activity might be due to the increment by CH_2 (*ca.* 1.5Å) in chain length and the change from primary amino group to secondary amino group in the dipeptide.

From the results obtained above both about induction and inhibition of germination, we can emphasize that a certain distance between primary amino group and free carboxyl group and conformation of the dipeptide most favourable for binding with the receptor site to induce or inhibit germination are required.

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Iron Carbonyls as Mild Friedel-Crafts Catalytic Agent[1]

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Iron carbonyls may act as an effective agent to moderate the Friedel-Crafts type reaction with allylic polyhalides.

Keywords——iron carbonyl; vinylene carbonate telomer; Friedel-Crafts reaction; allylic halide; coupling reaction

In the course of a study on the synthetic utility of the vinylenecarbonate telomers,[3] mild catalytic activity of diiron enneacarbonyl as well as an effectiveness of iron pentacarbonyl has been recognized in the Friedel-Crafts type alkylation of benzene with the allylic halides **2** and **3** readily derived from the vinylenecarbonate-polyhalomethane adducts **1**.

Scant information is available on catalytic ability of metal carbonyl[4] for the Friedel-Crafts type reaction, though there has been used such a wide variety of catalysts that it is difficult to assess their particular advantages.[5]

Dehydrohalogenation of the bromo (**1**, X=Br) and the chloro (**1**, X=Cl) telomers[6] was performed by the action of triethylamine in benzene to afford the reactive allylic halides **2** and **3**, respectively, as major products, which were sensitive toward nucleophiles such as water and amines to give 2-hydroxy-3, 3-dichloroacrolein and 4-hydroxy-5-dichloromethylene-2-oxazolidone.[7] The former halide **2** underwent smooth allylic rearrangement to the isomer **3**

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[1] This constitutes part XIII in the series, "Telomers and Oligomers of Vinylene Carbonate." Part XII: Y. Nii, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **26**, 1999 (1978).

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

[3] T. Kunieda and T. Takizawa, *Heterocycles*, **8**, 661 (1977).

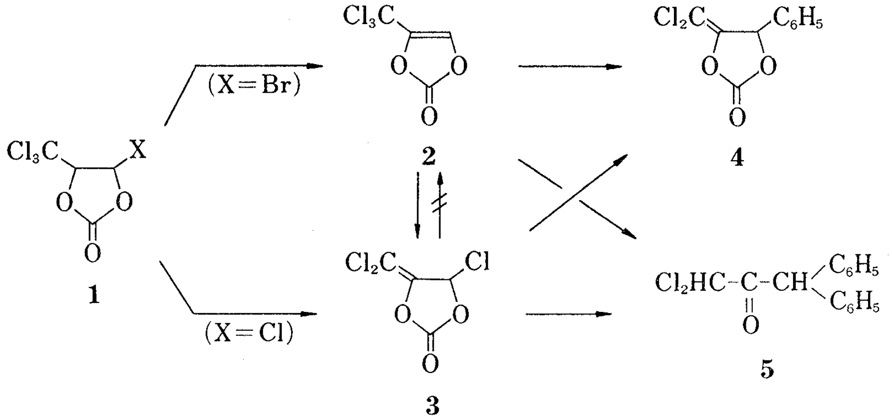
[4] *cf.* E. Yoshisato and S. Tsutsumi, *J. Org. Chem.*, **33**, 869 (1968).

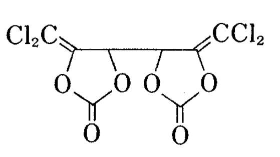
[5] G.A. Olah ed., "Friedel-Crafts and Related Reactions," Interscience publishers, Vol. 1, New York, 1963, p. 201.

[6] T. Tamura, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **39**, 38 (1974).

[7] T. Matsuura, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 1225 (1977).

in the presence of Lewis acid, stannic chloride but the reverse isomerization was not observed, which are consistent with the previous observation with a 3,3,3-trichloropropene system.[8]

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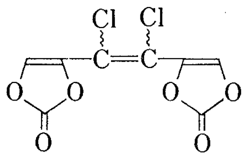
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Allylation of benzene with either the chloride **2** or **3** was smoothly effected using catalytic amount of diiron enneacarbonyl to give monophenylation product **4** (46%), while use of the convensional catalysts such as aluminium chloride and ferric chloride failed to yield compound **4** even under the milder conditions using moderating solvents and catalytic amount of the catalysts at low temperature but resulted in an exclusive formation of compound **5** which would arise from "two-fold" substitution involving rearylation of **4**.

Iron pentacarbonyl was also capable of effecting monophenylation to afford **4** as well as isomerization of **2** to **3**. Such a phenylation was not observed at the level of the telomers **1**. Other products isolated were the coupling compounds, **6** and **7**, which would be formed *via* π-allyl iron complexes.

Compound **4** may be formed by a Friedel-Crafts type reaction, but the actual catalytic species is not clear, since ferric chloride itself is unlikely operative in the present reaction, judging from no formation of compound **5**.

The reaction caused by iron carbonyls provides a route to permit an introduction of a functional allylic fragment into aromatics.

Experimental

Melting points are uncorrected. IR spectra were determined on a JASCO IRA-1 spectrophotometer. NMR spectra were measured on either a Hitachi R-24 (60 MHz) or a JEOL PS-100 (100 MHz) spectrometer with solvent as specified. Mass spectra were observed using a JEOL-JMS 01SG-2 mass-spectrometer at 75 eV by direct inlet.

4-(Trichloromethyl)-1,3-dioxol-2-one (2)——To a solution of *trans*-4-(trichloromethyl)-5-bromo-1,3-dioxolan-2-one[6] (7.5 g, 26 mmol) in dry benzene (60 ml) was dropwise added triethylamine (3.0 g, 30 ml) and it was gently refluxed for 3 hr. After removal of the precipitates by filtration, the filtrate was evaporated *in vacuo* to leave a dark oil. Chromatography of the residue on silica gel (*n*-hexane–benzene 20: 1) gave the dehydrobrominated trichloromethyl derivative (2) (4.0 g, 74. 6%) as a solid, which was further purified by recrystallization from *n*-hexane (or sublimation at 50—60° under 5 mmHg) to afford colorless

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[8] A.N. Nesmeyanov, R.Kh. Freidlina, and L.I. Zakharkin, *Quart. Rev.*, **10**, 330 (1956).

prisms: mp 63—65°; IR (KBr) 3145, 1850, 1825, 1670 cm^{-1}; NMR ($CDCl_3$) δ 7.36 (s, 1H); MS *m/e* 206 ($M^+ +4$), 204 ($M^+ +2$), 202 (M^+), 97 (base). *Anal.* Calcd. for $C_4HCl_3O_3$: C, 23.58; H, 0.49. Found: C, 23.22; H, 0.44.

4-(Dichloromethylene)-1,3-dioxolan-2-one (3)——a) Analogously to the procedure for the preparation of 2, treatment of *trans*-4-trichloromethyl-5-chloro-1,3-dioxolan-2-one⁶⁾ (100 g, 0.42 mol) with triethylamine (71 g, 0.7 mol) in benzene (300 ml) afforded the dichloromethylene compound **3** (64 g, 75%) as a major product in addition to the minor trichloromethyl derivative **2**, (4.7 g, 5.5%). Product **3** was crystallized on standing below 20° (mp 25—30°) and showed the following spectral data; IR (neat) 1940 (w), 1850, 1800, 1698 cm^{-1}; NMR ($CDCl_3$) δ 6.83 (s, 1H); MS *m/e* 206 ($M^+ +4$), 204 ($M^+ +2$), 202 (M^+), 134, 132, 130, 97 (base).

b) A solution of the allylic chloride **2** (0.54 g, 2.7 mmol) in benzene (10 ml) was refluxed in the presence of stannic chloride (0.7 g, 2.7 mmol) for 2 hr. The reaction mixture was worked up in the usual manner to give a nearly quantitative yield (0.5g) of the rearranged chloride **3**, which was identical with the authentic specimen.

3,3-Dichloro-2-hydroxyacrolein (Dichloropyruvaldehyde)——The chloride **3** was kept under a moist atmosphere at room temperature for a week. The solid deposited was recrystallized from *n*-hexane to give colorless needles, which were readily sublimated; mp 105—107°; IR (Nujol) 3210, 1670, 1615 cm^{-1}; NMR ($CDCl_3$) δ 9.78 (s, 1H), 6.05 (b.s, 1H, disappeared in addition of D_2O); MS *m/e* 144 ($M^+ +4$), 142 ($M^+ +2$), 140 (M^+), 112 ($M^+ -CO$), 76 (base).

4-Dichloromethylene-5-phenyl-1,3-dioxolan-2-one (4)——a) A solution of the chloride **3** (1.03 g, 5 mmol) in benzene (40 ml) was refluxed in the presence of catalytic amount of diiron enneacarbonyl (purchased from Aldrich Co.) (0.1 g, 0.27 mmol) under nitrogen atmosphere for 14.5 hr. After removal of the solvent, the residue was chromatographed on silica gel (*n*-hexane: benzene 1: 1) to afford the compound **4** (520 mg, 47% corrected yield) in addition to the unchanged material (100 mg, 10%) and the dimeric compounds as minor products. Recrystallization from CH_2Cl_2–*n*-hexane gave the mono-phenylated product as colorless pillows, mp 70—72°; IR (KBr) 1830, 1805, 1798 cm^{-1}; NMR ($CDCl_3$) δ 6.15 (s, 1H), 7.43 (s, 5H). *Anal.* Calcd. for $C_{10}H_6Cl_2O_3$: C, 48.99; H, 2.45. Found: C, 49.17; H, 2.53.

b) Analogously to the above procedure, the reaction of 4-trichloromethyl-1,3-dioxol-2-one (**2**) (1.0 g, 5 mmol) with iron pentacarbonyl (3 g, 15 mmol) in benzene (20 ml) (5 hr) gave the rearranged chloride **3** (0.35 g, 35%), phenylation product **4** (0.44 g, 37%) and coupling compounds **6** (0.1 g, 6%) and **7** (90 mg, 7%). Dimeric compounds showed the following properties. Compound **6**: mp 149—150° (from CH_2Cl_2–*n*-hexane); IR (Nujol) 3145, 1840, 1810, 1685 cm^{-1}; NMR ($CDCl_3$) δ 5.83 (s, 1H), 7.43 (s, 1H); MS *m/e* 340 ($M^+ +6$), 338 ($M^+ +4$), 336 ($M^+ +2$), 334 (M^+), 167 (base). *Anal.* Calcd. for $C_8H_2Cl_4O_6$: C, 28.57; H, 0.60. Found: C, 28.71; H, 0.66. Compound **7**: mp 172—174° (from CH_3CN–*n*-hexane); IR (Nuj) 3110, 1835, 1800 cm^{-1}; NMR (CH_3CN) δ 7.62 (s, 1H), 7.90 (s, 1H); MS *m/e* 266 ($M^+ +2$), 264 (M^+), 113 (base). *Anal.* Calcd for $C_8H_2Cl_2O_6$: C, 36.23; H, 0.75. Found: C, 36.21; H, 0.71.

c) In the same way as above, the allylic chloride **3** (1.5 g, 7.4 mmol) gave compound **4** (0.24 g, 14%) and the dimer **6** (0.18 g, 15%) in addition to the unchanged material (0.9 g, 60%) on the treatment for 5 hr.

1,1-Dichloro-3,3-diphenyl-2-propanone (5)——To a cooled solution of the chloride **3** (1.8 g, 8.8 mmol) in benzene (20 ml) was added aluminium chloride (0.13 g, 1 mmol) and it was stirred under ice-cooling for 1 hr. The complexes were carefully destroyed with ice and the benzene layer was washed with H_2O and dried (Na_2SO_4). After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using *n*-hexane–benzene (10: 1) to give **5** as colorless crystals (1.95 g, 79%). Recrystallization from *n*-hexane gave colorless needles, mp 60—61°; IR (KBr) 1733, 1597 cm^{-1}; NMR ($CDCl_3$) δ 5.64 (s, 1H), 5.94 (s, 1H), 7.23 (s, 10H); MS *m/e* 282 ($M^+ +4$), 280 ($M^+ +2$), 278 (M^+), 243 ($M^+ -Cl$), 208 ($M^+ -Cl_2$), 167 (base). *Anal.* Calcd. for $C_{15}H_{12}Cl_2O$: C, 64.51; H, 4.30. Found: C, 64.50; H, 4.31.

This type reaction also proceeded smoothly in the presence of catalytic amounts of $AlCl_3$ and $FeCl_3$ to afford **5** with no detectable quantities of **4**, while the Lewis acids, $ZnCl_2$ and $SnCl_4$ were ineffective.