The Formation and Reaction of Carbonyl Ylide. The Copper Chelate-catalyzed Decomposition of 1-(Diazoacetyl)fluorenone in the Presence of Ethylenic and Acetylenic Compounds

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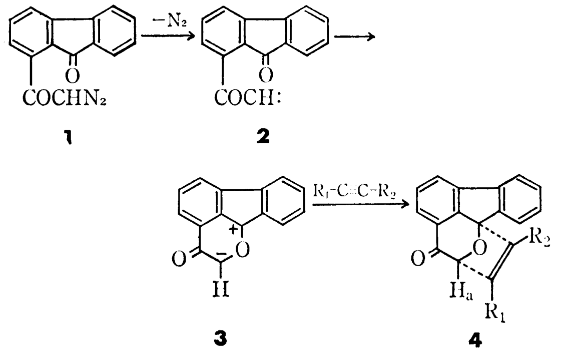
1,3-Dipolar cycloadducts were obtained by the copper chelate-catalyzed decomposition of 1-(diazoacetyl)-fluorenone in the presence of acetylenic and ethylenic dipolarophiles. The reaction proceeded *via* intermediate carbonyl ylide (**3**), which has been generated by the carbene-carbonyl reaction of **2**. The cycloaddition of **3** with ethylenic dipolarophiles was determined to proceed stereospecifically.

The thermolysis[1)] and photolysis[2)] of epoxides with electron-withdrawing groups, the thermolysis of 1,3,4-oxadiazolines,[3)] and the reaction of carbenes with carbonyl compounds[4,5)] have been known to be the general method of the formation of carbonyl ylides. In particular, the intramolecular carbene-carbonyl reaction has been recognized as one of the most convenient methods of the formation of cyclic carbonyl ylides.[5—7)] For example, as the first stable five-membered cyclic carbonyl ylide, isomünchnon was obtained by the $Cu(acac)_2$ catalyzed decomposition of *N*-methyl-*N*-(diazo-*p*-nitrophenylacetyl)benzamide.[6)] As a result of a continuing study of the intramolecular carbene-carbonyl reaction, we wish now to report the formation of carbonyl ylide by the copper chelate-catalyzed decomposition of 1-(diazoacetyl)fluorenone (**1**) and its cycloaddition with acetylenic and ethylenic dipolarophiles.

Results and Discussion

Cycloaddition with Acetylenic Dipolarophiles. When 1-(diazoacetyl)fluorenone (**1**) was decomposed in the presence of a 1.5 molar amount of dibenzoylacetylene and a catalytic amount of $Cu(acac)_2$ in absolute benzene at 80 °C, a cycloadduct (**4a**; $R_1=R_2=COPh$) was obtained in an 89% yield. The IR spectrum of **4a** shows a carbonyl band of cyclic ketone at 1704 cm^{-1} besides that of the benzoyl absorption at 1659 cm^{-1}, as is shown in Table 1. The methine proton, H_a, of **4a** shows a singlet at 4.22 τ which is at a field higher by 0.5 τ than those of other adducts with acetylenic dipolarophiles because of the shielding effect of the benzoyl group at the adjacent carbon. Dimethyl acetylenedicarboxylate also afforded an adduct (**4b**: $R_1=R_2=COOCH_3$) in a quantitative yield.



Although there are two possibilities in the direction of the cycloaddition of asymmetric acetylenes, methyl propiolate gave only one adduct (**4c**: $R_1=H$, $R_2=COOCH_3$, 80%), which exhibited a doublet methine signal of H_a at 4.78 τ and that of H_b at 2.48 τ coupled with one another ($J_{ab}=2.5$ Hz). This means that H_a and H_b are in a vicinal position and that R_2 is the methoxycarbonyl group. The NMR signal of methoxycarbonyl of **4c** at 6.51 τ is comparable to that of one OCH_3 (at 6.56 τ) of the adduct of dimethyl acetylenedicarboxylate (**4b**). Phenylacetylene yielded an adduct with a similar direction of cycloaddition (**4d**: $R_1=H$, $R_2=Ph$) in an 86% yield.

On the other hand, methyl phenylpropiolate yielded two cycloadducts, **4e** (24%) and **4f** (30%). The similarity of their IR spectra demonstrates that they are isomers different in the direction of cycloaddition. The singlet of **4e** at 6.69 τ was assigned to the methoxycarbonyl group at the R_2 position in comparison with that of **4c** (at 6.51 τ). Therefore, the singlet of **4f** at 6.30 τ was assigned to methoxycarbonyl at R_1. In general, the methoxycarbonyl group at R_2 has a methyl signal at a higher field than that of R_1 because of the

Table 1. Spectral properties of cycloadducts of **3** with acetylenic dipolarophiles

Adduct	R_1	R_2	IR (KBr, cm^{-1})		NMR ($CDCl_3$, τ)			
					H_a	H_b	$OCH_3(R_1)$	$OCH_3(R_2)$
4a	PhCO	PhCO	1704	1659	4.22(s)	—	—	—
4b	COOMe	COOMe	1707	1729	4.57(s)	—	6.23	6.55
4c	H_b	COOMe	1701	1725	4.78(d)[a)]	2.48(d)[a)]	—	6.51
4d	H_b	Ph	1706		4.77(d)[b)]	3.15(d)[b)]	—	—
4e	Ph	COOMe	1700	1710	4.40(s)	—	—	6.69
4f	COOMe	Ph	1707[c)]		4.50(s)	—	6.30	—

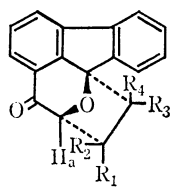
a) $J_{ab}=2.5$ Hz. b) $J_{ab}=2.4$ Hz. c) A broad absorption was observed.

anisotropy of the fluorene ring.

Because of the contribution of a resonance formula $H\text{-}\overset{+}{C}{=}\overset{-}{C}\text{-}COOCH_3$ in methyl propiolate, the α-carbon with an increased electron density attacks the positively charged C_9 of the fluorene ring of carbonyl ylide (**3**) to give **4c**. In the case of phenylacetylene, π-π interaction[11] between the phenyl group and the fluorene ring regulates the direction of cycloaddtition, affording **4d**. In the addition of methyl phenylpropiolate, electronic interaction and π-π interaction compete; two products, **4e** and **4f**, are thus formed.

Cycloaddition of 3 with Ethylenic Dipolarophiles. Ethylenic dipolarophiles also gave cycloadducts (**5**) in high yields (Table 3). The configuration of the adducts were determined on the basis of their NMR properties. The reaction with *trans*-1,2-dibenzoylethylene gave a single adduct (**5a**), which showed doublet methine signals of H_a and H_c at 4.88 τ and 4.46 τ, and a double doublet of H_b at 5.10 τ. From the small value of the coupling constant between H_a and H_b (J_{ab}=1.6 Hz), H_a and H_b are decided to be in the *trans* configuration. The coupling constant, J_{bc}, (=4.9 Hz) also indicates that H_b and H_c are *trans*. Therefore, the structure of **5a** was determined to be as is shown in Table 2.

In general, the *cis* coupling constants of methine protons in **5** have larger values (8.0—10.6 Hz) than those of *trans* protons (1.6—6.9 Hz) in this ring system.[8-10] For example, in the two adducts of dimethyl fumarate, the minor adduct, mp 142—144 °C, was assigned to **5b**, in which H_a and H_b are *trans* (J_{ab}= 1.4 Hz) and H_b and H_c are *trans* (J_{bc}=5.6 Hz).[10] On the contrary, in the major adduct, mp 210—213 °C, the large coupling constant of J_{ab}=8.0 Hz indicates that H_a and H_b are *cis*, while the small value of J_{bc} (=5.8 Hz) shows H_b and H_c are *trans*. An inspection of the Dreiding model of these adducts indicates that the newly formed tetrahydrofuran ring is perpendicular to the fluorene ring and that R_4 is situated under the plane of the fluorene ring. Therefore, when R_4 is the methoxycarbonyl group, the ring current of the fluorene ring causes an upper-field shift of the methyl signals, as may be seen in the NMR spectrum of **4b**.



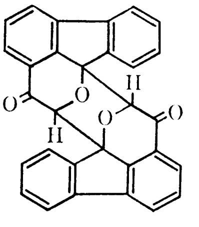
(**5**)

In the reactions with asymmetric olefins, such as methyl cinnamate or methyl *p*-bromocinnamate, a single adduct was obtained; it was assigned the structure shown in Table 2 (R_1=COOCH$_3$ and R_4=Ar) on the basis of the values of the coupling constants (see Table 2) and the chemical shift of methoxycarbonyl (6.20 and 6.23 τ).

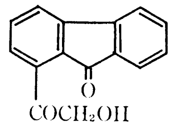
trans-Stilbene gave an adudct with a structure similar to **5a** in a 26% yield, besides a dimer(**6**) of the carbonyl ylide (70%). However, *cis*-stilbene did not form an adduct, but yielded the dimer in an 84% yield and 1-(hydroxyacetyl)fluorenone (**7**) in a 3% yield. The formation of the dimer suggests that the dipolarophilicity of *trans*-stilbene and *cis*-stilbene is lower than that of the other dipolarophiles cited above.

Styrene is much more reactive than stilbenes and affords an adduct (**5g**) which shows an H_a resonance as a double doublet coupling with both H_b and $H_{b'}$ (J_{ab}=1.7 (*trans*) and $J_{ab'}$=8.5 Hz (*cis*)). Thus, R_4 is decided to be phenyl in **5g**. Methyl methacrylate gave an adduct (**5h**) in which R_3 was assigned to methoxycarbonyl, because the methoxy signal was at 6.28 τ and H_a was a double doublet. The configuration of these adducts reveals that the phenyl (or *p*-bromophenyl) group is located at the R_4 position in the adducts of phenyl-substituted ethylenic dipolarophiles, such as methyl cinnamate, methyl *p*-bromocinnamate, *trans*-stilbene, and styrene. This directing effect seems to be caused by the π-π interaction[11] between the phenyl ring of dipolarophiles and the fluorene ring of the carbonyl ylide (**3**), which might be parallel in the transition state.

When the diazo compound (**1**) was catalytically decomposed without dipolarophile, the reaction mixture turned red[12] and was then decolorized after a few ten minutes. The treatment of the reaction mixture gave, quantitatively, a white crystalline product of the head-to-tail dimer of the carbonyl ylide.[5] Since, the attempt at the isolation of the carbonyl ylide (**2**) was unsuccessful, further studies to synthesize a stable carbonyl ylide of this type are now in progress.



(**6**)



(**7**)

Experimental[13]

Materials. Fluorenone-1-carboxylic acid was prepared by the CrO_3 oxidation of fluoranthene,[14] and was treated with thionyl chloride to give the corresponding acid chloride.

1-(Diazoacetyl)fluorenone (1) was prepared by the reaction of excess diazomethane with the corresponding acid chloride according to the usual method;[15] yellow plates, mp 149—151 °C; IR(KBr), 2120 (C=N$_2$), 1698 (C=O), and 1600 cm^{-1} (carbonyl of diazoketone). Found: C, 72.67; H, 3.39; N, 11.35%. Calcd for $C_{15}H_8O_2N_2$: C, 72.57; H, 3.25; N, 11.29%.

Dipolarophiles. Dibenzoylacetylene,[16] dimethyl acetylenedicarboxylate,[17] methyl phenylpropiolate,[18] methyl *p*-bromocinnamate,[19] and *trans*-dibenzoylethylene[20] were prepared by the procedure described in the literature. Other crystalline dipolarophiles, such as dimethyl fumarate, methyl cinnamate, and *trans*-stilbene, were used after the purification of commercial reagents by recrystallization. Liquid dipolarophiles, methyl propiolate, phenylacetylene, styrene, and methyl methacrylate, were purified by distillation im-

TABLE 2. SPECTRAL PROPERTIES OF CYCLOADDUCTS OF **3** WITH ETHYLENIC DIPOLAROPHILES

Adduct	R_1	R_2	R_3	R_4	IR (KBr, cm^{-1})		NMR (CDCl$_3$, τ)[b]				OCH$_3$			
							H_a	H_b	H_c	$H_{b'}$	R_1	R_2	R_3	R_4
5a	PhCO	H_b	H_c	PhCO	1700	1685 1673	4.88(d) $J_{ab}=1.6$ (*trans*)	5.10(dd) $J_{bc}=4.9$ (*trans*)	4.46(d)	—	—	—	—	—
5b	COOMe	H_b	H_c	COOMe	1700	1734	4.82(d) $J_{ab}=1.4$ (*trans*)	6.20(dd) $J_{bc}=5.6$ (*trans*)	5.83(d)	—	6.20	—	—	6.83
5c	H_b	COOMe	COOMe	H_c	1700	1732	4.83(d) $J_{ab}=8.0$ (*cis*)	5.60(dd) $J_{bc}=5.8$ (*trans*)	6.30(d)	—	—	6.53	6.31	—
5d	COOMe	H_b	H_c	Ph	1699	1735	4.77(d) $J_{ab}=1.7$ (*trans*)	6.48(dd) $J_{bc}=6.9$ (*trans*)	5.64(d)	—	6.20	—	—	—
5e	COOMe	H_b	H_c	Ar[c]	1700	1736	4.78(d) $J_{ab}=1.7$ (*trans*)	6.57(dd) $J_{bc}=6.8$ (*trans*)	5.70(d)	—	6.23	—	—	—
5f	Ph	H_b	H_c	Ph	1701		5.92(d) $J_{ab}=1.6$ (*trans*)	6.20(dd) $J_{bc}=6.8$ (*trans*)	6.00(d)	—	—	—	—	—
5g	H_b	H_b	H_c	Ph	1687		4.97(dd) $J_{ab}=1.7$ (*trans*) $J_{ab'}=8.5$ (*cis*)	6.77(oct) $J_{bc}=6.8$ (*trans*) $J_{b'c}=10.6$ (*cis*)	7.68(dd) $J_{bb'}=13.8$ (*geminal*)	5.99(dd)	—	—	—	—
5h	H_b	H_b	COOMe	Me[a]	1702	1713	4.99(dd) $J_{ab}=1.6$ (*trans*)	6.55(dd) $J_{ab'}=8.8$ (*cis*)	— $J_{bb'}=13.5$ (*geminal*)	8.11(dd)	—	—	6.28	—

a) 9.15 τ (s, CH_3). b) The coupling constants are shown in Hz. c) *p*-BrC_6H_4.

TABLE 3. YIELDS, MELTING POINTS, AND ANALYTICAL DATA OF CYCLOADDUCTS **4** AND **5**

Dipolarophile	Adduct	Yield	Mp (°C)	Found (%)		Calcd (%)		Molecular formula
				C	H	C	H	
$PhCO-C\equiv C-COPh$	**4a**	89	200—202	81.89	3.93	81.85	3.96	$C_{31}H_{18}O_4$
$CH_3OOC-C\equiv C-COOCH_3$	**4b**	100	144—146	69.60	3.95	69.61	3.89	$C_{21}H_{14}O_6$
$H-C\equiv C-COOCH_3$	**4c**	80	144—146	75.02	3.90	74.99	3.97	$C_{19}H_{12}O_4$
$Ph-C\equiv C-H$	**4d**	86	209—211	86.13	4.38	85.90	4.38	$C_{23}H_{14}O_2$
$Ph-C\equiv C-COOCH_3$	**4e**	24	208—209	80.02	4.26	78.93	4.24	$C_{25}H_{16}O_4$
	4f	30	161—163	78.85	4.32	78.93	4.24	
$PhCOCH=CHCOPh$ (*trans*)	**5a**	92	182—184	80.79	4.43	81.56	4.42	$C_{31}H_{20}O_4$
$CH_3OOCCH=CHCOOCH_3$ (*trans*)	**5b**	34	142—144	69.08	4.42	69.22	4.43	$C_{21}H_{16}O_6$
	5c	54	210—213	69.15	4.41	69.22	4.43	
$PhCH=CHCOOCH_3$	**5d**	66	173—175	78.39	4.77	78.52	4.74	$C_{25}H_{18}O_4$
p-$Br-C_6H_4CH=CHCOOCH_3$ (*trans*)	**5e**	66	179—181	65.42	3.73	65.09	3.72	$C_{25}H_{17}O_4Br$
$PhCH=CHPh$ (*trans*)	**5f**	26[a]	209—211	87.03	5.09	86.97	5.03	$C_{29}H_{20}O_2$
$PhCH=CH_2$	**5g**	79	211—213	84.82	4.90	85.16	4.97	$C_{23}H_{16}O_2$
$CH_2=C(CH_3)COOCH_3$	**5h**	88	184—187	74.90	5.14	74.99	5.03	$C_{20}H_{16}O_4$

a) In this reaction the dimer (**6**) was obtained in a 70% yield.

mediately before use.

General Procedure of the Decomposition of 1-(Diazoacetyl)-fluorenone (1) in the Presence of Dipolarophiles. 1-(Diazoacetyl)fluorenone (0.25 g, 1 mmol) was added, in small portions, to a benzene solution (30 ml) of a 1.5—3.0 molar amount of dipolarophile and a catalytic amount (0.02 g, 0.08 mmol) of $Cu(acac)_2$ at 80 °C. A vigorous evolution of nitrogen gas was observed immediately after the addition. The reaction mixture was separated by column chromatography on silica gel, using benzene as the eluent. The physical properties of the cycloadducts obtained are listed in Tables 1 and 2, while the yields, melting point, and results of elemental analyses are shown in Table 3.

Formation of Dimer (6). 1-(Diazoacetyl)fluorenone (0.25 g, 1 mmol) was decomposed in a benzene solution of a catalytic amount of $Cu(acac)_2$ by adding it in small portions. During the course of the addition, a vigorous evolution of nitrogen was observed and the reaction mixture turned red. After the red color has disappeared, the solvent was evaporated under reduced pressure. A white crystalline product was thus obtained in a quantitative yield; 0.22 g, mp>360 °C; IR (KBr), 1698 cm^{-1} (C=O). Found: C, 81.56; H, 3.69%. Calcd for $C_{30}H_{16}O_4$: C, 81.81; H, 3.66%.

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