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Reduction of Carbon Dioxide to Give Unstable Carbon Oxides. Electron Transfer from the Reduction Products of Carbon Dioxide with Benzoin Carbanion to Triphenylcarbenium Ion

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Synopsis. Reaction of the reduction products of carbon dioxide (CO_2) by benzoin carbanion with triphenylcarbenium ion (**1**) gave 1-(diphenylmethyl)-4-(triphenylmethyl)benzene (**2**) which was considered to be electron transfer product from the reduction products of CO_2 to **1**.

In the series of this study it has been reported that carbon dioxide (CO_2) or sulfur dioxide (SO_2) was reduced by benzoin carbanion[1] and that the reduction products formed had special reactivities.[2—5] Reduction products of SO_2 with benzoin carbanion reacted with cyclopentadiene to give oligomers which contained sulfur and oxygen atom in the ratio between $SO_{0.1}$ and $SO_{0.4}$.[2] Heating of reduction products of CO_2 by benzoin carbanion with sydnones gave saturated hydrocarbones.[3] Heating of the reduction products of CO_2 with $Na_2S_2O_4$ gave $(\!-C(SO_3Na)_2-\!)_n$.[4] Reaction of the reduction products of CO_2 with $PhI^+C^-(SO_2Ph)_2$ gave $:CH(SO_2Ph)$.[5] These results suggest that CO_2 or SO_2 is converted to unstable carbon oxides or unstable sulfur oxides. Although there is few report concerning unstable sulfur oxides, there have been many reports concerning unstable carbon oxides.[6] The unstable carbon oxides reported in the literatures are considered to exist as free species. However, the reduction products (presumably unstable carbon oxides) of CO_2 with benzoin carbanion not always exist as free species. In the present report it will be reported that the reduction products of CO_2 with benzoin carbanion act as electron donor to triphenylcarbenium ion (**1**). This fact suggests that the reduction products of CO_2 exist not only as free species but as an adduct with lithium.

Results and Discussion

Various electron-transfer reactions to triphenylcarbenium ion (**1**) have been reported. Electron-transfer reaction from sodium methoxide,[7] lithium alkanethiolate,[8] potassium *t*-butoxide,[9] and lithium amide[10] to **1** as well as electron-transfer reaction to **1** by means of electrochemical method[11] have been reported. It has been established that electron transfer to **1** gives trityl radical followed by conversion of the trityl radical to 1-(diphenylmethyl)-4-(triphenylmethyl)benzene (**2**) through intervention of Gombergs triphenylmethyl.[12]

When triphenylcarbenium hexafluorophosphate (**3**) was added to a solution containing reduction products of CO_2 with benzoin carbanion, formation of considerable amount of **2** was observed. Yields of **2** depend on the method of formation of benzoin carbanion. In the previous papers it has been reported that efficiency of formation of benzoin carbanion is higher in the reaction of benzoin with lithium diisopropylamide (LDA)[1] than in the reaction of benzoin with lithium.[5,13] Therefore, amount of the reduction products of CO_2 is larger in the reduction of CO_2 with benzoin carbanion formed using LDA than that using lithium. Yield of **2** was 21% based on benzoin used for the case of formation of benzoin carbanion by using LDA, and 4% for the case using lithium, respectively as is shown in Table 1.

One might suppose that other substances in the reaction solution than the reduction products of CO_2 bring about conversion of **1** to **2**. Therefore, five sorts of control experiments (Entries, 3—7) were undertaken as is shown in Table 1. Reaction of Entry 3 brought about polymerization of THF. Since heating of a mixture of **3** and reduction products of CO_2 did not bring about polymerization of THF, reaction of THF with **3** is not important in the reaction of **3** with the mixture of the reduction products of CO_2. Entries 4—7 did not give **2** at all.

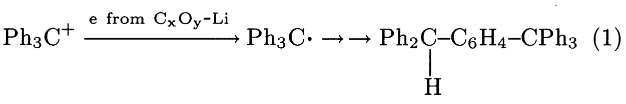
One might suspect that a small amount of benzoin carbanion remains without being quenched after the reaction of CO_2 with benzoin carbanion. In the previous paper[1] it was confirmed that the lower the reaction temperature of CO_2 with benzoin carbanion was the higher the yield of benzil was. This tendency was interpreted in terms of dependency of the solvation of the carbanion on the reaction temperature. Szwarc has reported that dissociation of the ion pair increases as the temperature of the solution decreases and that the increase of solvation reaches to maximum state at −70 °C.[14] It was confirmed that the reaction of benzoin carbanion with CO_2 at −95 °C does not bring about increase of the yield of benzil compared to that obtained at −78 °C. If benzoin carbanion is not completely quenched at low temperature, yield of benzil at −95 °C would not be same with that at −78 °C. Therefore, it can be concluded that saturation of increase of the yield of benzil with decreasing the reaction temperature corresponds to the saturation of solvation of ion pair reported by Szwarc. This consideration shows that benzoin carbanion is completely quenched at −78 °C. The fact that color of the solution of benzoin carbanion changes from intense orange red to yellow of benzil during the reaction with CO_2 supports this conclusion. About 20% isolated yield (vide ante) of **2** is too

Table 1. The Reaction Products of the Triphenylcarbenium Hexafluorophosphate (**3**) with Various Compounds

Entry	Reaction	Yield of **2**/%
1[a]	Reduction products of CO_2(LDA)[b]+**3**	21[d]+Ph_3CH (20[d])
2[a]	Reduction products of CO_2(Li)[c]+**3**	4[d]+Ph_3CH (20[d])
3[e]	THF+**3**	0[f]
4[e]	Li_2CO_3+THF+**3**	0[f]
5[e]	Diisopropylamine+THF+**3**	0[f]
6[e]	Li+THF+**3**	0[f]
7[e]	Benzoin+benzil+THF+**3**	0[f]

a) Experimental conditions are described in Experimental. b) Reduction products of CO_2 with benzoin carbanion which was formed using LDA. c) Reduction products of CO_2 with benzoin carbanion which was formed using Li. d) Yields were based on benzoin used. e) Control experiments 3-7 were carried out by heating under reflux for 1h. f) Mainly triphenylmethane was formed. Yield of it was not determined.

much to be attributed to the reaction of a small amount of remained benzoin carbanion with **1**. Therefore, formation of **2** can be attributed to the electron transfer from the reduction products (presumably unstable carbon oxides) of CO_2 to **1** as explained as following.



$$\mathrm{Ph_3C^+} \xrightarrow{\text{e from } C_xO_y\text{-Li}} \mathrm{Ph_3C\cdot} \to\to \mathrm{Ph_2}\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\mathrm{-C_6H_4-CPh_3} \qquad (1)$$

2

Althougn unstable carbon oxides formed in gas phase are reported to exist as free species in the literatures,[6] the unstable carbon oxides formed by the reaction of CO_2 with benzoin carbanion in solution presumably exist not only as free species but as adduct of unstable carbon oxides (C_xO_y) with lithium. An adduct of C_xO_y with Li and/or C_xO_y gives electron to **1** to give **2**.

Experimental

General Procedures. ^{1}H NMR, ^{13}C NMR, and mass spectra were recorded using instruments described in the previous paper.[5] Other procedures were also described in the previous papers.[1] Commercially available triphenylmethylcarbenium hexafluorophosphate (Aldrich Chem. Co.) was used.

Preparation of Benzoin Carbanion by the Reaction of Benzoin and LDA and the Reaction of the Benzoin Carbanion with CO_2. The procedure previously reported for preparation of carbanion using LDA[2] was slightly modified as below. A 100 ml two-necked flask with septum cap was purged by dry and oxygen free nitrogen. A portion (16 ml) of absolute THF was injected through a serum cap using a syringe. Slightly excess than 0.009 mol of dried diisopropylamine was added to THF using a syringe. This solution was degassed using liquid nitrogen and nitrogen gas deoxygenated with an Oxy-Trap (Alltech).[15] Slightly excess amount than 0.009 mol of butyllithium/hexane was added to the solution at −22 °C using a syringe. After the mixture was stirred using a magnetic stirrer for 10 min at −22 °C, 16 ml of THF solution of benzoin (0.0045 mol), which was degassed by above stated method, was injected to this mixture using a syringe, and the resulting intense orange red mixture was stirred for 10 min at −22 °C, and then stirred for 0.5 h at 0 °C. The mixture was then immersed into a cooling bath maintained at −78 °C. To this solution CO_2, which was deoxygenated with an Oxy-Trap,[16] was bubbled through a delivery tube for 1.0 h.

Preparation of Benzoin Carbanion by the Reaction of Benzoin and Li and the Reaction of the Benzoin Carbanion with CO_2. The procedure of preparation of benzoin carbanion by the reaction of benzoin and Li and the reaction of the carbanion formed with CO_2 was described in the previous paper.[5] 0.009 g atom of lithium and 0.0045 mol of benzoin were reacted to form benzoin carbanion.

Reaction of Triphenylcarbenium Hexafluorophosphate (3) with the Reduction products of CO_2. After finishing of the reduction of CO_2 with benzoin carbanion 0.0026 mol or 0.0018 mol of **3** was added to the reaction mixture at −78 °C. The reaction solution was gradually warmed up to room temperature and then was heated under reflux for 1 h under nitrogen bubbling.

Isolation of and Characterization of 1-(Diphenylmethyl)-4-(triphenylmethyl)benzene (2). After finishing of the reaction of **3** with the reduction products of CO_2, the solution was evaporated to give a residue. The residue was separated by means of silica-gel column chromatography using chloroform as an eluent. A fraction eluted earlier than a fraction of benzil was a mixture of triphenylmethane, and **2**. The mixture was separated by means of TLC using a mixture of hexane and chloroform (8:2 v/v) to give pure **2**.

^{1}H NMR of **2** ($CDCl_3$) δ=5.5 (s, 1H), 7.0—7.5 (m, 29H). ^{13}C NMR of this compound coincided well with those of **2** reported in the literature.[11] MP 225—227 °C (lit, 225—227 °C[17]). Calcd for $C_{38}H_{30}$: M^+, 486.2348. Found: m/z 486.2350. Because of little difference of polarity of **2** and triphenylmethene, accurate quantitative separation of these products was difficult by TLC. Therefore, amounts of triphenylmethane and **2** were estimated from ^{1}H NMR spectrum in $CDCl_3$ of a mixture of these two compounds using absorption signals of phenyl group at 7.0—7.5 ppm, signals of methine proton of triphenylmethane at 5.56 ppm and methine proton of **2** at 5.5 ppm. Separation and characterization of decomposition products of **3** were not carried out.

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13) As was shown in Refs. 1 and 5 the reaction of CO_2 with benzoin carbanion formed using LDA or Li gave a mixture of benzil and benzoin in a proportion of 49 : 51 or 20 : 55, respectively.

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15) The solution was frozen using liquid nitrogen and gas was exhaused. Then nitrogen gas, which was deoxygenated with an Oxy-Trap (Alltech), was introduced. The nitrogen was exhausted and the solution was melted. Then the solution was frozen again and deoxygenated nitrogen was introduced. These procedures were repeated several times.

16) When degassification of THF solution of benzoin or diisopropylamine and deoxygenation of CO_2 were not carried out, in addition to **2** small amount of bis(triphenylmethyl) peroxide was obtained.

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