Reaction of Azobenzene with Dichlorocarbene in Phase-transfer-catalyzed System

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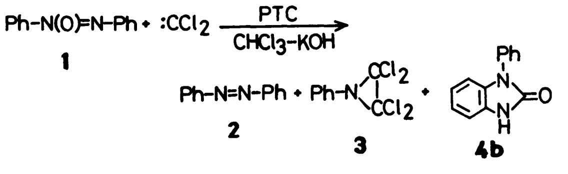
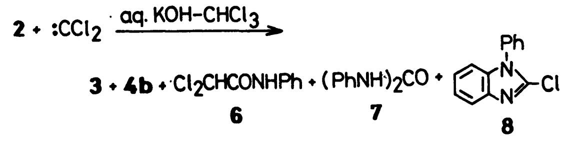
Synopsis. Azobenzene (**2**) reacted with dichlorocarbene at 40 °C in the presence of several phase-transfer catalysts in a binary solvent ($CHCl_3$-aqueous KOH), giving 2,2,3,3-tetrachloro-1-phenylaziridine (**3**), 1-phenyl-1,3-dihydro-2*H*-benzimidazol-2-one (**4b**), dichloroacetanilide (6), *N*,*N*′-diphenylurea (**7**), and trace amounts of 2-chloro-1-phenylbenzimidazole (**8**).

We have recently reported the reaction of azoxybenzene (**1**) with dichlorocarbene (DC) in the presence of a phase-transfer-catalyst (PTC 18-crown-6 or tributylamine) in the binary solvent ($CHCl_3$-aq KOH), in which azobenzene (**2**), 2,2,3,3-tetrachloro-1-phenylaziridine (**3**), and 1-phenyl-1,3-dihydro-2*H*-benzimidazol-2-one (**4b**) were formed[1] (Eq. 1).



(1)

These results are very different from those of Seyferth *et al.*,[2] who reported the reaction of **1** with DC generated from $PhHgCCl_2Br$ in benzene, giving **2**, **3**, and 1,1-dichloro-*N*-phenylmethanimine (**5**) as products. Especially, the formation of **4b** in the reaction (Eq. 1) led us to study the reaction of **2** with DC, where **3**, **4b**, dichloroacetanilide (**6**), *N*,*N*′-diphenylurea (**7**), and 2-chloro-1-phenylbenzimidazole (**8**) (trace amounts) were formed (Eq. 2).

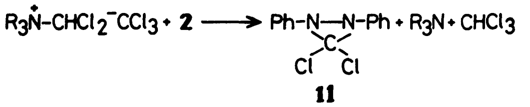


(2)

The results are summarized in Table 1. The compound (**8**) was produced in trace amounts in every run. The results that **4**, **6**, **7**, and **8** were obtained are conspicuously different from those of Seyferth *et al.*[2] and Sasaki *et al.*[3] With TBA the product yields are higher than with 18-crown-6: The higher catalytic activity of the former is atrributed to the intermediate formation of trialkyl(dichloromethyl)ammonium trichloromethanide (Eq. 4), as represented in Eqs. 3—5.[4]

$$NaOH + CHCl_3 \longrightarrow :CCl_2 \xrightarrow{R_3N} R_3\overset{+}{N}\text{-}\overset{-}{C}Cl_2 \qquad (3)$$

$$R_3\overset{+}{N}\text{-}\overset{-}{C}Cl_2 + HCCl_3 \longrightarrow R_3\overset{+}{N}CHCl_2{}^{-}CCl_3 \qquad (4)$$



$$R_3\overset{+}{N}\text{-}CHCl_2{}^{-}CCl_3 + \mathbf{2} \longrightarrow Ph\text{-}N\text{—}N\text{-}Ph\ (CCl_2\ \text{bridge}) + R_3N + CHCl_3 \qquad (5)$$

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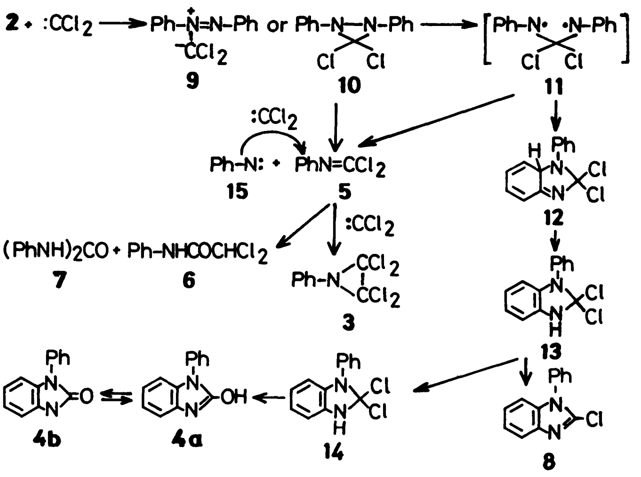
Table 1. Reactions of azobenzene (**2**) with dichlorocarbene[a)]

Run	Reaction time	Product/%[b)]				Conversion[c)]
	h	**4b**	**6**	**7**	**3**	%
1	0.5	14.7	5.3	1.2	6.2	37.1
2	1	13.7	5.8	1.0	7.6	58.7
3	2	13.0	5.1	0.8	9.4	67.3
4	4	10.2	3.8	0.3	10.8	72.0
5	7	6.5	2.8	0.1	10.2	74.0
6[d)]	0.5	34.9	7.6	3.1	10.9	49.3
7[d)]	1	21.6	7.6	trace	12.7	70.6
8[d)]	2	22.3	5.5	trace	14.8	75.5
9[d)]	4	15.5	4.2	0.4	31.0	76.7
10[d)]	7	11.7	3.7	0.3	29.0	78.7
11[e)]	4	13.2	3.7	trace	29.0	81.0
12[f)]	4	4.6	4.0	trace	—	20.7

a) Reaction conditions: **2** 15.0 mmol; $CHCl_3$ 226 mmol; aq KOH (50%) 223 mmol; temperature 40 °C; 18-crown-6 0.39 mmol. b) Based on **1** consumed. c) Conversion of **2**. d) Tributylamine (TBA, 0.39 mmol) used in the place of 18-crown-6. e) Benzyltriethylammonium chloride (0.38 mmol) used in the place of 18-crown-6. f) Benzyltributylphosphonium chloride (0.39 mmol) used in the place of 18-crown-6.

The PTCs other than 18-crown-6 and TBA were tested (Runs 11 and 12). Although benzyltriethylammonium chloride is reported to be very effective,[5] its activity is quite similar to TBA under the present conditions. However, benzyltributylphosphonium chloride is much less effective: the poor migratory aptitude of the corresponding ion pair (Eq. 5) from the aqueous to the organic layer may be responsible for it.

The reaction path is shown in Scheme 1.

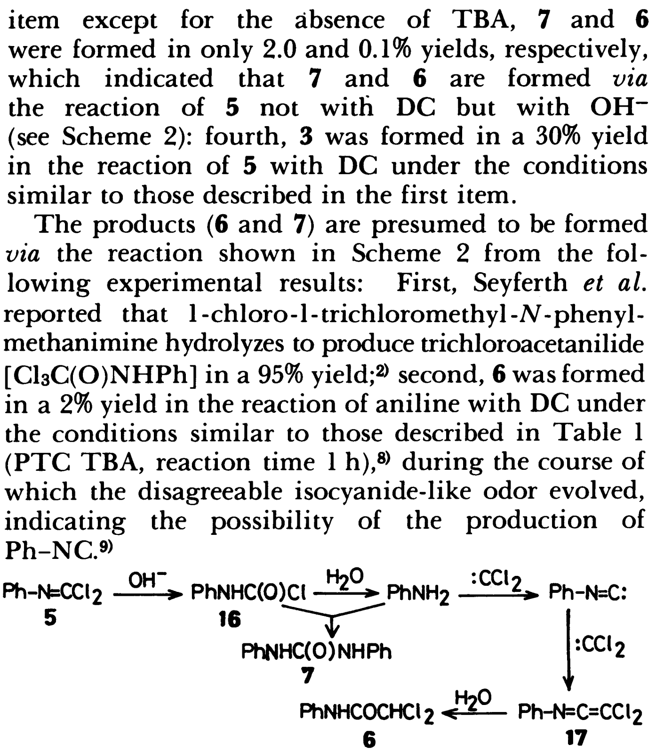


Scheme 1.

The formation of **15** and **5** may be formed *via* an acylic (9) or a cyclic (**10**) intermediate.[2] Further, the intermediacy of **10** is required, because the benzimidazole derivatives (**4** and **8**) are expected to be formed from **11**.[3]

The reaction sequences (**5**+**15**→**3**+**6**+**7**) are proposed from the following results (see Experimental): First, **6** was not formed in the reaction of **3** with DC under the conditions (PTC TBA, reaction time 4 h) similar to those described in Table 1, whereas the reaction of carbanilides with sodium hypochlorite giving 1,3-dihydro-2*H*-benzimidazol-2-ones was reported by Rosanti[6] and Oftedahl *et al.*;[7] second, **6** was not formed in the reaction of **7** with DC under the same conditions to those described in the first item; third, in the reaction of **5** with DC under the same conditions as those described in the first item except for the absence of TBA, **7** and **6** were formed in only 2.0 and 0.1% yields, respectively, which indicated that **7** and **6** are formed *via* the reaction of **5** not with DC but with OH^- (see Scheme 2): fourth, **3** was formed in a 30% yield in the reaction of **5** with DC under the conditions similar to those described in the first item.

The products (**6** and **7**) are presumed to be formed *via* the reaction shown in Scheme 2 from the following experimental results: First, Seyferth *et al.* reported that 1-chloro-1-trichloromethyl-*N*-phenylmethanimine hydrolyzes to produce trichloroacetanilide [$Cl_3C(O)NHPh$] in a 95% yield;[2] second, **6** was formed in a 2% yield in the reaction of aniline with DC under the conditions similar to those described in Table 1 (PTC TBA, reaction time 1 h),[8] during the course of which the disagreeable isocyanide-like odor evolved, indicating the possibility of the production of Ph-NC.[9]



Scheme 2.

In conclusion it is found that the kind of products depends largely on reaction conditions-especially polarities of solvents.

Experimental

General Comments. The products were identified by using NMR and Mass spectrometers, UV and IR spectrophotometer, and elemental analyses. The boiling point of ligroin used was 80—100 °C. All the capillary melting points were uncorrected.

Reaction of Azobenzene (2) with Dichlorocarbene for Isolation of the Products. The reaction and the isolation of products were carried out according to the procedure described in the revious work,[1] where the physical and chemical properties of **3** and **4b** were indicated.

2-Chloro-1-phenylbenzimidazole (8); mp 67—68 °C; IR (KBr) 1600, 1450, 760, 740, 690 cm^{-1}; NMR (DMSO-d_6) δ=7.7 (s, 1-phenyl 5H), 7.2—7.5 (m, phenyl 4H); Found: C, 68.66; H, 4.11; N, 12.43%; M$^+$ 228. Calcd for $C_{13}H_9ClN_2$: C, 68.27; H, 3.94; N, 12.25%; M, 228.

Dichloroacetanilide (6); mp 117—118.5 °C; IR (KBr) 3260, 1670, 1550, 1240, 860, 810, 760, 730, 690, 670 cm^{-1}; NMR (DMSO-d_6) δ=10.5 (s, NH 1H), 7.1—7.7 (m, phenyl 5H), 6.6 (s, CH 1H); Found: C, 47.51; H, 3.31; N, 7.08%; M$^+$, 203. Calcd for $C_8H_7Cl_2NO$: C, 47.17; H, 3.44; N, 6.88%, M, 203.

N,N′-Diphenylurea (7); mp 238—239 °C; IR (KBr) 3300, 1650, 1590, 1230, 750, 690 cm^{-1}; NMR (DMSO-d_6) δ=8.6 (s, NH 2H), 6.8—7.8 (m, phenyl 10H); Anal. ($C_{13}H_{12}N_2O$) C. H. N.

The NMR and IR spectra show that 2-hydroxy-1-phenylbenzimidazole (**4a**) considerably tautomerizes to **4b**.

Reaction of 2,2,3,3-Tetrachloro-1-phenylaziridine (3) or N,N′-diphenylurea (7) with Dichlorocarbene. To an 18 ml chloroform solution containing 18 mmol of **3** (3.85 g) or **7** (3.18 g) and 0.076 g (0.41 mol) of TBA was added a 25 g (223 mmol) aqueous KOH (50 wt%) solution. After the mixture was stirred for 4 h at 40 °C, it was processed according to the method described in the reaction of **2** with DC. In the both reactions **6** was not obtained but the substrate was recovered.

Reaction of 1,1-Dichloro-N-phenylmethanimine (5) with Dichlorocarbene. In the reaction of **5** (2.61 g, 15 mmol), prepared according to the method of Seyferth *et al.*,[2] with DC under the same conditions as those in the reaction of **3** with DC except for the absence of TBA, **7** and **6** were obtained 0.031 g (2%) and 0.0016 g (0.1%), respectively [both yields are based on **5** consumed (60% conversion)].

Reaction of Aniline with Dichlorocarbene. In the reaction of aniline (1.38 g, 15 mmol) with DC under the same conditions as those in the reaction of **3** with DC, **6** was obtained in a 2% yield (0.06 g).

The determination of products was carried out according to the method described in the previous paper.[1]

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