

Reduction of Sulfur Dioxide and Carbon Dioxide with Benzoin Carbanion. Oxygen Transfer from Products Formed by the Reduction of Sulfur Dioxide to 7,7,8,8-Tetracyanoquinodimethane

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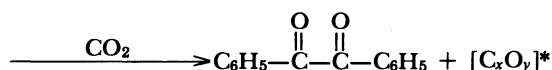
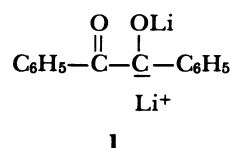
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A reaction of sulfur dioxide (SO_2) with benzoin carbanion (the lithium salt of benzoin dianion, **1**) in tetrahydrofuran (THF) gave a mixture of benzil (**2**) and benzoin (**3**) in yields of 83 and 17%, respectively, irrespective of the reaction temperature between -78 and 25°C . The reaction of carbon dioxide (CO_2) with **1** in THF gave a mixture of **2** and **3** accompanied by the formation of a small amount of lithium benzoate (**4**). The proportion of **2** in a mixture of **2** and **3** formed in the reaction of CO_2 with **1** were 49, 30, and 20% at -78 , -22 , and 25°C , respectively. The reaction of SO_2 with **1** in the presence of 7,7,8,8-tetracyanoquinodimethane (TCNQ) gave oligomers of TCNQ with a yield of 60%, in which some parts of the cyano groups were transformed to carboxylato groups.

From the view point of the use of resources it is important to investigate the reaction of sulfur dioxide (SO_2) or carbon dioxide (CO_2) with organic compounds. Especially, reductions of CO_2 or SO_2 have been extensively investigated for many years. It has been reported that a reduction of SO_2 with hydrogen sulfide,¹ methane,² carbon,³ carbon monoxide⁴ gave elemental sulfur. A reduction of CO_2 in the presence of various catalysts have been reported to give formic acid,⁵ methanol,⁶ or methane.⁷ Electrochemical or photoelectrochemical reduction of CO_2 has also been investigated.⁸ In these reactions SO_2 or CO_2 is converted to compounds having relatively low reactivity, such as carbon monoxide, formic acid, methanol, or elemental sulfur. If a reduction of SO_2 or CO_2 is conducted using mild reducing reagents, there is a possibility that unstable oxides, which are very reactive, may be formed. If we can use the high reactivity of these unstable oxides effectively, there is a possibility that we can fruitfully utilize SO_2 or CO_2 . An outline of this concept for the reduction of SO_2 was shown in a previous paper.⁹ That for the reduction of CO_2 is shown in Scheme 1.

Various types of sulfur oxides are known.¹⁰ Unstable sulfur monoxide has been known.¹¹ There might be other unstable sulfur oxides which have not been reported. Recently, unstable carbon oxides such as C_2O_2^+ ,¹² C_2O_2^- ,¹³ C_2O ,¹⁴ and C_3O ¹⁵ have been reported. In a previous paper the reduction of SO_2 with a mild reducing reagent, benzoin carbanion (the lithium salt of benzoin dianion, **1**), was reported to give unstable sulfur oxides which gave sulfur atoms to

cyclopentadiene to form oligomers having sulfide linkages.⁹ Although **1** has not been used as a reducing reagent in synthetic organic chemistry, it was found in a previous paper⁹ that **1** reduced SO_2 . In the present report it will be described that CO_2 is also reduced with **1**. The reaction scheme of a reduction of SO_2 with **1** was shown in the previous paper.⁹ That for the reduction of CO_2 with **1** is shown as follows:

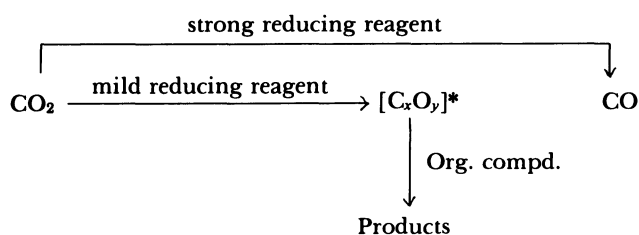


In addition to this result it will be described that the reduction products of SO_2 with **1** have sufficient reactivity to give an oxygen atom to 7,7,8,8-tetracyanoquinodimethane (TCNQ) and that the reduction products of CO_2 with **1** do not have sufficient reactivity to react with TCNQ.

Results and Discussion

Reaction of Benzoin Carbanion **1 with SO_2 (System A) or CO_2 (System B).** Reactions of **1** with SO_2 or CO_2 were carried out in tetrahydrofuran (THF) at three reaction temperatures -78 , -22 , and 25°C . The products were divided into water-soluble and -insoluble portions. Proportions of benzil (**2**) and benzoin (**3**) (the ratio of **2** to **3**) were measured from the NMR spectra of the water-insoluble portion and the yield of lithium benzoate (**4**) was measured from the NMR spectra of materials in the water-soluble portion (see Experimental).

In system A there was no **4** in the water-soluble portion and there were no organic compounds other than **2**, **3**, trace amounts of benzoic acid, and a small



Scheme 1.

Table 1. Products and Yields in the Reaction of Benzoin Carbanion **1** with SO₂ or CO₂ in THF

Reaction	Temp	Proportion (%) ^{a)} of benzil and benzoin Benzil (2) / Benzoin (3)	Yield (%) ^{b)}	
	°C		Lithium benzoate (4)	Benzoic acid
SO ₂ ^{c)}	25	83 / 17	0	Trace
	-22			
	-78			
CO ₂ ^{d)}	25	20 / 80 ^{e)}	4 ^{f)}	0
	-22	30 / 70 ^{e)}	10 ^{f)}	0
	-78	49 / 51 ^{e)}	18 ^{f)}	0

a) Proportions mean the ratio of **2** to **3**. b) 0.5 mol of product $\times 100$ / mol of **3** used. c) Proportion in the system A means actual yield.¹⁶⁾ Since several runs at three reaction temperature gave products having almost same proportions of **2** and **3**, the average value of the proportions was calculated. Although the yield of **2** in system A was reported to be 85% in the previous paper,⁹⁾ several times of reinvestigation showed that 83% was correct value. d) Actual yield of **2** or **3** can be calculated by multiplying proportion of them with (100-yield of **4**)/100.¹⁷⁾ e) Average values of three runs at each temperature are shown. f) Average values of two runs at each temperature are shown.

amount of the reaction products of SO₂ with diisopropylamine in the water-insoluble portion,¹⁶⁾ proportion of **2** and **3** being shown in Table 1.

Since in system B a small amount of **4** was formed and was found in the water-soluble portion, its yields were measured at three reaction temperature (Table 1). The proportions of **2** and **3** in the water-insoluble portion were measured (Table 1).¹⁷⁾

Since one might suppose that a small amount of the oxygen contained in CO₂ or SO₂ or in the reaction vessel as an impurity plays an important role in the production of benzil, a reaction of **1** with air was undertaken at -22 °C in order to show that the reaction product of **1** with air was mainly **4**. Therefore, such a possibility can be excluded.

The possibility that oxygen of **4** comes from the oxygen contained as an impurity in the reaction vessel can be excluded for the following reasons. The facts that system A does not give **4** and scarcely gives benzoic acid and that the purity of CO₂ is more than 99 vol% exclude the existence of oxygen in system B. The fact that the yields of **2** and **4** increase as the reaction temperature decreases suggests that these two compounds are oxidation products of **1** with CO₂.

In system B, the lower was the reaction temperature, the higher was the yield of **2**. An increase in the yield of the oxidation product of **1** with a decreasing reaction temperature is, presumably, concerned with a change in the solvation of reaction intermediate (adduct of **1** with SO₂ or CO₂). Szwarc et al. have suggested that a decrease in the temperature facilitates the formation of a solvent-separated ion pair by the solvation of an ion pair.¹⁸⁾ If in system A the intermediate is well solvated and a change in temperature does not have any effect on the solvation, the yield of **2** is expected not to be affected by a change in the reaction temperature. If in system B the intermediate is poorly solvated at room temperature and the solvation of the intermediate is facilitated as the temperature decreases, the yield of **2** is expected to

be affected by a change in the reaction temperature. The well-solvated structure of the intermediate presumably has a higher probability of an oxidation-reduction reaction than a poorly solvated one.

It was confirmed by means of TLC and gel-permeation chromatography of the products that elemental sulfur was not formed in system A. It was also confirmed by means of GLC or NMR analyses that carbon monoxide or formic acid was not formed in system B. These facts indicate the possibility that unstable oxides are formed in system A or B. Several attempts for their isolation were unsuccessful, presumably because of their instabilities.

In order to check the reactivities of the unstable oxides or intermediate formed in a reaction of SO₂ or CO₂ with **1**, the reaction of **1** with a mixture of TCNQ with an excess amount of SO₂ or CO₂ was carried out.

Reaction of Benzoin Carbanion **1 with a Mixture of TCNQ and SO₂ (System C) or CO₂ (System D).** An experiment in which air or nitrogen was used in place of SO₂ or CO₂ was also carried out. The reaction products were mainly salt (LiTCNQ) and oligomers of TCNQ. The IR spectrum of the salt (KTCNQ, see Experimental) is well coincident with that of the authentic sample prepared by the method of Melby¹⁹⁾ and other workers.²⁰⁾ Yields of the salt are shown in Table 2. Low yields of KTCNQ in the reaction in the presence of air or nitrogen are presumably attributed to hydrolysis of LiTCNQ or KTCNQ during the separation procedure (contact with saturated aqueous KCl solution) because of the strong basicity of the products.²¹⁾ The highest yield of KTCNQ was obtained in system D, as is shown in Table 2.

Oligomers of TCNQ formed in the reactions were separated; their yields are shown in Table 2. The yield of the oligomer of TCNQ was obtained in system C. The IR spectra of these oligomers obtained by four sorts of reactions were similar. The IR absorptions at 1587 and 1360 cm⁻¹ for the oligomers indicate the presence of carboxylato groups.²²⁾ The IR absorption

Table 2. Yields of the Oligomers of TCNQ and KTCNQ Obtained by the Reaction of Benzoin Carbanion **1** with a Mixture of TCNQ and SO₂, CO₂, Air, or Nitrogen at -22°C in THF

Reaction	Yield (%) of the oligomer of TCNQ ^{a)}	Yield (%) of KTCNQ ^{b)}
SO ₂	60	31
CO ₂	7	74
Air	13	7
Nitrogen	7	5

a) Yields were calculated as 100×wt of oligomer/wt of TCNQ used.³⁰⁾ b) LiTCNQ formed was converted to KTCNQ (see work-up procedure in Experimental). Yields were calculated as 100×mol of KTCNQ/mol of TCNQ used.

of a COO⁻ symmetric stretching vibration at a relatively low frequency, such as 1360 cm⁻¹, has been reported for formates²³⁾ or metal salts of amino acids.²⁴⁾ The absence of IR absorption of 1540 and 860 cm⁻¹, which are seen in a spectrum of TCNQ, indicates that all of the TCNQ used were consumed. Two ¹³C NMR signals at δ 160 and 170 in ¹³C NMR of the oligomers indicate the presence of carboxylato groups. Steric crowding of the groups in the oligomers presumably brings about a slight upfield shift of the carboxylato group compared to the value reported in the literature (δ 170–185).²⁵⁾ The difference in the chemical shift of these two signals is presumably attributed to different structures to which the carboxylato groups are attached. Elemental analyses of the oligomer obtained in system C indicated that N/C (ratio of N and C content) was 0.29, which was less than 0.39 (the calculated value for TCNQ). This fact indicates that the formation of the carboxylato group brought about the removal of a nitrogen atom from the oligomer of TCNQ. The molecular weight of these oligomers (calibrated to the molecular weight of standard polystyrene) was between 800–200 judged from the analyses by means of gel-permeation chromatography.

These above-stated facts show that in system C TCNQ was converted to low molecular weight oligomers of TCNQ in which some of the CN groups are transformed to a carboxylato group in considerable yield. One might suppose that the oxygen of the carboxylato group in this oligomer of TCNQ comes about from the moisture or oxygen contained in the reaction vessel as an impurity. However, the fact that only system C gave an oligomer having a carboxylato group in high yield and that other reactions carried out using CO₂, air or nitrogen by almost the same procedure as system C, did not give the oligomer so much supports the conclusion that the oxygen of the carboxylato group of the oligomer obtained in the former reaction comes about from the reduction products of SO₂. The formation of the oligomer of TCNQ in a yield of around 10% (see Table 2) is presumably concerned with the hydrolyses of TCNQ by the moisture contained in the reaction vessel as an impurity or hydrolysis during the work-up procedure by moisture in the atmosphere. Therefore, it can be concluded that the oxygen of the carboxylato group in

a small amount of the oligomer obtained in system D does not come from the reduction products of CO₂.

The fact that the oligomer of TCNQ, having a carboxylato group, is formed in system C presumably indicates that an oxygen atom transfers from the formed unstable sulfur oxides to TCNQ. Previously, unstable sulfur oxides were trapped (see previous paper) and IR spectra were shown (see Fig. 4 in that paper).⁹⁾ Although one might suppose that water is possibly formed by a reduction of SO₂ with **1** and it hydrolyzes the CN groups of TCNQ to form a carboxylato group, the fact that system D, in which the reduction of CO₂ with **1** also possibly gives water, slightly gives a carboxylato group suggests the possibility that a carboxylato group is formed by an oxygen transfer from the formed unstable oxides. In order to show that the formation of oligomer in 60% yield in system C can not be attributed to a hydrolysis of the CN group by the formed water, a control experiment was carried out.²⁶⁾ Since water formed, even if the reduction gives water in system C, is far less than the water added in the control experiment, it can be considered that 60% yield of the oligomer is too high to be attributed to hydrolyses by a small amount of the formed water.

The sulfur-transfer reaction in the previous paper gave an oligomer of cyclopentadiene which contained almost 20 wt% of sulfur.⁹⁾ On the other hand, the oligomer of TCNQ obtained in system C was found to have only less than 1 wt% of sulfur. It is not yet clear why TCNQ does not accept sulfur so much but accept oxygen atoms from the formed unstable sulfur oxides.

The reaction of unstable sulfur oxides or carbon oxides formed in system A or B with various reagents are now being investigated.

Experimental

General Procedures. The IR spectra were measured using a JEOL Fourier transform IR spectrophotometer. The ¹H NMR spectra were recorded on a JEOL Fourier transform NMR spectrometer operating at 89.55 MHz and a JNM-PMX 60SI NMR spectrometer operating at 60 MHz. The ¹³C NMR spectra were recorded on a JEOL Fourier transform NMR spectrometer operating at 22.50 MHz. Thin-layer chromatography separations were carried out on silica

gel (Merk Art. 5717). Sulfur dioxide was distilled over phosphorous pentaoxide prior to use. Tetrahydrofuran was distilled over LiAlH_4 under a nitrogen atmosphere immediately prior to use. Diisopropylamine was distilled and dried over molecular sieves. Reagent-grade TCNQ was recrystallized from ethyl acetate prior to use. All other chemicals were of reagent grade and were obtained from commercial sources. In all reactions in the present report two-necked round-bottomed flask, one neck of which was capped with a serum cap and the other neck of which was installed with a delivery tube for SO_2 , CO_2 , air, or nitrogen, was used.

Reaction of Benzoin Carbanion 1 with SO_2 (System A) or CO_2 (System B). Since it has been reported that two sites of benzoin are converted to anion,²⁷⁾ slight excess amount of lithium diisopropylamide (LDA) compared to 2 equivalent of benzoin was used to form 1. To a THF solution of 1, formed using 3 mmol of benzoin with the same procedure as that described in a previous paper,⁹⁾ 9 mmol of SO_2 or a large excess amount of CO_2 was bubbled as gas through a delivery tube. During the introduction of SO_2 or CO_2 into the reaction solution, the solution changed in color from orange-red to dark red (almost black), and then to yellow. In the case of the reaction of CO_2 , the introduction of CO_2 was continued for at least 30 minutes after the reaction mixture changed in color to yellow. After the completion of the introduction of SO_2 or CO_2 , THF was evaporated to give a yellow residue. The residue was washed with water several times in order to separate the products into a water-soluble portion and a water-insoluble organic portion. From the water-insoluble organic portion 2 and 3 were separated by means of preparative TLC using chloroform as an eluent; their structures were confirmed by comparisons of their IR and NMR spectra with those of authentic samples. For quantitative analyses the water-insoluble organic products were dissolved in CDCl_3 and their ^1H NMR were taken to give a ratio of 2 to 3 from signals of methine (δ 6.06) and aromatic protons (δ 7.17–8.17). Since benzoic acid was not formed in system B and was formed in only trace amount in system A, 2 and 3 are the only components derived from 1 in the water-insoluble portion (the proportions are shown in Table 1). The water-soluble portion was evaporated to give a white residue. This residue was treated several times with silica-gel column chromatography using water as an eluent to give pure 4, the structure of which was confirmed by a comparison of their IR and NMR spectra with authentic samples. For quantitative analyses hexamethyldisiloxane was added to the white residue and its ^1H NMR spectra were taken in CD_3OD in order to measure the ratio of CH_3 protons of hexamethyldisiloxane (δ 0.07) and aromatic protons (δ 7.2–7.4 and 7.8–8.0) of 4.

Reaction of Benzoin Carbanion 1 with a Mixture of TCNQ and SO_2 (System C). To 3 mmol of TCNQ in a nitrogen-containing two-necked 200 ml round-bottomed flask, 120 ml of absolute THF was added using a syringe and stirred for 30 minutes at room temperature under nitrogen atmosphere to obtain a homogeneous solution. This mixture was cooled to -22°C and 20 mmol of SO_2 was introduced through delivery tube to this mixture. To this mixture THF solution of 3 mmol of 1, which was prepared in other 100 ml two necked round-bottomed flask, was added dropwise through a serum cap using a syringe at -22°C .

Work-up Procedure for the Reactions of the Systems C, D, E, and F. THF was evaporated from the reaction solutions to give residues. Each residue was treated with two different separation procedures in order to isolate metal-TCNQ salt and the oligomer of TCNQ.

One separation procedure is that for the separation of the metal-TCNQ salt. Since LiTCNQ has been known to be a little soluble in water and organic solvents (about 1%¹⁹⁾), LiTCNQ was converted to KTCNQ , which was reported to be practically insoluble in water or organic solvents, in order to separate the metal-TCNQ salt from the reaction mixture. In this separation procedure 50 ml of saturated aqueous potassium chloride and 100 ml of ethyl acetate was added to the residue. The resulting mixture was shaken and filtered to give a purple powder, followed by washing it with water several times and then with ethyl acetate several times. The obtained powder was dried and elemental analyses were undertaken to show it to be KTCNQ (Found: C, 59.25; H, 1.66; N, 22.33; K, 16.25%. Calcd for $\text{C}_{12}\text{H}_4\text{N}_4\text{K}$: C, 59.24, H, 1.66; N, 23.02, K, 16.07%). Since there is no method for the purification of this salt (other than washing), a little discrepancy between the observed and calculated N contents is unavoidable. Analyses of potassium were undertaken using sodium tetraphenylborate.

In another separation procedure the residue was extracted with ethyl acetate several times and the extracts were treated with preparative TLC using ethyl acetate as an eluent to give oligomers of TCNQ. 2 and 3 were located in the range of a larger R_f value than 0.75. The oligomer of TCNQ obtained in system C or D were located in a TLC plate in the range of $R_f=0.05\text{--}0.60$ or $R_f=0.03\text{--}0.08$, respectively. The oligomers obtained in systems E and F were located in the range $R_f=0.03\text{--}0.27$. The obtained oligomers of TCNQ were colored dark brown. In the latter cases there was a trace amount of blue powder, which were located in the TLC plate in the range $R_f=0.35\text{--}0.68$, which showed an IR spectra different from those of the oligomer shown in Table 2. Since the amount of this blue powder was less than those located in $R_f=0.03\text{--}0.27$, this powder was not characterized and was not included in the oligomer shown in Table 2.

Reaction of Benzoin Carbanion 1 with a Mixture of TCNQ and CO_2 (System D). To a homogeneous mixture of 3 mmol of TCNQ and 120 ml of absolute THF in a nitrogen-containing two-necked 200 ml round-bottomed flask, CO_2 , which was passed through an drying reagent, was introduced through a delivery tube for 30 minutes at -22°C (during the introduction of CO_2 a part of CO_2 escapes from a needle which is attached to a serum cap). A 3-mmol THF solution of 1, which was prepared in other 100 ml two-necked round-bottomed flask, was added dropwise to the THF solution of TCNQ, which was saturated with CO_2 . During the addition of 1 CO_2 was continued to be introduced through a delivery tube. To our knowledge the solubility of CO_2 in THF has not been reported. However, the solubility of CO_2 in dichloromethane,²⁸⁾ cyclohexane,²⁹⁾ or dimethyl sulfoxide²⁹⁾ at above room temperature has been reported. Since the solubilities in these solvents are not so much different from each other, the solubility of CO_2 in THF can be assumed to be not so much different from the solubilities in these three solvents. Since we can assume that a decrease in the temperature from room temperature to -22°C brings about at least a two-fold increase in the solubility of CO_2 (on

the basis of the data in those literatures),^{28,29} we can assume that the contained CO₂ is at least 9 times greater than TCNQ in the reaction mixture.

Reaction of Benzoin Carbanion 1 with TCNQ in the Presence of Air (System E). Almost the same reaction procedure that for system D was adopted, except for the use of air, which was passed through a 10% KOH aqueous solution in order to remove the CO₂ contained in air and drying reagent, in place of CO₂.

Reaction of Benzoin Carbanion 1 with TCNQ in the presence of Nitrogen Atmosphere (System F). Almost the same reaction procedure as that used in system D was adopted, except for the use of nitrogen, which was passed through a drying reagent, in place of CO₂.

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- 16) In the system A the weight of the water-insoluble portion, which contained the reaction products of diisopropylamine with SO₂ in the amount of 6 mol% of the sum of 2 and 3, was 2–3 wt% more than the weight of 3 used.
- 17) In the system B the weight of the water-insoluble portion, which contained the reaction products of diisopropylamine with CO₂ in the amount of 3 mol% of the sum of 2 and 3, was less than the weight of 3 used by the weight correspondent to a decrease owing to the formation of 4.
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- 21) In the system E or F ethyl acetate solution obtained from work-up procedure for separation of KTCNQ (contact with aqueous KCl solution) contained larger amount of oligomer of TCNQ (30% yield, compare with the yields in Table 2) than those obtained by the separation procedure of oligomer (TLC procedure without contact with water).
- 22) Oligomer contained in the ethyl acetate solution obtained from the separation procedure of KTCNQ in the systems E and F (see Ref. 21) also showed IR spectra having absorptions at 1587 and 1360 cm⁻¹. The fact that contact of the products with aqueous KCl solution gave oligomer having IR absorptions at 1587 and 1360 cm⁻¹ supports conclusion that these absorptions can be attributed to carboxylato group.
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- 26) After 13 ml of 1 mol dm⁻³ aqueous hydrochloric acid solution, amount of which was enough to neutralize the basic material, was added to the reaction solution of the system F carried out using 3 mmol of benzoin, the whole solution was evaporated and extracted with ethyl acetate. The oligomer of TCNQ was separated from this extract by means of TLC to show that the yield of oligomer was 30%.
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- 30) IR spectra of the oligomers obtained in the system D, E, and F showed contamination of small amount of LiTCNQ in the oligomer separated with TLC. Therefore, actual yields of the oligomers in these three cases are a little lower than those shown in Table 2. Since solubility of LiTCNQ in ethyl acetate is relatively small and R_f of LiTCNQ is very low, contamination of LiTCNQ in the oligomer obtained in the system C can be neglected.