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REACTIONS OF COPPER-CARBENOIDS WITH SULFOXIDES

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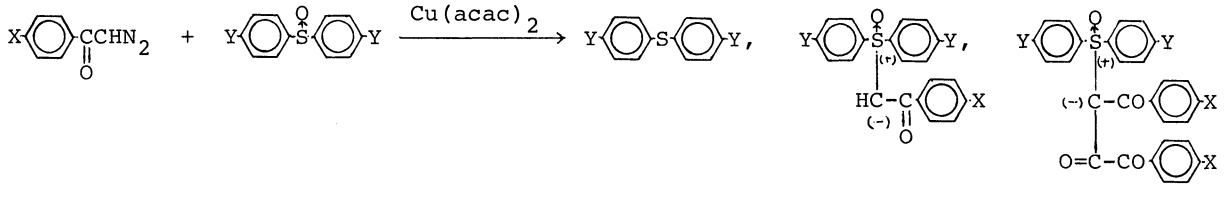
The copper chelate-catalyzed reaction of α-diazoacetophenones with substituted diphenyl sulfoxides gave two types of products, diaryl sulfides (V) and oxosulfonium ylides (VI), of which ratios depended on the substituents of α-diazoacetophenones and of diaryl sulfoxides. The oxosulfonium ylides exhibit a novel reaction with phenylglyoxal affording oxosulfonium glyoxalylphenacylides (VII) in the presence of copper acetylacetonate. When copper-phthalocyanine was employed as a catalyst, the reaction gave a lactone (X) besides (V).

Many studies have been carried out on the formation of stable sulfonium ylides by the reaction of carbenes with sulfides,[1] but only a few papers were published on the reaction of carbenes with sulfoxides.[2,3] Dost and Gosselck[2] reported the formation of oxosulfonium ylides in the reaction of carbenes with dimethyl sulfoxide. However, two kinds of paths may be expected in the reaction of copper-carbenoids (I') with sulfoxides (II). The one is electrophilic attack of the carbenoid-carbon on the oxygen atom of sulfoxide (path A),[4] and the other is the attack of the carbenoid-carbon on the sulfur atom of sulfoxide (path B). We wish to report in this communication that the copper chelate-catalyzed reaction of substituted α-diazoacetophenones with substituted diphenyl sulfoxides gives various products formed by paths A and B.

A benzene solution of p-substituted α-diazoacetophenone (I, 0.01 mol) was added dropwise to a benzene solution of p-substituted diphenyl sulfoxide (II, 0.02 mol) containing a catalytic amount (7.6×10^{-4} mol) of copper acetylacetonate ($Cu(acac)_2$) at 50 or 80°C during the course of more than five hours. An evolution of almost theoretical amount of nitrogen was observed, and p-substituted diphenyl sulfides (V), oxosulfonium ylides (VI), and oxosulfonium glyoxalylphenacylides (VII) were obtained accompanying small amounts of p-substituted benzoic acids (VIII) and p-substituted dibenzoylethylenes (IX). Diaryl sulfides (V) were identified by the comparison of their IR spectra with those of the authentic samples. The structures of VI and VII were determined by elemental analyses and IR and NMR spectra. The yields of reaction products are shown in Table 1.



(I) (II) (V) (VI) (VII)

Table 1. Yields of Reaction Products

Run	Substituent X	Substituent Y	Temp. (°C)	Reaction Products V (%)	VI (%)	VII (%)
a	H	H	50	25.2	-	14.0
			80	19.8	-	9.0
b	Cl	H	50	42.0	-	20.0
			80	22.1	-	12.6
c	OCH_3	H	50	46.0	25.5	-
			80	27.3	-	10.3
d	OC_2H_5	H	50	28.9	16.6	-
			80	18.9	-	16.6
e	H	Cl	50	30.1	33.4	-
			80	40.6	22.0	-
f	H	CH_3	50	25.5	-	8.5
			80	48.7	-	15.9
g	OCH_3	CH_3	50	33.7	-	10.9
			80	26.6	-	25.2

The formation of sulfides according to the path A was not affected by the substituent on diaryl sulfoxides, but affected by the reaction temperature.

It is noteworthy that the sulfonium ylides (VI) were obtained in the reactions at 50°C, when X is an electron-releasing group and Y is hydrogen atom (runs C and d) or X is hydrogen atom and Y is an electron-attraction group (run e). The ylides (VIc, and VId) were converted into the corresponding glyoxalylphenacylides (VIIc and VIId) in yields of 30-34% when the ylide was heated with p-methoxy or p-ethoxy-phenylglyoxal (IV) in benzene at 80°C in the presence of $Cu(acac)_2$. If the experiments were carried out at 50°C or in the absence of $Cu(acac)_2$, no glyoxalylphenacylides were obtained recovering starting materials (VIc and VId). Bis(p-methoxyphenyl)oxosulfonium ylide (VIc, X=OCH_3, Y=H) also reacted with phenylglyoxal in benzene at 50°C in the presence of $Cu(acac)_2$ to give the corresponding glyoxalylphenacylide (VII) in 44% yield. Therefore, it can be recognized that the glyoxalylphenacylides (VII) are formed by the interaction between ylides (VI) and glyoxals (IV), produced in the course of the

Table 2. Spectral Data

Product	X	Y	IR (KBr, cm^{-1}) Ylide C=O	IR (KBr, cm^{-1}) Arom. C=O	IR (KBr, cm^{-1}) S-O	NMR ($CDCl_3$, τ) Ylide CH[5]	NMR ($CDCl_3$, τ) CH_3 or C_2H_5	NMR ($CDCl_3$, τ) Arom. H
VIc	OCH_3	H	1530	-	1090	4.7(bs, 1H)	6.18(s, 3H)	3.15, 2.15 (ABq,4H) 1.8-2.6(m, 10H)
VId	OC_2H_5	H	1540	-	1080	4.5(bs, 1H)	8.57(t, 3H) 5.88(q, 2H)	1.8-3.2(m, 14H)
VIe	H	Cl	1550	-	1090	-	-	1.9-2.8(m)
VIIa	H	H	1570	1675	1080	-	-	1.9-2.8(m)
VIIb	Cl	H	1585	1675	1090	-	-	1.9-2.6(m)
VIIc	OCH_3	H	1580	1675	1090	-	6.30(s, 3H) 6.20(s, 3H)	1.9-3.5(m, 18H)
VIId	OC_2H_5	H	1590	1660	1060	-	8.73(t, 3H) 8.64(t, 3H) 5.7-6.3(m, 4H)	1.7-3.5(m, 18H)
VIIf	H	CH_3	1590	1680	1080	-	7.6 (s, 6H)	2.0-2.8(m, 18H)
VIIg	OCH_3	CH_3	1580	1680	1080	-	6.28(s, 3H) 6.20(s, 3H) 7.6 (s, 6H)	2.0-2.9(m, 16H)

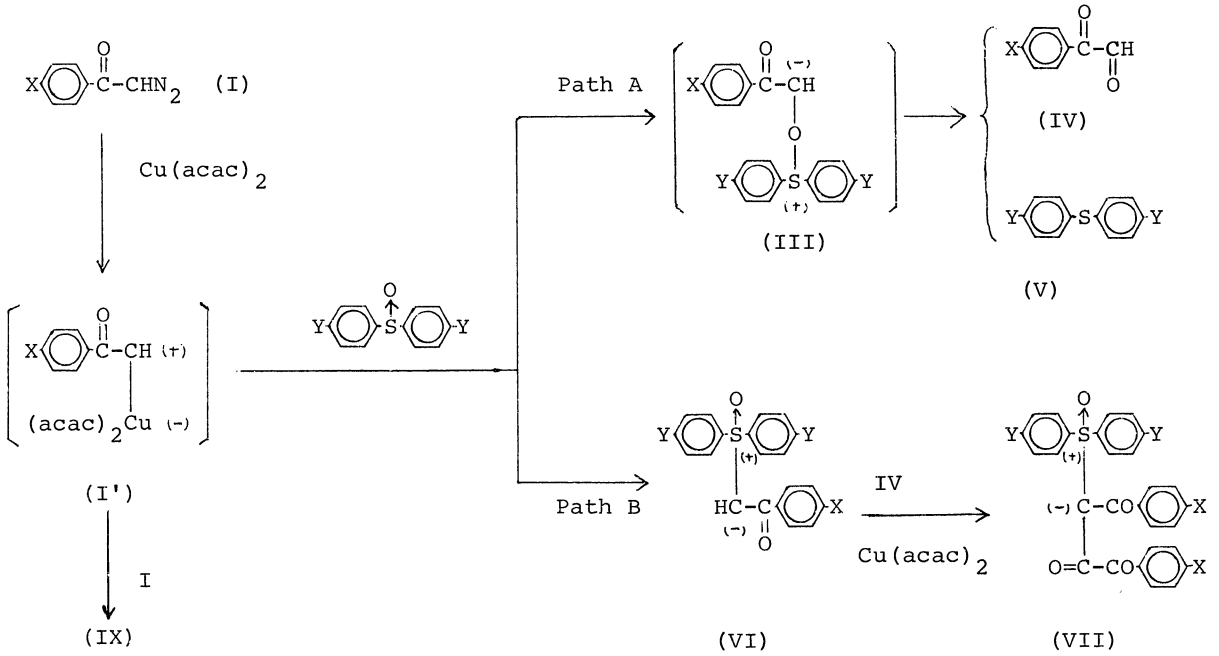
Table 3. Melting Points and Analytical Data

Product	mp(°C)	Found(%) C	Found(%) H	Found(%) S	Calcd(%) C	Calcd(%) H	Calcd(%) S	Molecular Formula
VIc	187-188	71.68	5.14	9.02	71.99	5.18	9.15	$C_{21}H_{18}O_3S$
VId	226-228	72.31	5.45	8.43	72.51	5.53	8.86	$C_{22}H_{20}O_3S$
VIe	233-234	62.08	3.51	8.32	61.70	3.62	8.23	$C_{20}H_{14}O_2SCl_2$
VIIa	202-203	74.55	4.33	6.83	74.33	4.46	7.08	$C_{28}H_{20}O_4S$
VIIb	219-220	64.38	3.34	6.30	64.50	3.45	6.15	$C_{28}H_{18}O_4SCl_2$
VIIc	230-231	70.64	4.58	6.04	70.30	4.72	6.26	$C_{30}H_{24}O_6S$
VIId	173-174	70.83	5.20	5.42	71.10	5.22	5.92	$C_{32}H_{28}O_6S$
VIIf	190-191	75.31	5.12	6.56	74.99	5.03	6.67	$C_{30}H_{24}O_4S$
VIIg	130-131	71.34	5.20	5.80	71.10	5.22	5.93	$C_{32}H_{28}O_6S$

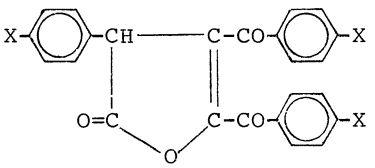
reaction, followed by the dehydrogenation by oxygen contained in the reaction systems. The result of experiment cited above and the fact that no VI was isolated in runs a and b even at 50°C suggest that unsubstituted and p-chlorophenylglyoxals have higher re-

activities than those of p-alkoxyphenylglyoxals. The electron attracting group (p-Cl) on ylide (VIe) seems to retard the reaction (run e) and the electron-releasing group (p-CH_3) on VIf and VIg accelerates the reaction with phenylglyoxals (runs f and g). The detailed studies on this step are under way. The failure of isolation of glyoxals (IV), in spite of detailed investigation of reaction products, suggests that the glyoxals react with copper carbenoids[6] to give tarry products, or decompose to afford the corresponding substituted benzoic acids (VIII).

The mechanism of the formation of reaction products is explained as follows:



When copper-phthalocyanine was employed as a catalyst, the reaction gave a lactone (X) in yields of 10-13%, besides V and IX without isolation of VI and VII. Details of this reaction will be discussed elsewhere.



(X)

References

1) W.Ando, T.Yagihara, S.Tosune, and T.Migita, J. Amer. Chem. Soc., 91, 2786 (1969).
2) F.Dost and J.Gosselck, Tetrahedron Lett., 1970, 5091.
3) J.Diekmann, J. Org. Chem., 30, 2272 (1965).
4) (a) R.Oda, M.Mieno, and Y.Hayashi, Tetrahedron Lett., 1967, 2363.
(b) R.O.Hutchins, D.Hoke, J.Keogh, and D.Kobayashi, ibid., 1969, 3495.
5) (a) K.W.Ratts and A.N.Yao, J. Org. Chem., 31, 1185 (1966).
(b) A.W.Johnson and R.T.Amel, Tetrahedron Lett., 1966, 819.
6) Tarry oligomers were obtained in the copper chelate-catalyzed reaction of α-diazoacetophenone with benzaldehyde [(M.Takebayashi, T.Ibata, and K.Ueda, Bull. Chem. Soc. Japan, 43, 1500 (1970)].

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