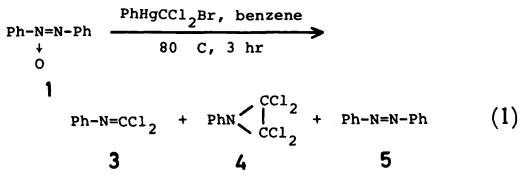
# Reactions of Azoxybenzene with Dichlorocarbene in the Phase-transfer-catalyzed System

Shizen SEKIGUCHI,* and Tomohisa FUJIU
*Department of Synthetic Chemistry, Faculty of Engineering, Gunma University, Ten-jin cho, Kiryu, Gunma 376*
(Received March 8, 1984)

**Synopsis.** Azoxybenzene (**1**) reacted with dichlorocarbene (**2**) at 40 °C in the presence of a phase-transfer catalyst (18-crown-6 or tributylamine) in a binary solvent ($CHCl_3$–aqueous KOH), giving 2,2,3,3-tetrachloro-1-phenylaziridine (**4**), azobenzene (**5**), and 2-hydroxy-1-phenylbenzimidazole.

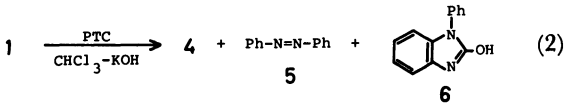
The phase-transfer technique has been regarded as a useful tool in improving the preparative processes and syntheses used in laboratories. Although the reactions of dihalocarbenes with olefins,[1-3] amides,[4] imines,[5] alcohols[6] and adamantane[7] have already been studied, only a few studies involving the addition of dichlorocarbenes to -N(O)=N- (azoxy) bonds have been published.

Seyferth and his coworkers have reported the reaction of azoxybenzene (**1**) with dichlorocarbene (**2**) in benzene, in which phenyl(bromodichloromethyl)mercury ($PhHgCCl_2Br$) was used as a source reagent of **2**. They found that 1,1-dichloro-*N*-phenylmethanimine (**3**, yield 3%), 2,2,3,3-tetrachloro-1-phenylaziridine (**4**, yield 12%) and azobenzene (**5**, yield 6%) were formed (Eq. 1).[8]



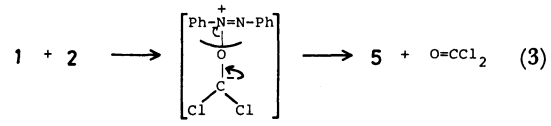
(1)

We have also carried out a reaction of **1** with **2** in the presence of 18-crown-6 or tributylamine as a phase-transfer catalyst (PTC) under the phase-transfer-catalyzed conditions (50% aqueous KOH–$CHCl_3$), in which the different products, except for **4** and **5**, were formed (Eq. 2). The results are indicated in Table 1.



(2)

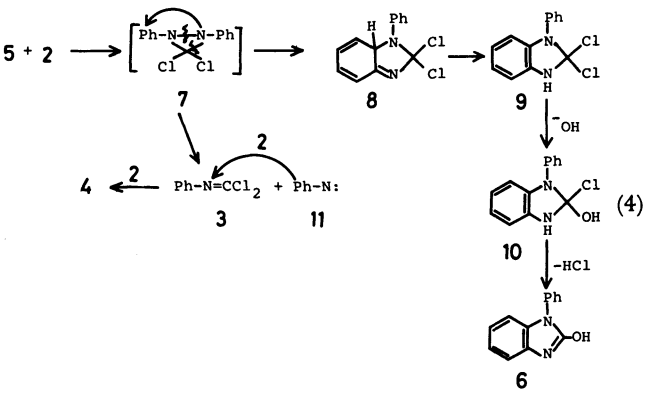
Azobenzene (**5**) is probably formed *via* the following path (Eq. 3).[9,10] In such polar solvents as chloroform



(3)

the intermediate shown in the bracket (Eq. 3) might reasonably be considered to intervene with the electrophilic character of **2**.

Further, in order to elucidate the formation path of **4** and **6**, a reaction of **5** with **2** under the same conditions described in Table 1 (PTC tributylamine; temp 40 °C; time 4 h) was carried out, in which **4** and **6** were formed in 31.0 and 15.5% yields (based on **5** consumed), respectively. These results would indicate that **4** and **6** are formed *via* the following path (Eq. 4).[11]



(4)

It is not clear, at present, whether the N-N bond fission in **7** is heterolytic or homolytic. The intermediacy of **7**, however, is reasonable from considering the formation of **4** and **6**.[11,12] As is shown in Eq. 3, the abstraction of an oxygen atom by **2** is interesting and such a reductive function of **2** would be excepted to attract attention.

TABLE 1. REACTION OF AZOXYBENZENE WITH DICHLOROCARBENE IN THE PRESENCE OF PHASE TRANSFER CATALYSTS

| 1 mmol | $CHCl_3$ mmol | aq KOH (50%) mmol | Temp °C | Time h | Product/%[a] 4 | 5 | 6 | Conv. % |
|---|---|---|---|---|---|---|---|---|
| | | | | | 18-Crown-6[b] | | | |
| 30.0 | 419 | 446 | 40 | 10 | 36.8 | 3.0 | 1.7 | 35.0 |
| | | | | | Tributylamine[c] | | | |
| | | | 40 | 4 | 42.0 | 5.3 | 8.5 | 37.6 |
| | | | 10 | 24 | 32.2 | 6.1 | 4.2 | 37.1 |

a) Based on the azoxybenzene consumed. b) 18-Crown-6 0.76 mmol. c) Tributylamine 0.76 mmol.

## Experimental

*General Comments.* The products were identified using NMR and MS spectrometers, UV and IR spectrophotometers, and elemental analyses. All the capillary melting points were uncorrected.

*Preparation of Azoxybenzene (1).* Following a method described in the literature,[12] **1** was prepared from nitrobenzene, diarsenic trioxide, and sodium hydroxide (yield 65%): mp 34—35 °C (35.5—36.6 °C).[12]

*Reaction of Azoxybenzene (1) with Dichlorocarbene (2) for Isolation of the Products.* The preparative procedure was as follows: A solution of 5.95 g (30.0 mmol) of **1**, 0.204 g (0.76 mmol) of 18-crown-6, and 50.0 g (446 mmol) of aqueous KOH (50%) was added to an Erlenmeyer flask with a reflux condenser and a thermometer placed on a heating plate. The flask was covered with aluminium foil in order to shield it from light.

After the chloroform layer was filtered and concentrated, by aqueous $H_2SO_4$ (5N) and extracted with chloroform. Then, the extract was dried overnight over anhydrous $MgSO_4$. After the chloroform layer was filtered and concentrated, the residue was processed by column chromatography (silica gel [Wako gel C-200]-benzene).

In addition, **4** was seperated from unreacted **1**, **5**, and **6**, using a column [silica gel-ligroin (bp 80—100 °C)], and purified by reduced distillation [bp 70—72 °C/2.66 Pa[8]].

The ligroin fraction containing unreacted **1**, **5**, and **6** was processed by column chromatography [firstly, silica gel-benzene-ligroin (4:1 v/v), and secondly, silica gel-benzene-acetone (9:1 v/v)] giving the **6** fraction. It was concentrated and the residue was recrystallized from acetone, giving pure **6**.

After the residual ligroin fraction was concentrated, the residue was subjected to fractional crystallization from methanol, giving pure **1** (mp 35—36 °C) and **5** (mp 67.5—68 °C).

*2,2,3,3-Tetrachloro-1-phenylaziridine (4);* bp 70—72 °C/2.66 Pa (70—72 °C/Pa).[8]

*2-Hydroxy-1-phenylbenzimidazole (6);* mp 210 °C; $M^+$ 210; NMR (DMSO-$d_6$) $\delta$=11.1 (1H, s, broad, OH and NH), 7.7 (5H, s, 1-phenyl), and 7.2—7.5 (4H, m, phenyl); IR (KBr) 3400, 3100, 1750—1660, 1600, 1450, 760, 740, and 690 $cm^{-1}$; Anal. ($C_{13}H_{10}N_2O$) C. H. N. The chemical shift at $\delta$=11.1 and the absorption band at 1750—1660 $cm^{-1}$ clearly indicate that there are two tautomers (**6** and 2-oxo-1-phenyl-2,3-dihydrobenzimidazole).

*Reaction of Azobenzene (5) with Dichlorocarbene (2) for Isolation of the Products.* The preparative procedure was the same as that involved in the reaction of **1** with **2**.

*Determination of Products.* After the reaction was completed, the mixture was neutralized with aqueous $H_2SO_4$ (5M (1M=1 mol $dm^{-3}$)) to pH 6—7 and extracted with two 200 ml portions of chloroform. Then, the chloroform layer was dried over anhydrous $MgSO_4$.

After the chloroform layer was filtered and the filtrate was concentrated, the residue was diluted exactly to 50 ml with a mixed solvent [methanol-chloroform (7:3 v/v)]. A 5-ml portion of the solution was analyzed by HPLC under the following conditions to determine **6**: Column JASCO SC-02L (silica gel) 0.46$\phi$×25 cm, flow rate 1.0 ml/min, wave length 290 nm, solvent methanol-$H_2O$ (6:4 v/v), internal standard biphenyl.

The residual 45-ml solution was concentrated and subjected to column chromatography [silica gel (Wako gel C-200)-benzene] to remove residual tarry matter.

After the eluent was concentrated, it was diluted to 20 ml with a mixed solvent [methanol-chloroform (7:3 v/v)]. The solution was subjected to GLC (HITACHI 164) to determine **4**, unreacted **1**, and **5**. The operating conditions were as follows: column (0.5$\phi$×100 cm) Celite 545 impregnated with SE-30 (silicone) (10 wt%), column temperature 120 °C (for **4**) and 250 °C (for **1** and **5**), flow rate 20 (for **4**) and 10 ml/min (for **1** and **5**), carrier gas He; internal standard azobenzene (**5**) (for **4**) and benzyl benzoate (for **1** and **5**).

## References

1) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971).
2) M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, 4659 (**1969**).
3) S. Kwon, Y. Nishimura, M. Ikeda, and Y. Tamura, *Synthesis*, 249 (**1976**).
4) T. Saraie, T. Ishiguro, K. Kawashima, and K. Morita, *Tetrahedron Lett.*, 2121 (**1973**).
5) M. Makosza and A. Kacprowicz, *Roxz. Chem.*, **48**, 2929 (1974).
6) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Am. Chem. Soc.*, **93**, 1820 (1971).
7) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Am. Chem. Soc.*, **92**, 6670 (1970).
8) D. Seyferth, W. Tronich, and H.-m. Shin, *J. Org. Chem.*, **39**, 158 (1974).
9) E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **28**, 2460 (1963).
10) R. Oda, M. Mieno, and Y. Hayashi, *Tetrahedron Lett.*, 2363 (**1967**).
11) T. Sasaki, S. Eguchi, and T. Ogawa, *Heterocycles*, **3**, 193 (1975).
12) J. S. Buch and W. S. Ide, *Org. Synth.*, Coll. Vol. **II**, 57 (1948).