CHEMISTRY LETTERS, pp. 2009-2012, 1989.

Reduction of Carbon Dioxide with Benzoin Carbanion. Conversion of the Reduction Products of Carbon Dioxide to a Mixture of Saturated Hydrocarbons

Fuminori AKIYAMA
Chemical Research Institute of Non-aqueous Solutions,
Tohoku University, Sendai 980

Heating under reflux of the tetrahydrofuran solution of the reduction products of carbon dioxide with benzoin carbanion in the presence of N-*p*-nitrophenylsydnone gave a mixture of saturated hydrocarbons.

Interest has been stimulated in the reduction of carbon dioxide (CO_2) in view of the use of resources.[1] In the preceding paper, it was proposed that reduction of CO_2 with benzoin carbanion (1) led to activation of CO_2.[2] Capture of the reduction products of CO_2 by 1 with sodium dithionite was recently tried to show that oligomers having a repeating unit, $-C(SO_3Na)_2-$, were obtained by this reaction.[3] This observation led the author to carry out reaction of the reduction products of CO_2 with the compounds having ionic structure such as sydnones. In the present paper, it will be reported that N-*p*-nitrophenylsydnone (2) catalyzes conversion of the reduction products of CO_2 to a mixture of saturated hydrocarbons. Other two sydnones, N-phenylsydnone (3) and N-*p*-methoxyphenylsydnone (4), were also tested.

After completion of the reaction of CO_2 at -78 °C with 4.5 mmol of 1 prepared using lithium diisopropylamid by the reported procedure,[2,4] 15 ml of tetrahydrofuran (THF) solution of 1.58 mmol of 2 was added to the solution using a syringe. After addition of the solution of 2, a serum cap was put off and a Liebig condenser was put on. The solution was warmed and then heated to reflux, during which a constant nitrogen stream was bubbled through an inlet tube. During heating for less than 5 min, a characteristic color-change in the solution, from red to dark red (almost black) then to original red, was observed. Red precipitates formed at the end of the color-change was found to be due to an adduct of 2 with lithium carbonate. After reflux for 20 min, THF was evaporated and residue was separated by silica-gel chromatography using chloroform as eluent. A fraction eluted prior to benzil was characterized as a mixture of saturated hydrocarbons on the basis of ^{1}H NMR (1.25 ppm(1.07—1.70), 0.88ppm(0.7—1.07)) and IR spectra(2954, 2923, 2870, 2854, 1458, and 1377 cm^{-1}). The isolated yield and composition of hydrocarbons are shown in Table 1 (see Run 1). Analyses of the reaction mixture after the color-change showed that all benzoin (equal amounts of benzoin and benzil were found in the solution in the case of Ref. 2) was converted to benzil after heating; by heating the amount of benzil was doubled.

Table 1. Hydrocarbons formed by heating of the reduction products of CO_2 by 1 in the presence of sydnones

Run	Condition sydnone/1 Heating time	Color-change in the solution Time, t$^{a)}$	$\frac{\text{Benzoin}}{\text{Benzoin+Benzil}}$	Isolated yield of hydrocarbon$^{b)}$ (%)	Hydrocarbon$^{c)}$
1	2/1 = 0.35 20 min	red→dark red ——→ red 3—4 min	≒ 0	22	$C_{11}H_{24}$ — $C_{26}H_{54}$
2	3/1 = 1 2 h	orange→dark red ——→ red 1 h	≒ 0	16	$C_{11}H_{24}$ — $C_{18}H_{38}$
3	4/1 = 1 5 h	yellow→dark red ——→ red 3.5 h	≒ 0	15	$C_{11}H_{24}$ — $C_{18}H_{38}$
4	without sydnone 0	yellow	0.51	13	$C_{11}H_{24}$ — $C_{18}H_{38}$
5	without sydnone 5 h	yellow→black	0.14	13	$C_{11}H_{24}$ — $C_{18}H_{38}$

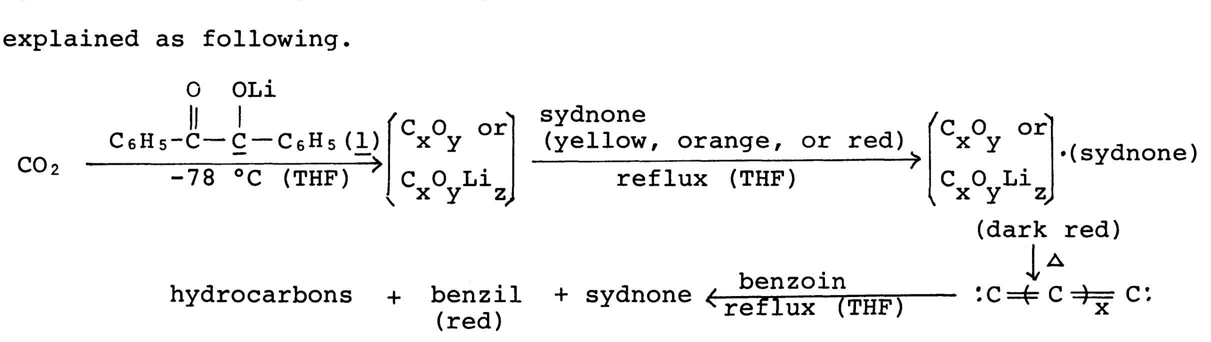
a) Time at which color-change from dark red to bright red was observed. When time t was converted to the time corresponding to the same sydnone concentration, a linear correlation between log(1/t) and Hammett constant σ of the substituent on sydnones was observed. b) 100×(g atom of carbon fixed)/(mol of CO_2 reduced). Amount of CO_2 reduced at -78 °C was calculated as 0.6 mol/1 mol of benzoin (sum of yields of benzil and lithium benzoate was about 60%, see Table 1 in Ref. 2). Low yields may be due to loss of lower hydrocarbons during evaporation of solvents.$^{5)}$ c) Compositions of hydrocarbons were determined by GLC and mass spectroscopy.

Similarly, THF solution of the reduction products was heated by addition of 4.5 mmol of 3 or 4 in place of 2 (1.58 mmol). The color-change in the solution from orange or yellow to dark red (almost black) then to bright red was observed by addition of 3 or 4 after heating for 1 or 3.5 h, respectively. In these two cases precipitates of an adduct of 3 or 4 with lithium carbonate were not formed. Isolated yields and compositions of hydrocarbons for these two cases are shown in Table 1 (Runs 2 and 3). In these two cases conversion of benzoin to benzil was also observed as shown in Table 1.

Control experiments, Runs 4 and 5 in Table 1, indicate that the reaction mixture of CO_2 with 1 contains low hydrocarbons even without heating (see Run 4) and that amount and composition of hydrocarbons were kept unchanged by heating without sydnone for 5 h (see Run 5). It was confirmed that n-hexane solution of n-butyl lithium used contained almost the same amount of hydrocarbons having the same composition as that observed in Runs 4 and 5. Since Run 1 gave higher hydrocarbons in higher yield than those in Runs 4 and 5, it can be concluded that higher ones in Run 1 are formed by thermal reaction of reduction products of CO_2 in the presence of 2.[6]

Another control experiment showed that heating of a mixture of 2, 3, or 4 with benzoin under reflux of THF gave neither reaction product nor color-change in the solution. Therefore, observations in Runs 1—3, i.e., 1) characteristic color-change, 2) conversion of benzoin to benzil, 3) recovery of sydnone as free sydnone or adduct with lithium carbonate, indicate that conversion of the reduction products of CO_2 to hydrocarbons took place not only in Run 1 but in Runs 2 and 3. Presumably the reaction with sydnones 3 or 4 gives volatile hydrocarbons, which are supposed to be lost during evaporation procedure of the solvents.[5]

Reactions of unstable carbon oxide C_2O with ethylenes[7] or THF[8] have been reported. Unstable carbon oxide such as C_3O[9], C_4O[10], or C_6O[10] has been considered to have the structure $:C{=}(C{=})_{x}C{=}O$. If reduction products C_xO_y or $C_xO_yLi_z$ formed in the reduction of CO_2 with 1 involve cumulene structure in their molecules and can eject polymerizable fragment such as $:C{=}(C{=})_{x}C:$, formation of hydrocarbons or oligomers having a repeating unit, $-C(Z)_2-$ can be tentatively explained as following.



If a molecule which does not transfer hydrogen atom but transfers other functional group Z to $:C{=}({=}C{=})_x{=}C:$ is present in the solution, oligomers having a repeating unit, $-C(Z)_2-$, such as $-C(SO_3Na)_2-$, may be formed.

The reactions of unstable reduction products of CO_2 by 1 with other various reagents are now being investigated.

References

1) The references are cited in the preceding paper.$^{2)}$

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

3) Heating of the reduction products of CO_2 with 1 in water solution of sodium dithionite gave a compound with no ^1H NMR signal but only one ^{13}C NMR signal at 75.4 ppm. Sufficient purification of it was hampered owing to its instability. However, NMR, IR data, and formation of the salt with benzylthiuronium chloride suggest that the compound is an oligomer having a repeating unit, $-C(SO_3Na)_2-$.

4) F. Akiyama, J. Polym. Sci., Polym. Lett. Ed., 24, 631 (1986).

5) GLC analyses of a mixture of hydrocarbons formed and the solvents were not performed because only very small amounts of hydrocarbons compared with solvents were formed. Therefore, evaporation of the solvents was necessary for the isolation of hydrocarbons formed.

6) The carbanion (1) could be formed by the reaction of benzoin with lithium metal at room temperature in THF and it was used for the reduction of CO_2 at -78 °C. Heating of the reduction products of CO_2 in this case in the presence of sydnone also gave hydrocarbons in lower yields than those shown in Table 1. Although low efficiency of formation of 1 using Li led to low yield of hydrocarbons, this fact indicates that hydrocarbons were formed even when n-hexane solution of n-BuLi was not used for the reaction.

7) K. D. Bayes, J. Am. Chem. Soc., 83, 3712 (1961); K. D. Bayes, ibid., 84, 4077 (1962); C. Willis and K. D. Bayes, ibid., 88, 3203 (1966); G. Parker, D. Wiseman, C. Winter, and C. Mackay, J. Org. Chem., 49, 4494 (1984).

8) T. R. Foubus, P. A. Birdsong, and P. B. Shevlin, J. Am. Chem. Soc., 100, 6425 (1978).

9) References are cited in the preceding paper.$^{2)}$

10) R. J. Van Zee, G. R. Smith, and W. Wetner, Jr, J. Am. Chem. Soc., 110, 609 (1988).

(Received September 1, 1989)