Notes

Reactivity of Carbon Disulfide with Aryl Radicals

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Carbon disulfide reacts with carbenes and thioketocarbenes to afford cycloaddition products on double bond C=S, and thus reacts with diaryldiazomethane[1] to yield 3,6-dimethylene-1,2,4,5-tetrathiocyclohexanes and with 1,2,3-benzothiadiazole[2] affording benzo-1,3-dithiol-2-thione, though the latter reaction may be seen as 1,3-dipolar addition. We wish to report some experimental results on the reactivity of carbon disulfide toward aryl radicals generated by reduction of aryldiazonium fluoroborates by iodide ions.[3] The reaction, carried out at room temperature by adding sodium iodide to a solution of the appropriate aryldiazonium fluoroborate (**1**) in a 1:1 acetone/carbon disulfide mixture, gives diaryl disulfide (**2**), diaryl trithiocarbonate (**3**), and small quantities of iodoarene (Scheme I).

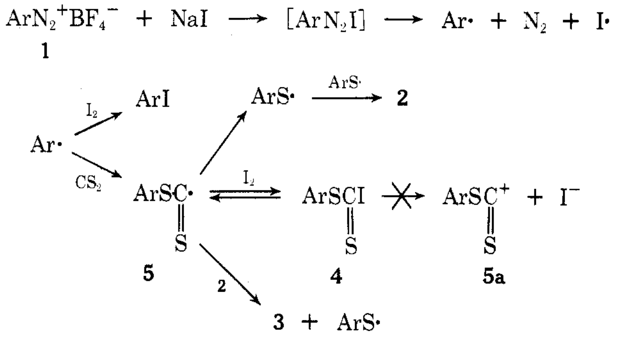
Scheme I

$$\underset{\mathbf{1}}{ArN_2{}^+BF_4{}^-} + CS_2 \xrightarrow{NaI} ArI + \underset{\mathbf{2}}{ArSSAr} + \underset{\mathbf{3}}{(ArS)_2CS}$$

As it can be seen in Table I, yields of disulfides are good, and this reaction may represent an alternative to the traditional Leukart reaction → oxidation pathway[4] to symmetrical disulfides, except for some derivatives such as OCH_3 and SCH_3.[5]

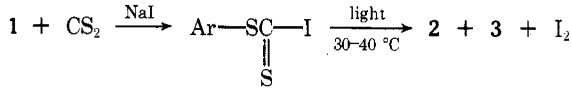
The first step of this reaction is very likely the attack of aryl radical on the sulfur atom of carbon disulfide leading to the radical **5**. Three kinds of reactions are possible from this intermediate: (1) loss of carbon monosulfide generating arylthio radicals which afford **2** by dimerization; (2) homolytic substitution SH2 on a sulfur atom of S–S bond of **2** to give **3**, and (3) reversible reaction with iodine to afford 4 (Scheme II).

Scheme II



The reaction carried out at 0 °C (under nitrogen) leads actually to the separation of the highly instable aryl iododithioformate (**4**) which is easily converted by light or heating at 30–40 °C into **2**, **3**, and iodine (Scheme III).

Scheme III



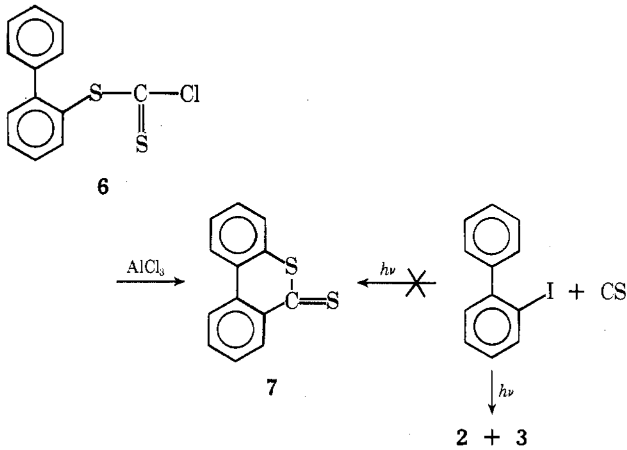
$$1 + CS_2 \xrightarrow{NaI} Ar{-}\underset{\underset{S}{\|}}{SC}{-}I \xrightarrow[30\text{–}40\ °C]{light} 2 + 3 + I_2$$

4

Ar = *o*-PhPh

A cationic mechanism with **5a** as intermediate can be ruled out by examining products of the heterolytic Friedel–Crafts type reaction[17] between 2-biphenylyl chlorodithioformate (**6**) and $AlCl_3$ in carbon disulfide. **2**, Ar = *o*-PhPh, and **3**, Ar = *o*-PhPh, are not present in the reaction mixture and dibenzo[*c*,*e*]thiin-2-thione (**7**) was obtained in quantitative yield. On the other hand, when 2-iodobiphenyl was photolyzed in an ether/carbon disulfide mixture the products isolated were **2**, Ar = *o*-PhPh, and **3**, Ar = *o*-PhPh, but no traces of **7** were found in agreement with results obtained from the decomposition of **1**, Ar = *o*-PhPh, with NaI (Scheme IV).

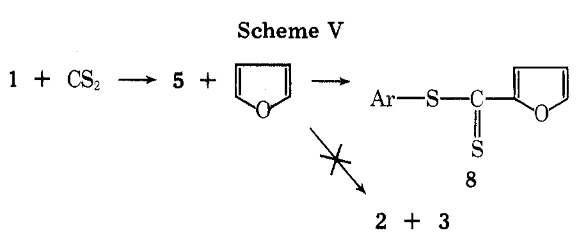
Scheme IV



The intervention of **5** as intermediate was further on demonstrated by decomposing **1**, Ar = Ph, in a 1:1 furan/carbon disulfide mixture. In this case aryl 2-dithiofuroate (**8**) was obtained in 75% yield together with trace amounts of **2**. No substitution products deriving from attack of aryl radicals on the furan ring were detected by GLC though the furan is known to be highly reactive in homolytic aromatic substitution.[18]

This fact indicates that carbon disulfide is an effective scavenger of aryl radicals (Scheme V).

Scheme V



Ar = Ph

Experimental Section

GLC analyses were carried out with a Varian 1440/1 instrument (5% SE-30 on a Varaport column). The reaction products were all identified by comparison (mixture melting point, NMR, and mass spectra) with authentic samples prepared independently. NMR spectra were recorded with a JEOL 60-MHz instrument and mass spectra with a JEOL D-100 instrument. All the aryldiazonium fluoroborates,[19] diphenyl trithiocarbonate (**3**),[20] and 2-mercaptobiphenyl[4] were prepared according to the procedures described in the literature. Only

Table I. Yields[a] of Ar–S–S–Ar (2) from Reaction of $ArN_2^+BF_4^-$ (1) with NaI in a 1:1 Acetone/Carbon Disulfide Mixture

Ar	Registry no.	Yield, %	Ar	Registry no.	Yield,[a] %
Phenyl[6]	882-33-7	47	*m*-Anisyl[11]	59014-89-0	46
o-Tolyl[7]	4032-80-8	60	*p*-Tolyl[12]	103-19-5	45
o-Anisyl[8]	13920-94-0	10	*p*-Anisyl[13]	5335-87-5	45
2-Biphenylyl[4]	19813-97-9	33	*p*-Nitrophenyl[14]	100-32-3	34
o-Phenylthiophenyl[9]	58074-47-8	45	*p*-Chlorophenyl[15]	1142-19-4	40
o-Methylthiophenyl[10]	59014-88-9	0	2,6-Xylyl[16]	2905-17-1	30

[a] Based on the starting aryldiazonium fluoroborate (**1**).

well-dried samples of diaryldiazonium fluoroborates were used. Carbon disulfide was dried with calcium chloride and then distilled twice. Acetone was refluxed over $KMnO_4$ and distilled over P_2O_5 twice.

Decomposition of Aryldiazonium Fluoroborate (1). General Procedure. The salt (0.01 mol) was dissolved in acetone (30 ml). To the solution was first added CS_2 (30 ml) and then NaI (1.5 g) in small quantities under stirring. After nitrogen evolution the mixture was refluxed for 30 min and the solvent evaporated. The crude was dissolved in chloroform, washed with water and dried and the solvent removed under vacuum. The mixture was analyzed on GLC or chromatographed on a silica gel column.

A. From **1** (R = Ph) diphenyl disulfide (**2**, 47%) and diphenyl trithiocarbonate (**3**, 35%) were separated by column chromatography on silica gel, using light petroleum as an eluent.

B. From **1** (R = *o*-PhPh) were obtained 2-iodobiphenyl, 2-biphenylyl disulfide (**2**, 33%), and a yellow product identified as di-2-biphenylyl trithiocarbonate (**3**, 30%): mp 119 °C; mass spectrum *m/e* 414 ($M\cdot^+$, 11), 370 (6), 338 (35), 229 (100), 197 (40), 185 (39), 184 (43), 152 (40). Anal. Calcd for $C_{25}H_{18}S_3$: C, 72.42; H, 4.38; S, 23.22. Found: C, 72.1; H, 4.4; S, 23.4.

C. From 1 (R = *o*-PhPh) at 0 °C. The salt (0.01 mol) was dissolved in acetone (30 ml) under nitrogen in the dark and CS_2 (30 ml) was added. The solution was cooled to −5 to 0 °C and NaI (1.5 g) was added slowly under stirring. After 10 min, the nitrogen flow was increased and the solvent evaporated at 0 °C. The crude was rapidly extracted with light petroleum, and the organic layer filtered on silica gel (*h* = 15 cm) under nitrogen. A dilute solution of 2-biphenylyl iododithioformate (**4**) was obtained, and was kept at −20 °C. This solution, gently heated at 30–40 °C, or exposed to uv light, rapidly affords iodine, 2-biphenylyl disulfide (**2**), and di-2-biphenylyl trithiocarbonate (**3**) identified by TLC. An alcoholic solution of **4** gives a positive test with alcoholic $AgNO_3$: mass spectrum *m/e* 356 ($M\cdot^+$) (0.5), 280 (100), 184 (35), 185 (45), 153 (100).

D. From 1 (R = Ph) in Furan. The salt (0.01 mol) was suspended in a furan (30 ml) and CS_2 (30 ml) mixture, and NaI (1.5 g) was added in small quantities under stirring at room temperature. The solution was stirred for 5 h, washed with water, and dried, and the solvent was evaporated. By column chromatography of the crude on silica gel were separated diphenyl disulfide (**2**, traces) and phenyl 2-dithiofuroate (**8**, 75% yield) as a red oil: bp 85 °C (1 mm); mass spectrum *m/e* 220 ($M\cdot^+$, 21), 111 ($M\cdot^+$ − PhS·, 100). Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.0; H, 3.65; S, 29.4.

Photolysis of 2-Iodobiphenyl. A solution of 2-iodobiphenyl (0.9 g, 0.005 mol) in Et_2O (8 ml) and CS_2 (2 ml) mixture was photolyzed using a low-pressure mercury lamp Hanau Type P.L. 368 for 12 h. By column chromatography of the reaction mixture on silica gel, unreacted starting product (0.7 g), 2-biphenylyl disulfide (**2**, 30%), and di-2-biphenylyl trithiocarbonate (**3**, 30%) were separated.

Reaction of 2-Biphenylyl Chlorodithioformate (6) with $AlCl_3$. A solution of **6** (2.4 g, 0.0092 mol) in CS_2 (35 ml) was added at room temperature to a suspension of $AlCl_3$ (1.37 g, 0.0103 mol) in CS_2 (23 ml) under stirring. The mixture was refluxed for 1 h, and then poured into a cold solution of $NaHCO_3$, then extracted with Et_2O. The organic layer was dried and the solvent removed under vacuum. Dibenzo[*c*,*e*]thiin-2-thione (**7**) was obtained in quantitative yield as a red solid, mp 106–107 °C, which crystallizes from light petroleum (bp 75–120 °C): mass spectrum *m/e* 228 ($M\cdot^+$, 100), 184 (65). Anal. Calcd for $C_{13}H_8S_2$: C, 68.38; H, 3.53; S, 28.08. Found: C, 68.4; H, 3.53; S, 28.2.

2-Biphenylyl chlorodithioformate (6) was prepared according to the general procedure described by Rivier:[21] bp 164–165 °C; mass spectrum *m/e* 264 ($M\cdot^+$, 15), 229 (14), 185 (100), 152 (29).

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Registry No.—**1** (R = Ph), 369-57-3; **1** (R = *o*-MePh), 2093-46-1; **1** (R = *o*-MeOPh), 17685-76-6; **1** (R = *o*-PhPh), 318-13-8; **1** (R = *o*-PhSPh), 59014-91-4; **1** (R = *o*-MeSPh), 52959-17-8; **1** (R = *m*-MeOPh), 17569-84-5; **1** (R = *p*-MePh), 459-44-9; **1** (R = *p*-MeOPh), 459-64-3; **1** (R = *p*-NO_2Ph), 456-27-9; **1** (R = *p*-ClPh), 673-41-6; **1** (R = 2,6-diMePh), 2192-33-8; **3** (R = Ph), 2314-54-7; **3** (R = *o*-PhPh), 59014-92-5; **4** (R = *o*-PhPh), 59014-93-6; **6**, 54199-77-8; **7**, 54199-60-9; **8** (R = Ph), 59014-94-7; NaI, 7681-82-5; carbon disulfide, 75-15-0; 2-iodobiphenyl, 2113-51-1.

References and Notes

(1) A. Schönberg, E. Frese, and K. H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).
(2) R. Huisgen and V. Weberndörfer, *Experientia*, **17**, 566 (1961).
(3) D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 1*, 105 (1972).
(4) E. E. Campaigne and S. W. Osborn, *J. Org. Chem.*, **22**, 561 (1957).
(5) In the latter case the main reaction product was benzo-1,3-dithiol-2-thione (work in progress).
(6) H. Lecker, *Ber.*, **58**, 409 (1925).
(7) F. Taboury, *Ann. Chim.*, **15**, 47 (1908).
(8) L. Gattermann, *Ber.*, **32**, 1136 (1899).
(9) L. Benati, P. C. Montevechi, A. Tundo, and G. Zanardi, *J. Org. Chem.*, in press.
(10) W. E. Parham and P. L. Stright, *J. Am. Chem. Soc.*, **78**, 4783 (1956).
(11) L. Colichman and D. L. Love, *J. Am. Chem. Soc.*, **75**, 5736 (1953).
(12) B. Holmberg, *Ber.*, **43**, 220 (1910).
(13) F. Fichter and W. Tamm, *Ber.*, **43**, 3032 (1910).
(14) T. Zincke and S. Lenhardt, *Justus Liebigs Ann. Chem.*, **400**, 7 (1913).
(15) J. Böeseken and D. A. W. Koning, *Recl. Trav. Chim. Pays-Bas*, **30**, 116 (1911).
(16) R. M. Pierson, A. J. Costanza and A. H. Weinstein, *J. Polym. Sci.*, **17**, 221 (1955).
(17) H. Viola, S. Scheithauer, and R. Mayer, *Chem. Ber.*, **101**, 3517 (1968).
(18) L. Benati, C. M. Camaggi, M. Tiecco, and A. Tundo, *J. Heterocycl. Chem.*, **9**, 919 (1972).
(19) D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc. C*, 1518 (1967).
(20) W. Autenrieth and H. Hefner, *Ber.*, **58**, 2151 (1925).
(21) H. Rivier, *Bull. Soc. Chim. Fr.*, **1**, 737 (1907).

A New Route to Acetylenes

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Most synthetic approaches to the formation of carbon–carbon triple bonds[1] involve eliminations which, unless the reactant is suitably constituted, can also lead to isomeric allenes, dienes, etc. A particularly useful acetylene synthesis, especially for strained cyclic acetylenes, is the conversion of an α-diketone to its bishydrazone, followed by oxidation (net *reduction* of carbon) with, e.g., mercuric oxide[2] or lead tetraacetate.[3]

In our quest for synthetic routes to a novel cyclic acetylene,