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Reactions of Diazoketones in the Presence of Metal Chelate. IV. Formation and Reaction of Carbonyl Ylides[1]

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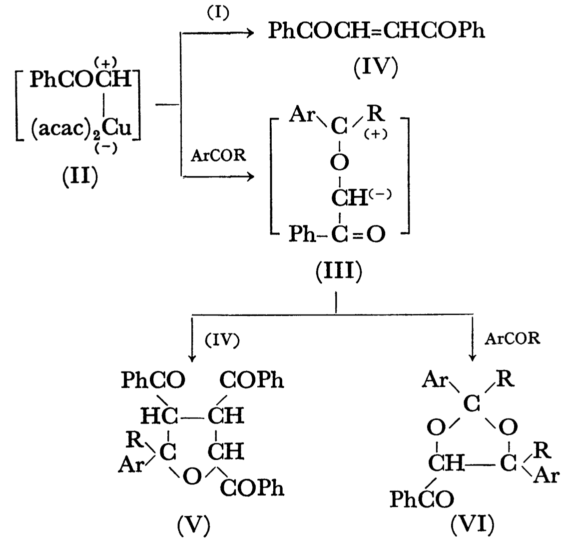
The copper chelate-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone was carried out in benzene. The reaction gave a dimer of a carbonyl ylide intermediate. The intermediate was trapped with dipolarophiles such as *trans*-dibenzoylethylene, ethyl fumarate, isoprene and dimethyl acetylenedicarboxylate, yielding 1,3-dipolar adducts in a stereospecific and stereoselective manner. Similar results were obtained in the catalytic decomposition of *o*-(*n*-butoxycarbonyl)-α-diazoacetophenone. The configuration of adducts and the mechanism of the reaction are discussed.

Carbonyl ylide has been reported as an intermediate in the cycloaddition of some oxiranes having electron attracting group-s to olefinic and acetylenic dipolarophiles.[2] The formation of carbonyl ylide is also expected in the reaction of carbene with carbonyl compound. However, very few example-s were found in the literature.[3] In a previous paper,[1a] we showed that the copper chelate catalyzed reaction of α-diazoacetophenone (I) with aromatic carbonyl compounds such as benzaldehyde and acetophenone gave the corresponding tetrahydrofurans (V) and dioxolanes (VI) accompanied by some by-products derived from benzoylcarbenes, and that the mechanism of the reaction could be explained by assuming a carbonyl ylide intermediate (III), produced by the reaction of a keto-carbene-copper chelate complex, copper carbenoid (II) with carbonyl compounds (Scheme 1).



Scheme 1.

This paper deals with the copper chelate-catalyzed decomposition of substituted α-diazoacetophenones having methoxycarbonyl group at *ortho*-position.

Results and Discussion

Catalytic Decomposition of o-*Methoxycarbonyl-α-diazoacetophenone (VII) in Benzene.* The bis(acetylacetonato)-copper-catalyzed decomposition of VII was carried out in benzene at 80°C under nitrogen. The reaction gave X as the principal product, which had a similar structure to that obtained by Zimmerman and Simkin[4] in the photochemical reaction of 2,3-epoxy-2-methyl-3-phenylindanone. The IR spectrum of X showed a streching vibration band of carbonyl group at 1712 cm^{-1} and an absorption band of newly formed ring-ether linkages at 1285 and 1260 cm^{-1}, and showed no carbonyl streching vibration band of ester group of the starting diazo compound. Ullman and Milks[5] have obtained an another type of dimer yielded by the 1,3-dipolar cycloaddition of benzopyrilium oxide to carbonyl group of indenone oxide in the thermal reaction of 2,3-diphenylindenone oxide. Ullman-type structure of our reaction product (X) may be ruled out by the absence of characteristic IR absorption bands of dioxolane[1a] in the region of 1100—1000 cm^{-1}. The failure of the isolation of indenone oxide (IXd) may support the structure Xa because Xb is the adduct of IXd and IXb.

Since none of the Wolff rearrangement products and formal dimers of *o*-methoxycarbonyl-benzoylcarbene were obtained during the reaction, one reasonable mechanism involves forming of a ketocarbene-copper chelate complex (VIII), a copper carbenoid, followed by the formation of a carbonyl ylide intermediate (IX), and a head-to-tail dimerization (Scheme 2).

This intermediate (IX) seems to be produced intramolecularly by electrophilic attack of carbenoid-carbon on carbonyl oxygen at *ortho*-position, contrary to the case of intermolecular reaction of a copper-carbenoid with methyl benzoate.[1a] Facilities for the formation of carbonyl ylide (IX) may be attributed to that the carbonyl group of *o*-substituent is close to the carbenoid

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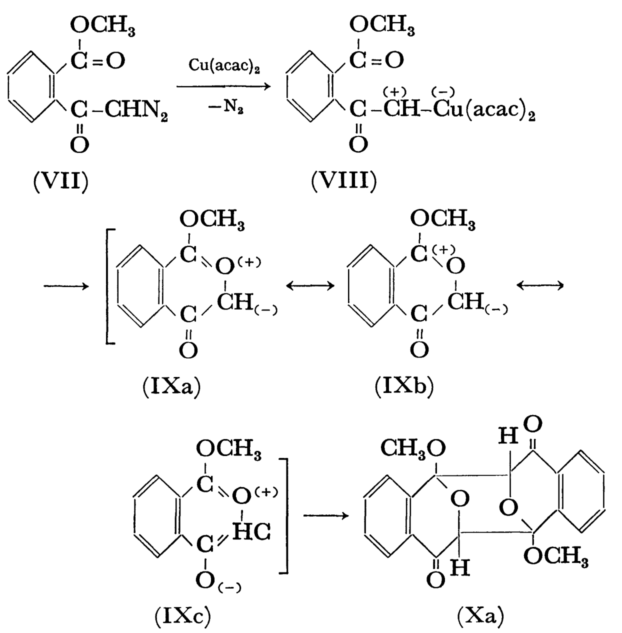
[1] a) Part III: M. Takebayashi, T. Ibata, and K. Ueda, This Bulletin, **43**, 1500 (1970). b) Presented in part at the 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., U.S.A., July, 1971. Abstracts of paper, p. 124. (c) Preliminary Communication: M. Takebayashi, T. Ibata, K. Ueda, and T. Ohashi, This Bulletin, **43**, 3964 (1970).

[2] a) H. Hamberger and R. Huisgen, *Chem. Commun.*, 1190 (1971). b) A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *Chem. Commun.*, 1192 (1971). c) References cited therein.

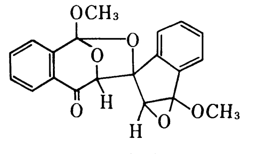
[3] R. Huisgen, and R. Bermes, *Angew. Chem.*, **75**, 630 (1963).

[4] H. E. Zimmerman and R. D. Simkin, *Tetrahedron Lett.*, 1847 (1964).

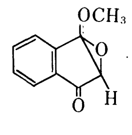
[5] E. F. Ullman and J. E. Milks, *J. Amer. Chem. Soc.*, **84**, 1315 (1962); *ibid.*, **86**, 3814 (1964).



Scheme 2.



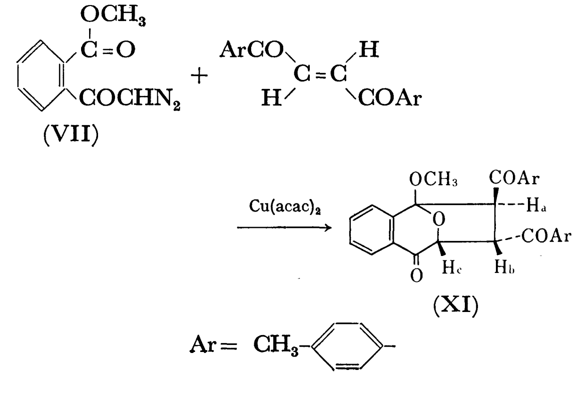
(Xb)



(IXd)

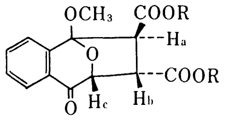
carbon atom (neighboring group participation), and that the newly created ring of IX is stabilized owing to the contribution of its canonical formula-e (IXa, IXb, and IXc). The contribution of IXc to the intermediate seems to be smaller than that of carbonyl ylide structure (IXa), because the color of the reaction mixture does not show the red color of benzopyrilium oxide,5) but maintain-s blue color of copper chelate during the reaction.

Reaction of o-*Methoxycarbonyl-α-diazoacetophenone (VII) with Unsaturated Compounds.* In order to investigate the reactivities of the carbonyl ylide toward dipolarophiles, the copper chelate-catalyzed decomposition of VII was carried out in the presence of unsaturated compounds. In the presence of *trans*-bis(*p*-methylbenzoyl)ethylene, the reaction gave an adduct (XI) in 75% yield. No cyclopropane derivatives, which would be formed by the reaction of the copper-carbenoid with the ethylenic compound, were recognized by the precise investigation of IR and NMR spectra of the reaction products. The coupling constants of NMR spectrum of XI show that H_a and H_b seems to be oriented in *trans*-configuration judging from its small value of $J_{a,b}=2.0$ Hz, whereas H_b and H_c to be in *cis*-configuration ($J_{b,c}=6.0$ Hz) from the analogy to the stereochemistry fo pyrrolidine system.6)



The results indicate that the addition of IX to the ethylenic compound may be stereospecific, and that the reaction may proceed through a concerted $({}_{\pi}4_s+{}_{\pi}2_s)$ type of cycloaddition according to the Woodward-Hoffman rule.7)

In a similar manner, the dipolar intermediate (IX) was trapped with diethyl and dimethyl fumarates to give adducts, XII and XIII, in yields of 59 and 70%, respectively.

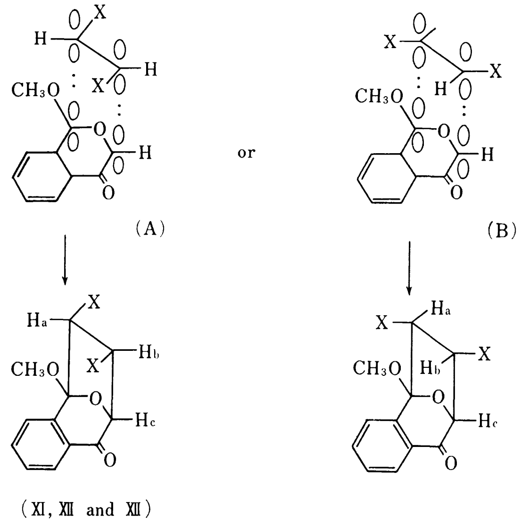


(XII) R: C_2H_5
(XIII) R: CH_3

The NMR spectra showed that the configurations concerning with H_a, H_b, and H_c of XII and XIII are quite same to that of XI.

Two kinds of transition states A and B, may be possible in the addition of IX to the ethylenic compounds (Scheme 3). The one (A) gives an adduct in which H_b and H_c are oriented in *cis*-configuration, whereas the other (B) leads to an adduct in which H_b and H_c are in *trans*-configuration. The fact that H_b and H_c of the adducts (XI, XII, and XIII) are oriented in *cis*-configuration indicates that the addition will take stereoselectively through A, owing to the overlapping of π-electrons of IX with those of acyl group of ethylenic compounds and/or to the repulsion of methoxy group of IX against acyl group of the ethylenic compounds.

The reaction of VII with dimethyl maleate seems to be remarkably slower than that with dimethyl fumarate,



Scheme 3.

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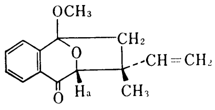
6) a) J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **48**, 2215 (1970). b) R. Huisgen, W. Scheer, G. Szeimies, and H. Hube, *Tetrahedron Lett.*, 397 (1966).

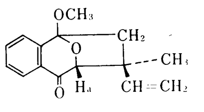
7) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry" Academic Press Inc, Weinheim (1970).

because the reaction of VII with a mixture of maleate and fumarate (99: 1), which contained almost equimolecular amount of dimethyl fumarate to VII, gave only an adduct (XIII) of IX to dimethyl fumarate in 70% yield. Dimethyl fumarate was found to be consumed completely during the reaction by the gas chromatographic analyses of recovered substrate.

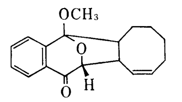
In the presence of isoprene, two stereoisomeric adducts, XIV and XV, were obtained in yields of 34 and 43%, respectively. The NMR spectra show that the H_a of XV is deshielded by 0.14 ppm in comparison with that of XIV owing to π-electrons of the ethenyl group. The results indicate that the isoprene reacts with the carbonyl ylide (IX) by 1,2-addition to give XIV and XV. Cyclooctadiene-1,3 also reacted with IX to afford a 1: 1 adduct in a 18% yield, whose structure was assumed to be XVI by the similarity to the reaction with isoprene.



(XIV)



(XV)

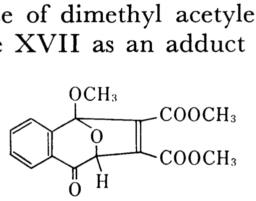


(XVI)

Methyl acrylate, *trans*-methyl crotonate, crotonaldehyde, acrylonitrile, and crotononitrile gave also cycloaddition products in high yields (60—90%).[8]

However, *cis*- and *trans*-stilbenes, maleic anhydride, chalcone and norbornadiene gave no cycloaddition products, although the reason is not clear. In these cases, the dimer (X) was obtained in 40—50% yield.

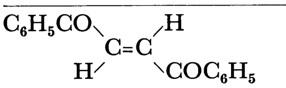
In the presence of dimethyl acetylenedicarboxylate, the reaction gave XVII as an adduct in 70% yield.



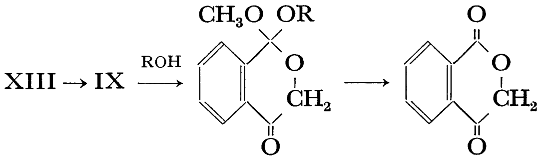
(XVII)

Similar results were obtained in the reaction of *o*-(*n*-butoxycarbonyl)-α-diazoacetophenone (VII′) as is shown in Table 1.

Table 1. Reaction of *o*-(*n*-butoxycarbonyl)-α-diazoacetophenone with dipolarophiles

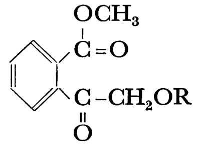
Dipolarophile		Adduct	
		Yield (%)	Mp (°C)
 $C_6H_5CO{-}CH{=}CH{-}COC_6H_5$	(XI′)	92	91—92
$H_3COOC{-}C{\equiv}C{-}COOCH_3$	(XVII′)	80	oil

The Catalytic Decomposition of o-*Methoxycarbonyl-α-diazoacetophenone (VII) in Protic Solvents.* The copper chelate-catalyzed decompositions of VII were carried out in protic solvents such as ethyl alcohol and dioxane-water. The reaction gave isochromanedione-1,4 (XVIII) in yields of 40—50%, without any insertion products (XIX) of the ketocarbene to O–H bond of ethyl alcohol and water. The formation of XVIII gives another support to the intermediacy of carbonyl ylide (IX) as is shown in Scheme 4.



(XVIII)

Scheme 4.



(XIX)

These results mentioned above suggest that the copper carbenoid (VIII) converts preferentially to give a carbonyl ylide intermediate (IX), followed by 1,3-dipolaraddition to unsaturated compounds.

Experimental

All melting and boiling points are uncorrected. The IR spectra were measured on a Hitachi Infrared Spectrometer, model EPI-S2. The NMR spectra were recorded at 60 Mc with a Varian Associates model A-60 Spectrometer, using tetramethylsilane as an internal standard.

Materials. o-*Alkoxycarbonyl-α-diazoacetophenones* were prepared starting from alkyl hydrogen phthalate according to the method of Hodson.[9]

o-*Methoxycarbonyl-α-diazoacetophenone*, mp 62.0—62.3°C. IR (KBr): 2200 (–N≡N), 1725 (ester C=O), 1605 (diazoketone C=O), 1370, and 740 cm^{-1} (Ph).

Found: C, 58.88; H, 3.89; N, 13.61%. Calcd for $C_{10}H_8O_3N_2$: C, 58.82; H, 3.95; N, 13.72%

o-(n-*Butoxycarbonyl*)-*α-diazoacetophenone*, oil, partially decomposes on standing at room temperature. IR (KBr); 2200 (–N≡N), 1725 (ester C=O), 1610 (diazoketone C=O), 1350, and 735 cm^{-1} (Ph).

Catalytic Decomposition of VII in Benzene. A solution of 2.0 g (0.01 mol) of VII and 0.05 g (1.9×10^{-4} mol) of $Cu(acac)_2$ in 50 m*l* of benzene was heated at 80°C under an atmosphere of nitrogen. The color of the reaction mixture turned dark-brown with an evolution of almost theoretical amount of nitrogen. After the reaction was over, the catalyst was separated by filtration and the solvent was removed by distillation. The residue was fractionated by silicagel chromatography (solvent: benzene) and a colorless crystalline product was obtained accompanied by a small amount of unknown solid. The structure of the crystalline product (X) was determined by elemental analyses and IR and NMR spectra after repeated crystallization from benzene-*n*-heptane, mp 233—235°C, yield 0.48 g (27%). IR (KBr): 1712 (ring C=O), 1285, 1260, 1237 (ring C=O and C–O–C), and 1052 cm^{-1} (C–O–CH_3)[10] NMR ($CDCl_3$): 1.7—2.7 (m, 8H, Ph), 5.08 (s, 1H, methyne-H), 5.62 (s, 1H, methyne-H), 6.30 (s, 3H, OCH_3), and 6.54 τ (s, 3H, OCH_3).

Found: C, 68.05; H, 4.32%. Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58%.

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[8] The detail will be published elsewhere.

[9] D. Hodson, G. Holt, and D. K. Wall, *J. Chem. Soc., C*, 971 (1970).

[10] No absorption band of ester group was observed.

Reaction of VII and VII′ with Ethylenic Compounds. A solution of VII or VII′ (0.01 mol) in 50 m*l* of benzene was added dropwise to a solution of Cu(acac)$_2$ (1.9×10^{-4} mol) and an unsaturated compound (0.01 mol) in 100 m*l* of benzene on stirring at 80°C under the atmosphere of nitrogen. The reaction products were separated by silica gel chromatography and were identified by elemental analyses and IR and NMR spectroscopy.

In the reaction of VII with trans-*bis*(p-*methylbenzoyl*)*ethylene*, a white crystalline product (XI), mp 193.0—194.0°C, was obtained without any other detectable by-products, yield 3.50 g (83%). IR (KBr): 1710 (ring C=O), 1280, 1240 (ring C–O–C), 1065 (C–O–CH$_3$), 833, and 772 cm^{-1} (Ph). NMR (CDCl$_3$): 1.7—2.8 (m, 12H, Ph), 4.65 (d, 1H, Hc), 4.93 (d, 1H, Ha), 5.26 (dd, 1H, Hb), 6.32 (s, 3H, OCH$_3$), and 7.54 τ (s, 6H, CH$_3$). $J_{a,b}=2.0$ Hz, $J_{b,c}=6.0$ Hz.

Found: C, 76.53; H, 5.47%. Calcd for $C_{28}H_{24}O_5$: C, 76.35; H, 5.49%.

In the reaction of VII′ with trans-*dibenzoylethylene*, a white crystalline adduct (XI′), mp 91.0—92.0°C, was isolated, yield 4.18 g (92%). IR (KBr): Nearly same to above concerning with characteristic bands. NMR (CDCl$_3$): 1.7—3.3 (m, 14H, Ph), 4.75 (d, 1H, Hc), 5.10 (d, 1H, Ha), 5.40 (dd, 1H, Hb), 6.0—6.25 (m, 2H, OCH$_2$), 8.0—9.0 (m, 4H, CH$_2$), and 9.10 τ (broad s, 3H, CH$_3$). $J_{a,b}=1.9$ Hz, $J_{b,c}=5.8$ Hz.

Found: C, 76.78; H, 5.76%. Calcd for $C_{29}H_{26}O_5$: C, 76.63; H, 5.77%.

In the reaction of VII with diethyl fumarate, an adduct (XII), mp 36.5—37.0°C, were obtained, yield 2.05 g (59%). NMR (CDCl$_3$): 1.7—3.0 (m, 4H, Ph), 5.20 (d, 1H, Hc), 5.73 (q, 2H, OCH$_2$), 6.02 (d, 1H, Ha), 6.12 (q, 2H, OCH$_2$), 6.40 (s, 3H, OCH$_3$), 6.52 (dd, 1H, Hb), 8.65 (t, 3H, CH$_3$), and 8.90 τ (t, 3H, CH$_3$). $J_{a,b}=1.8$ Hz, $J_{b,c}=5.8$ Hz. IR (KBr): 1735 (ester C=O), 1710 (ring C=O), 1288, 1232 (C–O–C), and 760 cm^{-1} (Ph).

Found: C, 61.76; H, 5.52%. Calcd for $C_{18}H_{20}O_7$: C, 62.06; H, 5.79%.

In the reaction of VII with dimethyl fumarate, a crystalline product (XIII), mp 110.5—111.0°C, was obtained, yield 2.25 g (70.3%). NMR (CDCl$_3$): 1.7—3.3 (m, 4H, Ph), 4.98 (d, 1H, Hc), 6.10 (d, 1H, Ha), 6.52 (dd, 1H, Hb), 6.20 (s, 3H, OCH$_3$), 6.40 (s, 3H, OCH$_3$), and 6.55 τ (s, 3H, OCH$_3$). $J_{a,b}=1.7$ Hz, $J_{b,c}=6.0$ Hz. IR (KBr): 1735 (ester C=O), 1710 (ring C=O), 1287, 1233 (ring C–O–C), 980, and 760 cm^{-1} (Ph).

Found: 59.86; H, 4.84%. Calcd for $C_{16}H_{18}O_7$: C, 60.00; H, 5.04%.

In the reaction of VII with isoprene, two kinds of liquid products (XIV and XV), were isolated in yields of 0.78 and 0.98 g (34 and 43%), respectively. IR (neat) of XIV: 1700 (C=O), 1635 (C=C), 1290 (ring C–O–C), 1050 (C–O–CH$_3$), and 765 cm^{-1} (Ph). NMR (CDCl$_3$) of XIV: 1.9—2.8 (m, 4H, Ph), 4.7—5.8 (m, 3H, CH=CH$_2$), 6.55 (s, 3H, OCH$_3$), 8.13 (s, 1H, methyne-H), 6.6—8.4 (m, 2H, CH$_2$), and 8.57 τ (s, 3H, CH$_3$).

Found: C, 73.41; H, 6.45%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%. IR (neat) of XV: The same above. NMR (CDCl$_3$) of XV: 1.9—2.8 (m, 4H, Ph), 4.7—5.8 (m, 3H, CH=CH$_2$), 6.55 (s, 3H, OCH$_3$), 8.32 (s, 1H, methyne-H), 6.6—8.4 (m, 2H, CH$_2$), and 8.55 τ (s, 3H, CH$_3$).

Found: C, 73.56; H, 6.35%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

In the reaction of VII with cyclooctadiene-1,3, a liquid product (XVI) and unidentified oil (XVI′) were obtained in yields of 0.49 g (18.4%) and 0.16 g, respectively. IR (neat) of XVI: 1700 (ring C=O), 1300, 1250 (ring C–O–C), 1060 (C-OCH$_3$), and 770 cm^{-1} (Ph). NMR (CDCl$_3$) of XVI: 1.7—2.7 (m, 4H, Ph), 4.0—5.5 (m, 2H, CH=CH), 6.50 (s, 3H, OCH$_3$), and 6.6—9.3 τ (m, 11H, CH and CH$_2$).

Found: C, 75.87; H, 7.12%. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

IR (neat) of XVI′: 1700 (ring C=O), 1290, 1250 (ring C–O–C), 1060 (C-OCH$_3$), 770, and 740 cm^{-1} (Ph). NMR (CDCl$_3$) of XVI′: 1.7—3.2 (m, 8H, Ph), 4.0—5.5 (m, contaminated with a trace of XVI), 6.55 (d, 6H, OCH$_3$), and 6.7—9.3 τ (m, 12H, CH and CH$_2$).

Reactions of VII and VII′ with Acetylenic Compounds. The reactions were carried out in similar manner as described above.

In the reaction of VII with dimethyl acetylenedicarboxylate, a liquid product (XVII) was obtained, yield 2.11 g (70.3%). NMR (CDCl$_3$): 1.9—2.7 (m, 4H, Ph). 4.50 (s, 1H, methyne-H), singlets at 6.17, 6.30 and 6.47 τ (9H, OCH$_3$). IR (neat): 1725 (ester C=O), 1715 (ring C=O), 1660 (C=C), 1270 (ring C–O–C) and 760 cm^{-1} (Ph).

Found: C, 60.45; H, 4.31%. Calcd for $C_{16}H_{14}O_7$: C, 60.38; H, 4.43%.

In the reaction of VII′ with dimethyl acetylenedicarboxylate, an oily product (XVII′) was isolated, yield 2.99 g (80%). NMR (CDCl$_3$): 2.0—2.7 (m, 4H, Ph), 4.60 (s, 1H, methyne-H), 6.1—6.4 (q, 2H, OCH$_2$), 6.20 (s, 6H, OCH$_3$) and 8.1—9.15 τ (m, 7H, CH$_2$ and CH$_3$). IR (neat): 1725 (ester C=O), 1715 (ring C=O), 1660 (C=C), 1260 (ring C–O–C) and 760 cm^{-1} (Ph).

Catalytic Decomposition of VII in Protic Solvents. The catalytic decomposition of VII (2 g, 0.01 mol) in 150 m*l* of a mixed solvent of dioxane and water (5:1) was carried out as mentioned above. A white crystalline product (XVIII), 101.0—102.5°C, was obtained, yield 0.81 g (50%). IR (KBr): 1725 (ring C=O), 1280, 1140 (ring C–O–C) and 763 cm^{-1} (Ph). NMR (CDCl$_3$): 1.6—2.3 (m, 4H, Ph) and 4.90 τ (s, 2H, CH$_2$).

Found: C, 66.38; H, 3.51%. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73%.

The same product (XVIII) was isolated in the reaction in ethyl alcohol (yield; 0.72 g, 44%).