2016 © *1991 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **64**, *2016—2018 (1991)* [Vol. 64, No. 6

Reduction of Carbon Dioxide to Give Unstable Carbon Oxides. An Attempt of Capture of Unstable Carbon Oxides Formed by the Reduction of Carbon Dioxide with Benzoin Carbanion Using Phenyliodonium Bis(phenylsulfonyl)methylide

Fuminori Akiyama
Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Sendai 980

(Received March 11, 1991)

Synopsis. Capture of unstable carbon oxides formed by the reduction of carbon dioxide (CO_2) with benzoin carbanion using phenyliodonium bis(phenylsulfonyl)methylide (**1**) was tried. In this reaction decomposition of the ylide **1** by the unstable carbon oxides was observed to give phenylsulfonylcarbene $:CH(SO_2Ph)$.

The reaction of CO_2 is receiving much attention in view of the use of resources. In most of many reactions of CO_2 reported, CO_2 combines with organic compounds keeping CO_2 unit to give carboxylic acids, carbonates, lactones, carbamates, substituted 5(2*H*)-oxazolones, and substituted 2-oxazolidinones as described in the preceding papers.[1] In a previous paper[2] of this study, a hypothesis that CO_2 can be converted to unstable carbon oxides by the reduction with mild reducing reagent such as benzoin carbanion and that the unstable carbon oxides formed have special reactivities, has been proposed. The preceding papers have shown that the reduction products of CO_2 with benzoin carbanion, which was formed using LDA, had special reactivities with sydnones,[3] and that carbon atom of unstable carbon oxides was captured by sodium dithionites.[1]

Unstable carbon oxides formed by the reduction of CO_2 with benzoin carbanion was considered to have the structure $:C\!\left(\!=\!C\!=\!\right)_{n}\!C{=}O$.[1] Various sorts of unstable carbon oxides such as C_2O,[4] C_3O,[5] C_4O,[6] and C_6O[6] have been reported to have the structure $:C\!\left(\!=\!C\!=\!\right)_{n}\!C{=}O$.[1] Since unstable carbon oxides are considered to have carbene and cumulene structures, it seems to be preferable to use substances having ability to eject carbene in order to capture such carbon oxides. Recently, it has been reported that phenyliodonium bis(phenylsulfonyl)methylide $PhI^{+}\text{-}C^{-}(SO_2Ph)_2$ (**1**) are able to eject carbene under mild conditions.[7] In the present report it will be shown that unstable carbon oxides formed by the reduction of CO_2 with benzoin carbanion show specific reaction behavior to phenyliodonium bis(phenylsulfonyl)methylide (**1**).

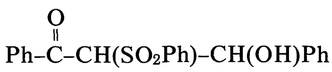
Results and Discussion

Benzoin carbanion was formed by the reaction of benzoin with lithium metal (see Experimental).[8] After treating of the THF solution of benzoin carbanion with CO_2 gas, the ylide **1** was added to this solution and the products were separated as described in Experimental. In this reaction mixture, besides benzoin, benzil, hydrobenzoin, and lithium benzoate, the insertion products of the carbene derived from the ylide **1** to benzoin were observed. The insertion products consisted of two isomers. Because of close R_f values of two isomers, relatively low solubilities, and a little instabilities of these isomers,[1] separation of two isomers were unsuccessful. However, analyses of a mixture of two isomers and trimethylsilylation and acetylation of these two isomers showed that the mixture consisted of isomer **2** and **3** (vide infra).

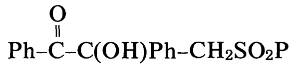
Mass spectroscopy indicated following peaks; *m*/*z* 366 (M^+, rel intensity 3), 259 (M^+ −CH(OH)Ph, 58), 125 (PhSO, 13), 118 (CHC(O)Ph, 31), and 105 (PhCO, 100). Measurement of molecular weight by means of vapor phase osmometry also showed that molecular weight of the mixture was 366. IR spectrum of the mixture indicated the absorptions at 3475 (OH), 1683 (C=O), 1302 and 1153 (SO_2), 1083 (C–O), 746 and 700 cm^{-1} (Ph).

^1H NMR spectrum of the mixture of two isomers indicated that the isomer **2** had signals at 7.0—8.0 ppm (Ph), 5.85—5.89 ppm (two doublets combined to give a triplet, HC(OH)(Ph) for two diastereomers of **2**), 4.30—4.51 ppm (two doublets, $HC(SO_2Ph)$ for two diastereomers of **2**). Double irradiation at 5.85—5.89 ppm converted two doublets at 4.30—4.51 ppm into two singlets. ^1H NMR spectrum of the mixture also indicated that isomer **3** had signals at 7.0—8.0 ppm (Ph) and 4.25—4.29 ppm (s,[10], CH_2SO_2Ph). Double irradiation technique for this case did not give any change in this apectrum.

^{13}C NMR of the two isomers were assigned reasonably as following (absorptions for phenyl groups appear at 124—141 ppm)


$Ph\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH(SO_2Ph)\text{-}CH(OH)Ph$ **2**

197.2 74.6 76.7 and 76.6 ppm


$Ph\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}C(OH)Ph\text{-}CH_2SO_2Ph$ **3**

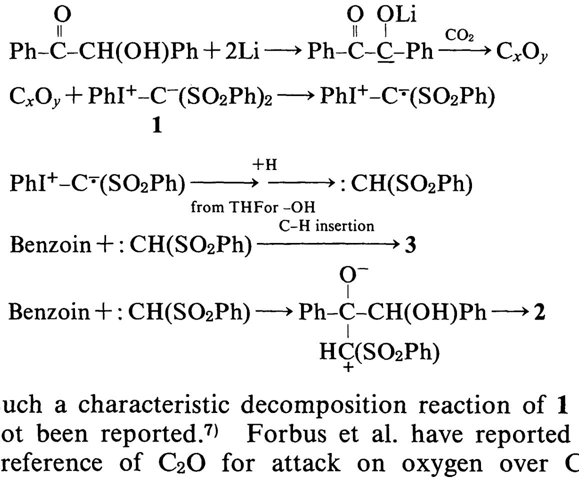
197.2 82.2 59.5 ppm

Trimethylsilylation of a mixture of **2** and **3** using trimethylchlorosilane, hexamethyldisilazane, and pyridine gave a rearranged silylated compound and a small amount of decomposition product, in addition to silylated products of **2** and **3**. R_f values of two silylated products of **2** and **3** were almost same and that of a rearranged silylated compound was slightly smaller than those of two silylated products of **2** and **3**. It was impossible to isolate the silylated product of **2** and **3** from a mixture of these compounds having similar R_f values by TLC or HPLC. Acetylation of a mixture of **2** and **3** by a mixture of acetic anhydride and pyridine showed disappearance of ^1H NMR absorption at 4.30—4.51 and 5.85—5.89 ppm, which are attributed to those of isomer **2** (vide ante), and appearrance of ^{1}H NMR absorption (singlet) at 6.72 ppm. Presumably the isomer **2** was dehydrated to give an olefin. By this acetylation the isomer **3** was converted to an acetylated product which showed ^{1}H NMR absorption at 4.29 ppm (2H, CH_2SO_2Ph) and 2.2 ppm (3H, CH_3CO). Unfortunately R_f values of an acetylated product of **3** and this decomposition product of **2** were almost same. Therefore, isolation of the acetylated product of **3** from this mixture by means of TLC or HPLC was impossible. However, this acetylation experiment indicated that ^{1}H NMR absorptions at 4.30—4.51 and 5.85—5.89 ppm can be attributed to one isomer **2** and a singlet at 4.25—4.29 ppm can be attributed to another isomer **3**.

Yields of **2** and **3** were 10 and 8 mol% based on ylide **1** used, respectively. Although the yields of the products **2** and **3** are relatively low, formation of **2** and **3** indicates that unstable carbon oxides formed by the reduction of CO_2 with benzoin carbanion decomposes ylide **1** to give a carbene and the carbene formed inserts to benzoin to give **2** and **3**.

One might suppose that ylide **1** is decomposed by the compounds which is present in the solution. In order to exclude this possibility, six sorts of control experiments were undertaken. The reactions of ylide **1** with following six mixtures were carried out at room temperature for 0.5 h. (a) Benzoin and THF; (b) Benzoin, Li, and THF; (c) Benzoin, benzaldehyde, and THF; (d) Benzoin, hydrobenzoin (see Experimental), THF; (e) Benzoin, benzil, and THF; (f) Benzoin, lithium benzoate, lithium carbonate, and THF. These six experiments gave only disulfone $CH_2(SO_2Ph)_2$ but did not give product **2** and **3**. Presumably ylide **1** abstracts hydrogen atom from THF to give disulfone. In the control expertiments the ylide **1** was remained as a powder at first and gradually dissolved in the THF solution by the reaction with THF in 0.5 h. On the other hand, ylide **1** decomposed in a few minutes when **1** was added to the solution containing reduction products of CO_2. These control experiments exclude the possibility that compounds in the solution other than reduction products of CO_2 (C_xO_y) decompose the ylide **1**. Therefore, it is probable that C_xO_y decompose the ylide **1**.

Reaction scheme is tentatively shown as following.



$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH(OH)Ph + 2Li \longrightarrow Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OLi}{|}}{\underline{C}}{-}Ph \xrightarrow{CO_2} C_xO_y} \qquad (1)$$

$$\mathrm{C_xO_y + \underset{\mathbf{1}}{PhI^+{-}C^-(SO_2Ph)_2} \longrightarrow PhI^+{-}C^{\underset{\cdot}{-}}(SO_2Ph)} \qquad (2)$$

$$\mathrm{PhI^+{-}C^{\underset{\cdot}{-}}(SO_2Ph) \xrightarrow[\text{from THFor -OH}]{+H} \longrightarrow :CH(SO_2Ph)} \qquad (3)$$

$$\mathrm{Benzoin + :CH(SO_2Ph) \xrightarrow{\text{C-H insertion}} \mathbf{3}} \qquad (4)$$

$$\mathrm{Benzoin + :CH(SO_2Ph) \longrightarrow Ph{-}\overset{\overset{O^-}{|}}{\underset{\underset{H\underset{+}{C}(SO_2Ph)}{|}}{C}}{-}CH(OH)Ph \longrightarrow \mathbf{2}} \qquad (5)$$

Such a characteristic decomposition reaction of **1** has not been reported.[7)] Forbus et al. have reported the preference of C_2O for attack on oxygen over C–H insertion.[4h)] In preceding paper carbon atom of unstable carbon oxide was captured by sulfur atom.[1)] The fact that C_xO_y showed characteristic behavior to sydnones[3)] can be explained by similar tendency of them. Presumably such a tendency of a preferential attack of C_xO_y on heteroatom such as sulfur atom over carbon atom of the ylide brings about elimination of a sulfonyl group as shown in the reaction (2). Although phenylsulfonylcarbene is considered to be formed as shown in reaction (3), detailed interpretation of this reaction can not be given in the present stage of this study. Insertion of phenylsulfonylcarbene to C–H bond of benzoin gives the isomer **3** as is shown in reaction (4). Attack of carbene to a carbon atom of C=O bond of ketones has been proposed to give dipolar intermediate[11)] as is shown in reaction (5). Rearrangement of an alkyl group in such a dipolar adduct does not seem to occur to so much extent in the reaction of simple ketones. However, rearrangement of CH(OH)Ph group to carbon atom of $CH(SO_2Ph)$ group seems to occur to some extent to give isomer **2**.

Although capture of carbon atom from unstable carbon oxides by ylides **1** was unsuccessful in the present report, the present results indicated that benzoin carbanion formed using Li metal reduced CO_2 to give C_xO_y, and that C_xO_y formed had special reactivity.

Experimental

General Procedures. The ^{1}H NMR spectra were recorded on JEOL Fourier transform NMR spectrometer operating at 89.55 MHz and Brooker AC 250T NMR spectrometer operating at 250 MHz. The ^{13}C NMR were recorded on a Brooker AC 250T NMR spectrometer. Mass spectra were recorded on JEOL JMS-DX-300 mass spectrometer. Other procedures and instruments were described in the previous paper.[2)]

Formation of Benzoin Carbanion and the Reaction of the Carbanion Formed with CO_2. Into the nitrogen containing 100 ml two-necked flask, in which 0.009 g atom of lithium powder was placed, 10 ml of THF, which was refluxed over $LiAlH_4$ under nitrogen atmosphere and distilled just before use, was injected through a serum cap using a syringe. To this mixture 16 ml of THF solution containing 0.0045 mol of benzoin was injected through a serum cap using a syringe, and the resulting mixture was stirred for 3 h at room temperature. The resulting dark red mixture was immersed in a cooling bath maintained at −78 °C. To this solution CO_2 was bubbled as gas through a delivery tube for 20 min. During the introduction of CO_2 a part of CO_2 escapes from a needle which is attached to a serum cap. After the reaction THF was evaporated and the residue was analyzed by same procedure as described in the previous paper.[2)] Yields of the reaction products were benzoin 55, benzil 20, hydrobenzoin 11,[12)] and lithium benzoate 3% based on benzoin used.[13)]

Reaction of the Reduction Products of CO_2 with Ylide 1. After the reaction of benzoin carbanion with CO_2 was finished as described above, a serum cap was put off and 0.0018 mol of ylide **1** was added at −78 °C as a powder through one neck of the flask. The resulting mixture was warmed to room temperature. A few minutes after warming up to room temperature the ylide seemed to decompose. The mixture was stirred for one hour at room temperature. THF was evaporated and the residue was separated by means of TLC using chloroform as an eluent. Crude mixture of **2** and **3** was again separated by means of TLC using a mixture of chloroform and ethyl acetate as an eluent. Yields of **2** and **3** were determined to be 10 and 8 mol% based on the ylide used from ^{1}H NMR spectrum. Although a mixture of **2** and **3** was slightly contaminated with decomposition products or hydrobenzoin because of difficulty of separation as mentioned above, satisfactory analytical result was obtained. Calcd for $C_{21}H_{18}O_4S$; M^+, 366.0926. Found: m/z 366.0930. This molecular formula of **2** and **3** and the fact shown by acetylation experiment that one isomer **2** has ^1H NMR absorptions at 4.30—4.51 and 5.85—5.89 ppm and another isomer **3** has a singlet at 4.25—4.29 ppm, together with fact shown by double irradiation technique that one isomer **2** consists of two diastereomers and another isomer **3** consists of one structure, indicate that structures of **2** and **3** are correct. Although disulfone was formed, quantitative analysis of it was not undertaken.

Author thanks to Dr. Hisahiro Hagiwara of this institute for measurement of mass spectra and helpful discussion.

References

1) F. Akiyama, *Bull. Chem. Soc. Jpn.*, **63**, 2131 (1990).

2) F. Akiyama, *Bull. Chem. Soc. Jpn.*, **61**, 3951 (1988).

3) F. Akiyama, *Chem. Lett.*, **1989**, 2009.

4) a) K. D. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961); b) K. D. Bayes, *ibid.*, **84**, 4077 (1962); c) C. Willis and K. D. Bayes, *ibid.*, **83**, 3203 (1966); d) R. T. Mullen and A. P. Wolf, *ibid.*, **84**, 3214 (1962); e) C. Devillers, *C. R. Acad. Sci. (Paris), Ser. C*, **262**, 1485 (1966); f) R. T. Baker, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc., A*, **1967**, 1641; g) G. R. Smith and W. Weltner, Jr, *J. Chem. Phys.*, **62**, 4592 (1975); h) T. R. Forbus, P. A. Birdsong, and P. B. Shevlin, *J. Am. Chem. Soc.*, **100**, 6425 (1978); i) G. Parker, D. Wiseman, C. Winter, and C. Mackay, *J. Org. Chem.*, **49**, 4494 (1984); j) O. Horie, W. Bauer, R. Meuser, V. H. Schmidt, and K. H. Becker, *Chem. Phys. Lett.*, **100**, 251 (1983); k) W. Bauer, R. Meuser, and K. H. Becker, *J. Photochem.*, **24**, 99 (1984); l) W. Bauer, K. H. Becker, and R. Meuser, *Ber. Bunsen-Ges. Phys. Chem.*, **89**, 340 (1985); m) C. Yamada, H. Kanamori, H. Horiguchi, S. Tsuchiya, and E. Hirota, *J. Chem. Phys.*, **84**, 2573 (1986); n) C. F. Chabalowski, R. T. Buenker, and S. D. Peyerimhoff, *J. Chem. Phys.*, **84**, 268 (1986).

5) a) R. L. Dekock and W. Weltner, Jr, *J. Am. Chem. Soc.*, **93**, 7106 (1971); b) R. D. Brown, F. W. Eastwood, P. S. Elmes, and P. D. Godfrey, *J. Am. Chem. Soc.*, **105**, 6496 (1983); c) R. D. Brown and E. N. Rice, *J. Am. Chem. Soc.*, **106**, 6475 (1954); d) T. B. Tang, H. Inokuchi, S. Saito, and E. Hirota, *Chem. Phys. Lett.*, **116**, 83 (1985).

6) a) R. J. Van Zee, G. R. Smith, and W. Weltner, Jr., *J. Am. Chem. Soc.*, **110**, 609 (1988); b) D. W. Ewing, *J. Am. Chem. Soc.*, **111**, 8809 (1989).

7) L. Hatjarapoglou, A. Varvoglis, N. W. Alcock, and G. A. Pike, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 2839.

8) When ylide **1** was added to the reaction mixture of CO_2 with benzoin carbanion formed using LDA, totally decomposition of the ylide **1** was observed to give disulfone. Presumably diisopropylamine decomposes ylide to give disulfone. Therefore, lithium was used to make benzoin carbanion.

9) During the separation procedure of a mixture of **2** and **3** by means of TLC or HPLC, decomposition of the isomers was observed to occur to some extent. During the separation procedure by means of HPLC elution time became very longer because of stuffing of the column.

10) Although this signal was observed as a singlet in the measurement by 90 MHz ^1H NMR this signal separated to a multiplet in the measurement by 250 MHz ^1H NMR. Presumably this separation can be attributed to a slight barrier for rotation around C–C bond since OH group locates between carbony and sulfonyl groups.

11) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York (1971), Chap. 11, p. 434.

12) Hydrobenzoin has been reported to be prepared by the reaction of benzoin with basic compound. For example, see A. Breuer and T. Zinke, *Liebigs Ann. Chem.*, **198**, 151 (1879). Therefore, hydrobenzoin is presumably formed during the reaction of benzoin with lithium at room temperature (vide ante).

13) Small amounts of benzaldehyde was formed. Since benzaldehyde was lost during evaporation procedure of THF, quantitative analyses of it was not undertaken. An unknown compound, which was found in near R_f range with hydrobenzoin, was obtained in a few wt% yield. It showed very low solubility, high melting point (220 °C). NMR spectra indicated that this compound had PhCH(OH) and PhC(OH) groups. Since this compound showed very peculiar behavior in NMR analyses including 2D NMR, which has not ever been reported in the literatures, structure can not be determined at present. Since this compound has same functional group with benzoin and it exists in small amount, it certainly has nothing to do with decomposition of the ylide **1**. Therefore, determination of the structure of this compound was postponed.