1,1,3-Tribromo-5-phenylpentane: NMR δ 2.04 (2H, q, $J=7.5$ Hz), 2.75 (4H, m), 4.03 (1H, quint $J=6.0$ Hz), 5.83 (1H, d.d, $J=8.0$ Hz, $J'=6.0$ Hz), 7.20 (5H, m). *Anal.* Calcd. for $C_{11}H_{13}Br_3$: C, 34.29; H, 3.38. Found: C, 34.57; H, 3.42.

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12) Melting points were determined in a Yanaco melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained on a Hitachi R-24 or a JEOL PS-100 in $CDCl_3$, unless otherwise stated, and IR spectra on a JASCO DS-402G spectrometer.
13) E.E. Harris and G.B. Frankforter, *J. Am. Chem. Soc.*, **48**, 3146 (1926).
14) W. von E. Doering and A.K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).
15) *cf.* W.M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. trav. Chim.*, **80**, 740 (1961).
16) G.H. Coleman, W.H. Holst, and R.D. Mazwell, *J. Am. Chem. Soc.*, **58**, 2310 (1936).

4-Bromo-5-dichloromethyl-1,3-dioxolan-2-one (**14d**): IR (neat) 1830 and 1790 (w) cm^{-1}. NMR δ 5.15 (1H, d.d, $J=4.0$ Hz, $J'=2.0$ Hz), 5.80 (1H, d, $J=4.0$ Hz), 6.50 (1H, d, $J=2.0$ Hz). *Anal.* Calcd. for $C_4H_3BrCl_2O_3$: C, 19.20; H, 1.20. Found: C, 19.14; H, 1.31.

4-Dichloromethyl-1,3-dioxolan-2-one (**14e**): IR (Nujol) 1835 (w) and 1800 cm^{-1}. NMR δ 4.65 (2H, m), 5.10 (1H, m), 6.00 (1H, d, $J=3.0$ Hz). *Anal.* Calcd. for $C_4H_4Cl_2O_3$: C, 28.07; H, 2.34. Found: C, 28.06; H, 2.70.

4-Methoxy-5-dichloromethyl-1,3-dioxolan-2-one (**14f**): IR (neat) 1840 cm^{-1}. NMR δ 3.62 (3H, s), 4.66 (1H, d.d, $J=4.0$ Hz, $J'=2.0$ Hz), 5.54 (1H, d, $J=2.0$ Hz), 6.00 (1H, d, $J=4.0$ Hz). *Anal.* Calcd. for $C_5H_6Cl_2O_4$: C, 29.85; H, 2.99. Found: C, 30.46; H, 3.28.

1,1,2,2-Tetrachloro-1,2-diphenylethane——A solution of benzotrichloride (5.9 g, 0.03 mol) and nickel carbonyl (10 g, 0.06 mol) in tetrahydrofuran (25 ml) was stirred at 40° for 4 hr under nitrogen gas. Work-up as above gave the dimer (1.73 g, 36% corrected yield 73%) in addition to the starting compound (3 g). Recrystallization from *n*-hexane gave colorless prisms, mp 162—164° (lit,[17] 161—162°). NMR δ 7.1—7.5 (m). *Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.50; H, 3.13. Found: C, 52.33; H, 3.14.

4-Chloro-5-dichloromethyl-1,3-dioxolan-2-one (**14c**)[6]——a) With Hexaethylphosphorous Triamide: To a solution of **13c** (3.6 g, 0.01 mol) and ethanol (0.8 g, 17 mmol) in dry ether (30 ml) was added the ether solution of hexaethylphosphorous triamide[18] (4.0 g, 16 mmol) prepared from phosphorous trichloride and diethylamine, under stirring at room temperature in the stream of nitrogen. The ether was removed *in vacuo* and the residue was chromatographed on silica gel to give **14c** (0.28 g, 9%) as an oil in addition to the unchanged **13c** (0.04 g).

b) With Iron Pentacarbonyl: The mixture of **13c** (4.8 g, 20 mmol) and iron carbonyl (7.7 g, 39 mmol) in tetrahydrofuran (25 ml) was gently refluxed for a week. Work-up as described for the reduction with nickel carbonyl gave **13c** (1.52 g) and **14c** (93 mg, 3%).

c) With Sodium Cyanoborohydride: The mixture of **13c** (2.0 g, 8 mmol) and sodium cyanoborohydride (1.0 g, 16 mmol) in hexamethylphosphoramide (10 ml) was warmed at 80° to 100° in the presence of sodium iodide (1.0 g) for 5 hr and poured into ice-water. It was extracted with benzene and the extract was evaporated to give oily products which were purified by chromatography on silica gel (*n*-hexane–benzene) to give **14c** (0.53 g, 31%) in addition to **13c** (0.33 g). In the reaction of **13d** under similar conditions, **14d** was isolated only in 10% yield.

Reaction of DDT (5) with Nickel Carbonyl in Dimethylformamide——A solution of **5** (DDT) (3.6 g, 0.01 mol) and nickel carbonyl (3.9 g, 0.023 mol) in dimethylformamide (30 ml) was warmed at 40° under nitrogen atmosphere for 2 days. The resulting green solution was poured into ice-water and the products deposited were extracted with benzene. The extract was washed with 10% sodium bicarbonate solution and water, and dried (sodium sulfate). Removal of the benzene gave a red oil which contained at least three major components (by the TLC analysis). Chromatography on silica gel followed by more careful rechromatography using *n*-hexane and benzene gave 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene (**9**), mp 87—88°, (0.15 g, 8.5%), and 2,2-bis(*p*-chlorophenyl)-1-chloroethylene (**10**), mp 60—65°, (0.25 g, 16%) in addition to the unchanged **5** (1.6 g). The combined bicarbonate solution and washings were acidified with hydrochloric acid and the products were extracted with benzene and chloroform. The combined extracts were dried and evaporated *in vacuo* to leave a solid which was separated by chromatography on silica gel (benzene–acetone) into 3,3-bis(*p*-chlorophenyl)acrylic acid (**11**), mp 178—179.5°, (0.2 g, 12%) and 2-chloro-3,3-bis(*p*-chlorophenyl)propionic acid (**12**), mp 187—189°, (0.35 g, 21%). Products had the following properties.

9[19]: NMR δ 7.18 (4H, d, $J=8.0$ Hz), 7.30 (4H, d, $J=8.0$ Hz). The infrared (IR) spectrum (Nujol) was identical with that of the authentic sample.

10[20]: NMR (CCl_4) δ 6.50 (1H, s), 7.20 (8H, m). This was identified by direct comparison with the compound prepared from **7**.

11[21]: NMR (DMSO-d_6) δ 6.38 (1H, s), 7.35 (8H, m), 12.30 (1H, broad s). *Anal.* Calcd. for $C_{15}H_{10}Cl_2O_2$: C, 61.43; H, 3.41. Found: C, 61.29; H, 3.25.

12: NMR (CH_3CN) δ 4.50 (1H, d, $J=11.0$ Hz), 5.07 (1H, d, $J=11.0$ Hz), 7.33 (8H, m). *Anal.* Calcd. for $C_{15}H_{11}Cl_3O_2$: C, 54.73; H, 3.34. Found: C, 54.66; H, 3.20.

Benzyl 5-O-(2,2,2-Trichloroethoxycarbonyl)-2,3-O-isopropylidene-D-lyxoside (20)——Benzyl 2,3-O-isopropylidene-D-lyxofuranoside (**21**) (5.6 g, 0.02 mol) prepared by the method of Brimacombe[22] was dissolved in dry pyridine (15 ml) and trichloroethyl chloroformate (7.0 g, 0.035 mol) was added under cooling. The mixture was kept at room temperature overnight and then poured into ice-water. It was extracted with benzene and the extract was washed with 10% hydrochloric acid and water, and dried. Removal of the

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benzene gave a solid which was recrystallized from *n*-hexane to give colorless needles, mp 58—60°, (7.7 g, 85%). IR (Nujol) 1760 cm^{-1}. NMR δ 1.29 (3H, s), 1.44 (3H, s), 4.2—4.8 (7H, m), 4.77 (2H, s), 5.12 (1H, s), 7.30 (5H, s). *Anal.* Calcd. for $C_{18}H_{21}O_7Cl_3$: C, 47.42; H, 4.61. Found: C, 47.83; H, 4.67.

Benzyl 2,3-O-Isopropylidene-D-lyxofuranoside (21)——A solution of **20** (2.5 g, 5.5 mol) and nickel carbonyl (3 g, 17 mmol) in dimethylformamide (10 ml) containing methanol (0.5 ml) was warmed at 40° under nitrogen gas for 20 hr. Then, water was added to the mixture and the compounds deposited were extracted with benzene. The benzene layer was dried and evaporated *in vacuo* to leave a syrup which was chromatographed on silica gel to give unchanged **20** (1.1 g) and the alcohol **21** (0.77 g, 52%, corrected yield 90%). Recrystallization from *n*-hexane gave colorless crystals, mp 80—83°. IR (Nujol) 3380 cm^{-1}. *Anal.* Calcd. for $C_{15}H_{20}O_5$: C, 64.29; H, 7.14. Found: C, 64.35; H, 7.22.