

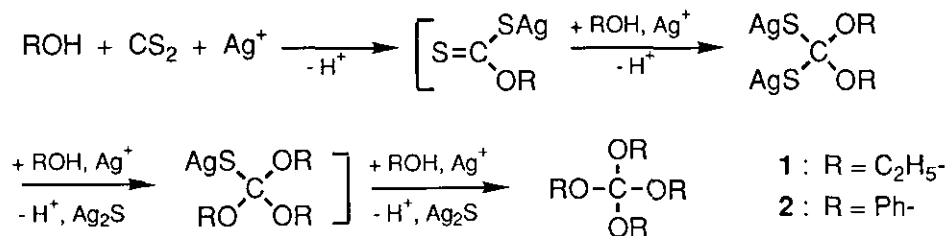
SILVER(I) ION-MEDIATED DESULFURIZATION-CONDENSATION OF
CARBON DISULFIDE WITH SOME HYDROXYL COMPOUNDS

Isao Shibuya,* Yasuo Gama, and Masao Shimizu

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba,
Ibaraki 305, Japan

Abstract - The title reaction with ethanol and phenol gave tetraethyl and tetraphenyl orthocarbonate, respectively, in good yields. Diols, such as benzene-1,2-dimethanol, *meso*-hydrobenzoin, and cathecol, afforded spiro orthocarbonic acid esters. In the same manner, 2-anilinoethanol, *N*-methylantranilic acid, and salicylic acid led to some novel spirobicycles.

In the previous paper we reported that the desulfurization-condensation of thiocarbonyl compounds with active methylenes, amines and diols under mild conditions gives olefins, imines and acetals, respectively.¹ We also demonstrated that thioketones are an efficient unique protecting agent for hydroxyl groups of polyols and glycosides.^{2,3} Carbon disulfide, a simple thiocarbonyl compound, is expected to be a useful material for synthesizing orthocarbonic acid esters and their related compounds if it is enough reactive to hydroxyl group. However, actually it has been hardly used due to lack of the reactivity, and more reactive and specific reagents such as chloropicrin, trichloroacetonitrile, trichloromethanesulfonyl chloride, and *N*-trichloromethyl carboimide dichloride have been frequently used for preparing them.⁴ In our serial study, we attempted the title reaction with ethanol, phenol, diols, 2-anilinoethanol, *N*-methylantranilic acid, and salicylic acid, and found that the use of a silver salt with these hydroxyl compounds activates carbon disulfide to afford their products.

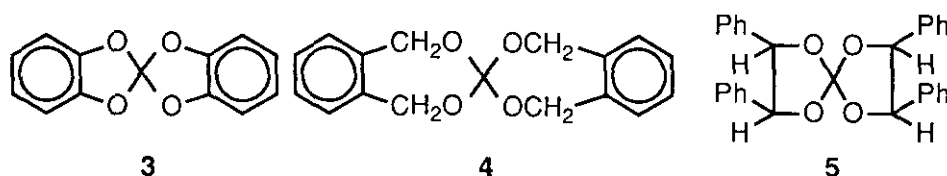


Scheme 1

At first, we tried the reaction of carbon disulfide with silver trifluoroacetate in ethanol-triethylamine at room temperature, and we obtained tetraethyl orthocarbonate (**1**), which is known to be given by the reaction of hazardous chloropicrin with sodium ethoxide.⁵ Tetraphenyl orthocarbonate (**2**), prepared from *N*-trichloromethyl carboimide dichloride and phenol,⁶ was also obtained in a good yield by the similar way.

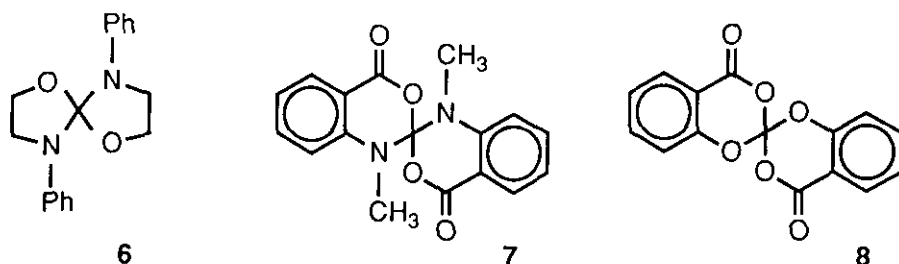
This new reaction would be considered to proceed as follow: carbon disulfide is desulfurized through successive condensation of four hydroxyl groups along the plausible pathway shown as Scheme 1, and produces **1** or **2** with liberating silver sulfide.

It has been reported that the reaction of carbon disulfide with cyclic dibutyltin dialkoxide,^{7,8} affords spiro orthocarbonates. On the other hand, the application to the title reaction with diols such as catechol, benzene-1,2-dimethanol, and *meso*-hydrobenzoin gave directly the corresponding spiro orthocarbonates, 2,2'-spirobi[benzo-1,3-dioxolane] (**3**), 2,2'-spirobi[5,6-benzo-1,3-dioxepane] (**4**), and 2,2'-spirobi[4,5-diphenyl-1,3-dioxolane] (**5**), respectively, by the same pathway as Scheme 1.



Furthermore we examined the desulfurization-condensation with 2-anilinoethanol and *N*-methylantranilic acid, and we obtained the condensation products 2,2'-spirobi[3-phenyl-1,3-oxazolane] (**6**) and 2,2'-2*H*,2*H*'-spirobi[benzo-1,3-oxazin-4-one] (**7**) in 76 and 73% yields, respectively. The relatively high yields of **6** and **7**, compared with those of **4** and **5**, may be assumed that these amino compounds and carbon disulfide form previously the 2:1 adducts, ammonium dithiocarbamates, and the adducts are desulfurized with silver ion to give **6** and **7**. Moreover, in the desulfurization-condensation of α - or β -hydroxy carboxylic acids, salicylic acid gave only novel 2,2'-2*H*,2*H*'-spirobi[benzo-1,3-dioxane-4-one] (**8**) in spite of a low yield.

In conclusion, we found that carbon disulfide is not only conveniently available to the synthesis of orthocarbonic acid esters by using a silver salt as a desulfurizing agent, but also through this desulfurization-condensation some novel spirobicycles are prepared from *N*-substituted amino compounds, such as 2-anilinoethanol, *N*-methylantranilic acid, and salicylic acid, as well as diols.



EXPERIMENTAL

All melting points were measured on a Mettler FP90 microscope plate, and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 300BB spectrometer in the solution of CDCl₃ using TMS as an internal standard. The MS spectra were taken on a Shimadzu (GCMS-QP2000A) spectrometer. IR

spectra were measured on a JASCO (FT-5300) spectrophotometer using KBr disks.

Preparation of tetraethyl orthocarbonate (1).

To a solution of triethylamine (5.0 g, 50 mmol), and carbon disulfide (0.76 g, 10 mmol) in ethanol (10 mL), silver trifluoroacetate (9.05 g, 41 mmol) was added over 5 min with stirring and the reaction mixture was continuously stirred for 5 h at rt. After removal of the solvent by evaporation, resulting tetraethyl orthocarbonate was subsequently distilled at 158 - 162°C (lit.,⁵ 158 - 161°C) to give **1** (1.17 g, 61%).

Preparation of tetraphenyl orthocarbonate (2).

To a solution of carbon disulfide (76 mg, 1 mmol), phenol (470 mg, 5 mmol) and triethylamine (710 mg, 7 mmol) in acetonitrile (5 mL), silver trifluoroacetate (1.10 g, 5 mmol) was added bit by bit with stirring at rt and the reaction mixture was allowed to stand overnight. After removal of silver sulfide by filtration, organic layer was passed through on a silica gel column (Merck silica gel 60, hexane : ethyl acetate = 1 : 1) to give colorless powder of **2** (261 mg, 68%); mp 97°C, (lit.,⁶ 98°C).

Typical procedure for preparing 3 - 8.

A typical experimental procedure for the reaction of carbon disulfide with catechol in the presence of silver trifluoroacetate was as follow: to a solution of carbon disulfide (76 mg, 1 mmol), catechol (264 mg, 2.4 mmol), and triethylamine (710 mg, 7 mmol) in acetonitrile (5 mL), silver trifluoroacetate (1.10 g, 5 mmol) was bit by bit added over 3 min with stirring on an ice-water bath. The reaction mixture was continuously stirred for 5 h at rt. After evaporation of the solvent under reduced pressure, ethyl acetate was added to the residue, and silver sulfide was removed by filtration. The resulting organic layer was passed through on a silica gel column (the same conditions as **2**) to give colorless powder of 2,2'-spirobi[benzo-1,3-dioxolane] (**3**) (170 mg, 75%); mp 110°C, (lit.,⁶ 110°C).

According to the above-mentioned method, products (**4** - **8**) were also obtained. Their characterization data were shown below.

2,2'-Spirobi[5,6-benzo-1,3-dioxepane] (4).

Colorless powder; yield 88 mg (31%); mp 252°C (hexane); ¹H NMR δ = 5.02 (*s*, 8H), 7.07 ~ 7.26 (*m*, 8H); ¹³C NMR δ = 65.8, 126.1, 126.2, 127.0, 136.4; MS *m/z* 284 (*M*⁺); IR ν 1499, 1140, 1118, 1105, 992, 750 *cm*⁻¹. Anal. Calcd for C₁₇H₁₆O₄: C, 71.82; H, 5.67. Found: C, 71.82; H, 5.67.

2,2'-Spirobi[4,5-diphenyl-1,3-dioxolane] (5).

Colorless powder; yield 80 mg (33%); mp 125°C (isopropyl ether); ¹H NMR δ = 5.73 (*s*, 4H), 7.08 ~ 7.25 (*m*, 20H); ¹³C NMR δ = 81.8, 82.5, 126.8, 126.9, 127.7, 127.8, 127.9, 134.1, 134.9, 136.0; MS *m/z* 436 (*M*⁺), 240; IR ν 1499, 1321, 1192, 1071 *cm*⁻¹. Anal. Calcd for C₂₉H₂₄O₄: C, 79.80; H, 5.54. Found: C, 79.81; H, 5.61.

2,2'-Spirobi[3-phenyl-1,3-oxazolane] (6).

Colorless powder; yield 215 mg (76%); mp 110°C (isopropyl ether); ¹H NMR δ = 3.86 (*m*, 4H), 4.25 (*m*, 4H), 6.78 - 7.51 (*m*, 10H); ¹³C NMR δ = 45.1, 46.4, 61.2, 62.4, 114.8, 118.2, 119.4, 124.0, 128.7, 129.0, 138.2, 142.1; MS *m/z* 282 (*M*⁺); IR ν 1601, 1505, 1358, 1244, 1045 *cm*⁻¹. Anal. Calcd for C₁₇H₁₈N₂O₂: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.53; H, 6.36; N, 9.78.

2,2'-2H,2H'-Spirobi[benzo-1,3-oxazin-4-one] (7).

Colorless powder; yield 235 mg (73%); mp 181°C (ethyl acetate); ¹H NMR δ = 2.98 (*s*, 3H), 3.47 (*s*, 3H),

6.98 ~ 8.06 (*m*, 8H); ^{13}C NMR δ = 31.5, 34.5, 111.1, 111.2, 113.6, 113.9, 118.6, 120.8, 123.5, 126.6, 130.4, 132.1, 136.6, 137.7, 146.4, 148.9, 159.0; MS m/z 310 (M^+), 266, 181, 134; IR ν 1751 ($\text{C}=\text{O}$), 1726 ($\text{C}=\text{O}$), 1606, 1358, 1028 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$: C, 65.80; H, 4.55; N, 9.03. Found: C, 65.84; H, 4.58; N, 8.95.

2,2'-2H,2H'-Spiro[benzo-1,3-dioxane-4-one] (8).

Colorless powder; yield 57 mg (20%); mp 150°C (ethyl acetate); ^1H NMR δ = 7.04 ~ 7.19 (*m*); ^{13}C NMR δ = 111.5, 116.8, 124.9, 130.2, 137.6, 153.0, 156.8; MS m/z 284 (M^+), 240, 212, 168; IR ν 1757 ($\text{C}=\text{O}$), 1618, 1467, 1296, 1199, 953 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_8\text{O}_6$: C, 63.39; H, 2.84. Found: C, 63.38; H, 2.79.

REFERENCES

1. I. Shibuya, Y. Taguchi, T. Tsuchiya, A. Oishi, and E. Katoh, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3048.
2. I. Shibuya, E. Katoh, Y. Gama, A. Oishi, Y. Taguchi, and T. Tsuchiya, *Heterocycles*, 1996, **43**, 851.
3. Y. Gama, I. Shibuya, and E. Katoh, *Carbohydr. Lett.*, to be submitted
4. W. Kantlehner, B. Funke, E. Haug, P. Spech, L. Kienitz, and T. Maier, *Synthesis*, 1977, 73.
5. J. D. Roberts and R. E. McMahon, *Org. Synth., Coll. Vol.*, 1963, **IV**, 457.
6. K. Findeisen, K. Wagner, and H. Holtschmidt, *Synthesis*, 1972, 599.
7. S. Sakai, Y. Kobayashi, K. Itoh, and Y. Ishii, *J. Org. Chem.*, 1970, **35**, 2347.
8. S. Sakai, Y. Kobayashi, and Y. Ishii, *J. Org. Chem.*, 1971, **36**, 1176.

Received, 10th November, 1997