Reaction of Diazo Ketones in the Presence of Metal Chelates. VII. 1,3-Dipolar Cycloaddition of 1-Methoxybenzo[*c*]pyrylium-4-olate with Acetylenic Dipolarophiles

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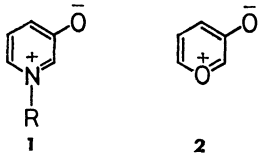
The $Cu(acac)_2$ catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**3**) in the presence of acetylenic dipolarophiles gave cycloadducts of the dipolarophiles with 1-methoxybenzo[*c*]pyrylium-4-olate generated by the intramolecular carbene-carbonyl reaction of the corresponding carbene. The direction of the cycloadditions of unsymmetrically substituted acetylenes has been determined on the basis of the NMR coupling pattern and chemical shift of the bridgehead methine protons of the adducts. Treatment of **3** with strong dipolarophiles such as dibenzoylacetylene or dimethyl acetylenedicarboxylate gave spiro pyrazoles by the direct cycloaddition of **3** and acetylenes followed by the elimination of methanol.

The 1,3-dipolar cycloaddition of pyridinium-3-olates (**1**) have recently been extensively studied by Katritzky *et al.*[1] Only a few papers exist however on the reaction of pyrylium-3-olates (**2**),[2] having isoelectronic structures with pyridinium-3-olate, due to the low stability and difficulty formation of **2**. The reported methods for the formation of pyrylium-3-olates were the thermal and photochemical cleavage of the corresponding epoxides.[2] In the previous paper the formation of benzo[*c*]-pyrylium-4-olate (**5**) was reported in which the contribution of the carbonyl ylide type resonance formula (**5b**), in the copper chelate-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**3**) *via* intramolecular carbene-carbonyl reaction.[3] In this paper the cycloaddition of the carbonyl ylide with acetylenic dipolarophiles will be described.



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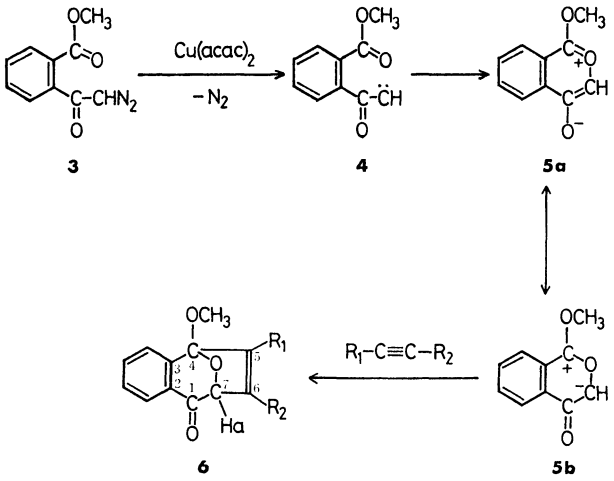
Results and Discussion

The $Cu(acac)_2$ catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**3**) in benzene at 80 °C in the presence of 1.2 mol equivalents of dibenzoylacetylene gave two products. The main product (66% yield) was assigned as 5,6-dibenzoyl-4-methoxy-4,7-epoxy-2,3-benzo-2,5-cycloheptadien-1-one (**6a**) on the basis of the spectral and analytical data. The IR spectrum of **6a** shows carbonyl bands of cyclic ketone and benzoyl groups at 1710 and 1660 cm^{-1}, respectively, together with an ethylenic band at 1630 cm^{-1}. The NMR spectrum of **6a** has a singlet signal of the methoxyl group at δ 3.73 and that of a bridgehead proton at δ 5.75 together with the multiplet signal of the aromatic protons.

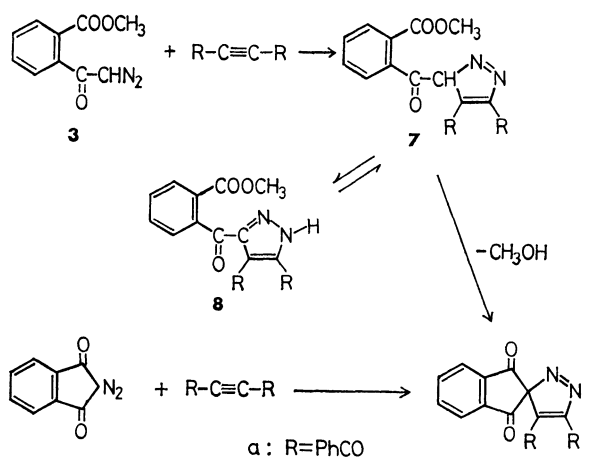
The formation of **6a** is reasonably explained by the 1,3-dipolar cycloaddition of dibenzoylacetylene with 1-methoxybenzo[*c*]pyrylium-4-olate (**5**) which is derived by the intramolecular carbene-carbonyl reaction of the *o*-methoxycarbonylbenzoylcarbene intermediate (**4**) generated by the $Cu(acac)_2$ catalyzed decomposition of **3**



Scheme 1.

(Scheme 1).

The other product contains nitrogen and has a molecular formula $C_{25}H_{14}O_4N_2$ which corresponds to the compound obtained by the elimination of CH_3OH from a 1:1 adduct of the diazo ketone and dibenzoylacetylene. The absence of methoxyl and methine signals in the NMR spectrum agrees with the molecular formula. The IR spectrum shows strained carbonyl and benzoyl bands at 1748 and 1680 cm^{-1} respectively and also shows an ethylenic band at 1650 cm^{-1}. Heating of the 1:1 mixture of the diazo ketone and dibenzoylacetylene in xylene at 120 °C without $Cu(acac)_2$ catalyst gave the same product in high yield. The nitrogen containing product was assigned as 4′,5′-dibenzoylspiro[indan-2,3′-[3*H*]pyrazole]-1,3-dione (**9a**) on the following basis. The cycloaddition of diazo ketones toward electron-deficient acetylenes has been reported to give pyrazoles.[4] The cycloaddition of the diazo ketone (**3**) towards dibenzoylacetylene gives pyrazole (**7a**) which may be in equilibrium with pyrazole (**8a**) by a 1,3-proton shift. The intramolecular elimination of methanol from the pyrazole (**7a**) may give 4′,5′-dibenzoylspiro[indan-2,3′-[3*H*]pyrazole]-1,3-dione (**9a**). The structure of the spiro pyrazole (**9a**) was confirmed by comparison of the spectral properties with an authentic sample prepared by the cycloaddition of 2-diazo-1,3-indandione with dibenzoylacetylene.[5] In



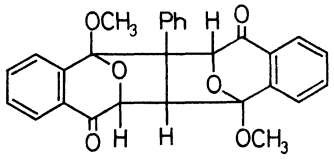
Scheme 2.

order to ascertain the intermediacy of the pyrazole **7a** and **8a**, an absolute benzene solution of equimolar amounts of the diazo ketone (**3**) and dibenzoylacetylene was heated at 60 °C for 6 h. In the IR spectrum of the reaction mixture (after evaporation of benzene under reduced pressure below 50 °C) the characteristic absorption of the diazo group at 2150 cm^{-1} disappeared. The carbonyl bands at 1710 and 1660 cm^{-1} (broad) remained unchanged and a broad band appeared at 3270 cm^{-1}. The NMR spectrum exhibited a singlet of the methoxyl methyl group at δ 3.70 together with a multiplet of aromatic protons. Column chromatography of the reaction mixture on silica gel did not isolate the intermediate **7a** or **8a** but gave the spiro pyrazole (**9a**) in high yield. Fractional recrystallization of the reaction mixture from a mixture of benzene–heptane below 60 °C gave colorless crystals, which were assigned to pyrazole (**8a**) on the basis of analytical and spectral data (see experimental section). Treatment of the pyrazole (**8a**) on silica gel or heating it at 110 °C for 5 h gave the spiro pyrazole (**9a**) quantitatively.

The reaction of **3** with dimethyl acetylenedicarboxylate with $Cu(acac)_2$ catalyst gave a small amount (4%) of the corresponding spiro pyrazole (**9a**) together with cycloadduct (**6b**; 73%) of the benzopyrylium-4-olate (**5**). The spiro pyrazole (**9b**) was also confirmed by comparison with an authentic sample prepared by a similar method as cited above.

In the reactions with asymmetric acetylenes there exist two possibilities in the direction of the cycloaddition giving two isomers. Methyl propiolate however gave only one adduct (**6c**: R_1=$COOCH_3$, R_2=H) in 44% yield despite a detailed inspection of the reaction mixture by column chromatography. The structure of **6c** was characterized by the NMR coupling pattern of two methine protons of the adduct. Both bridgehead methine protons (H_a) and vinyl protons (H_b) show doublet signals coupled with one another (J=2.8 Hz) at δ 5.16 and 7.21 ppm, respectively. This indicates that H_a and H_b are located in vicinal positions (C-7 and C-6).[6]

Phenylacetylene gave two adducts (**6d**: R_1=Ph, R_2=H and **6e**: R_1=H, R_2=Ph) in 45% and 13% yields respectively, together with isochroman-1,4-dione (**10**; 8%) and a 1:2 adduct (**11**; in 5% yield). The structure of the major adduct **6d** was assigned on the basis of the coupling pattern of the methine protons similar to that with **6c** (Table 1). The minor adduct **6e** showed singlet methine proton signals at δ 5.61 and 6.80 ppm indicating that the vinyl proton is located on C-5 and consequently the phenyl group is attached to C-6. The 1:2 adduct is tentatively assigned as **11** on the basis of the elemental analysis and spectroscopic data. The NMR spectrum shows the chemical shifts of two methoxyl groups at δ 3.86 (s) and 3.53 (s) and those of methine protons at δ 6.50 (d), 5.38 (d), and 5.27 (s) and a singlet signal of phenyl protons at δ 7.23 except for a multiplet of aromatic protons. The value of the coupling constant, J=2.4 Hz, for the two doublet methine protons indicates that the two vicinal protons are in a trans configuration.[7] The precise configuration of the 1:2 adduct has however not been determined.



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Methyl phenylpropiolate gave a small amount (6%) of an adduct (**6f**) and isochromandione (**10**, 58%) in

Table 1. Yields and ^{1}H-NMR data of 1,3-dipolar cycloadducts (**6**)

Adduct	R_1	R_2	Yield/%	NMR (δ/ppm, in $CDCl_3$)					
				OCH_3	OCH_3	H_a	H_b(=R_2)	H_c(=R_1)	J_{ab}/Hz
6a	PhCO	PhCO	66	3.73	—	5.75 (s)	—	—	—
6b	$COOCH_3$	$COOCH_3$	73	3.83	3.67	5.46 (s)	—	—	—
6c	$COOCH_3$	H	44	3.70	3.53	5.16 (d)	7.21 (d)	—	2.8
6d	Ph	H	9(45)[a]	3.49	—	5.21 (d)	6.68 (d)	—	2.6
6e	H	Ph	0(13)[a]	3.65	—	5.61 (s)	—	6.80(s)	—
6f	$COOCH_3$	Ph	6(39)[a]	3.73	3.63	5.55 (s)	—	—	—
6g	Ph	$COOCH_3$	0(9)[a]	3.72	3.40	5.48 (s)	—	—	—
6h[b]	COOH	Ph		3.74[c]	—	5.67 (s)[c]	—	—	—

a) Neat dipolarophile was used as the solvent instead of benzene. b) **6h** was obtained by the hydrolysis of **6f**.
c) The NMR spectrum was measured in $CDCl_3$–pyridine solution.

the reaction according to the general procedure (in benzene). When the decomposition was conducted in neat methyl phenylpropiolate (large excess), the yield of the adduct (**6f**) was improved (39%) and the yield of **10** decreased (7%). Moreover, another isomer (**6g**) was obtained in 9% yield. In the previously cited adducts (**6a**—**6g**), the chemical shifts of the bridgehead protons (H_a) are revealed to be affected by the substituents on C-6. The deshielding effect of the C-6 substituent on the chemical shift of H_a decreases in the following order, phenyl (**6e**, 5.61 ppm), methoxycarbonyl (**6b**, 5.46), hydrogen (**6c**, 5.16; **6d**, 5.12). The major adduct (**6f**) shows the chemical shift of H_a at 5.55 ppm which is closer to the value for **6e** than **6b**. The value of the minor adduct (**6g**) corresponds to that of **6b** (5.46 ppm) which has a methoxycarbonyl group on C-6 indicating that the methoxycarbonyl group is on C-6 in the minor adduct (**6g**). These assignments were confirmed by means of conversion of the major adduct (**6f**) into **6e** *via* hydrolysis followed by the decarboxylation.

The reactions when conducted in benzene solution as is shown in the general procedure, the yields of the adducts of these acetylenic dipolarophiles decrease in the order: dimethyl acetylenedicarboxylate>dibenzoylacetylene>methyl propiolate>methyl phenylpropiolate ≈phenylacetylene>diphenylacetylene (no reaction). The order of the reactivities of the dipolarophiles are consistent with their reactivities toward 3-methyl-2,4-diphenyloxazolium-5-olate having an azomethine ylide system.[8] The intermediate benzopyrylium-4-olate (**5**) reacts competitively with the dipolarophile or water (a contaminant in the reaction system) affording the adduct or isochromandione due to the low dipolarophilicity of methyl phenylpropiolate and phenylacetylene.

The preferential formation of the cycloadduct (**6c**) in the reaction of methyl propiolate is reasonably explained by the dipolar interaction between the dipole and the dipolarophile considering the dipolar structure, $H-\overset{\delta+}{C}\equiv\overset{\delta-}{C}-COOCH_3$, of methyl propiolate and a resonance formula **5b** for benzopyrylium-4-olate. The regioselectivity of the reaction of phenylacetylene and methyl phenylpropiolate with **5** is difficult to explain only on the basis of the dipolar interaction as cited above. 3-Phenylphthalazinium-1-olate, having an isoelectronic system with benzopyrylium-4-olate (**5**), has been reported to give two cycloadducts in the reaction with phenylacetylene.[9] The steric factor and π-π interaction[10] between the substituents of the dipole (**5**) and dipolarophiles may also effect the direction of cycloaddition.

Experimental

All melting points were taken with a Yanagimoto Melting Point Apparatus and are uncorrected. The IR spectra were measured on a Hitachi Infrared Spectrometer model EPI-S2. Unless otherwise indicated ^{1}H-NMR spectra were recorded in $CDCl_3$ solution at 60 MHz on a Varian Spectrometer model A-60 or EM-360 using tetramethylsilane as an internal standard.

Materials. *o*-Methoxycarbonyl-α-diazoacetophenone (**3**) was prepared by the method of Hudson;[11] mp 62.0—62.5 °C.

Dipolarophiles. Dibenzoylacetylene,[12] dimethyl acetylenedicarboxylate,[13] and methyl phenylpropiolate[14] were prepared by procedures described in the literature. Methyl propiolate, phenylacetylene, and diphenylacetylene were used after purification of commercial reagents by distillation or recrystallization.

General Procedure of the Cu(acac)$_2$ Catalyzed Decomposition of o-Methoxycarbonyl-α-diazoacetophenone (3) in the Presence of Acetylenic Dipolarophiles. To an absolute benzene solution (50 ml) containing a catalytic amount of $Cu(acac)_2$ and a 1.2—2.0 molar amount of the dipolarophile was added a benzene solution (20 ml) of the diazo ketone (**3**) with magnetic stirring at 80 °C. Almost quantitative amounts of nitrogen gas were evolved and the reaction mixture turned colorless. After heating for 2 h the benzene was removed under reduced pressure, and the residue fractionated by column chromatography (silica gel–benzene).

Decomposition of 3 in the Presence of Dibenzoylacetylene by General Procedure: In the reaction of **3** (2.0 g, 9.8 mmol) and dibenzoylacetylene (2.75 g, 12 mmol) two products were obtained.

Cycloadduct (6a): Colorless crystals; yield 2.65 g (66%); mp 146—148 °C; IR (KBr) 1710, 1660 (C=O), 1630 cm^{-1} (C=C). Found: C, 75.90; H, 4.28%. Calcd for $C_{26}H_{18}O_5$: C, 76.09; H, 4.42%.

Spiro Pyrazole (9a): Pale yellow crystals; yield 0.38 g (10%); mp 234—235 °C; IR (KBr) 1748, 1680 (C=O), 1650 cm^{-1} (C=C). Found: C, 73.56; H, 3.48; N, 6.89%. Calcd for $C_{25}H_{14}O_4N_2$: C, 73.88; H, 3.47; N, 6.90%.

Reaction of 3 with Dibenzoylacetylene at High Temperature Without Catalyst: A xylene solution of **3** (0.21 g, 1 mmol) and dibenzoylacetylene (0.24 g, 1 mmol) was heated at 120 °C for 7 h. Evaporation of xylene under reduced pressure and recrystallization gave **9a** in 95% yield.

Reaction of 3 with Dibenzoylacetylene at Low Temperature Without Catalyst: A benzene solution of **3** (0.21 g, 1 mmol) and dibenzoylacetylene (0.24 g, 1 mmol) was heated at 60 °C for 6 h. Two careful recrystallizations of the product from a mixture of benzene–heptane below 60 °C gave colorless crystals (**8a**); yield 0.328 g (81%); mp 67.5—68.5 °C; IR (KBr) 3270 (NH), 1710 (ester C=O), 1660 cm^{-1} (C=O); NMR (in $CDCl_3$) δ 3.73 (s, 3H, OCH_3), 7.3—7.7 (m, 14H, aromatic), and 12.2 ppm (broad s, 1H, NH). Found: C, 71.11; H, 4.16; N, 6.63%. Calcd for $C_{26}H_{18}O_5N_2$: C, 71.22; H, 4.14; N, 6.39%.

Thermal Decomposition of 8a: Treatment of **8a** (0.086 g, 0.2 mmol) at 110 °C for 5 h yielded spiro pyrazole (**9a**) in quantitative yield after the evaporation of the solvent under reduced pressure.

Reaction of 2-Diazo-1,3-indandione with Dibenzoylacetylene: A mixed solution of 2-diazo-1,3-indandione (0.344 g, 2 mmol) and dibenzoylacetylene (0.468 g, 2 mmol) in xylene was heated at 140 °C for 5 h. Evaporation of the solvent gave a pale yellow crystalline product in quantitative yield. The IR spectrum of the product was identical to that of **9a** obtained in the reaction of **3** and dibenzoylacetylene.

Decomposition of 3 in the Presence of Dimethyl Acetylenedicarboxylate by General Procedure: The reaction of **3** (2.0 g, 9.8 mmol) and dimethyl acetylenedicarboxylate (1.7 g, 12 mmol) gave two products.

Cycloadduct (6b): Yield 2.0 g (73%); mp 79—80 °C; IR (KBr) 1720 (broad, ester and ring C=O), 1650 cm^{-1} (C=C). Found: C, 60.24; H, 4.34%. Calcd for $C_{16}H_{14}O_7$: C, 60.38; H, 4.43%.

Spiro Pyrazole (9b): Yield 0.12 g (4%); mp 187.5—188.5 °C; IR (KBr) 1745 (broad, ester and indandione C=O), 1675 cm^{-1} (C=C); NMR (in $CDCl_3$) δ 4.05 (s, 3H, OCH_3), 4.09 (s, 3H, OCH_3), 7.1—8.2 ppm (m, 4H, aromatic). Found:

C, 57.13; H, 3.40; N, 8.87%. Calcd for $C_{15}H_{10}O_6N_2$: C, 57.33; H, 3.21; N, 8.92%.

Reaction of 2-Diazo-1,3-indandione with Dimethyl Acetylenedicarboxylate: A xylene solution of 2-diazo-1,3-indandione (0.344 g, 2 mmol) and dimethyl acetylenedicarboxylate (0.31 g, 2.2 mmol) was heated at 140 °C for 6 h. Evaporation of the solvent under reduced pressure gave a crystalline product (0.540 g, 85%) which showed no mixed melting point depression with **9b** obtained in the reaction of **3** and dimethyl acetylenedicarboxylate.

Decomposition of 3 in the Presence of Methyl Propiolate by General Procedure: Reaction of **3** (0.284 g, 1.4 mmol) and methyl propiolate (0.22 g, 2.5 mmol) gave an adduct (**6c**); yield 0.160 g (44%); mp 87—88 °C; IR (KBr) 1710 (C=O), 1630 cm^{-1} (C=C). Found: C, 64.57; H, 4.63%. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65%.

Decomposition of 3 in the Presence of Phenylacetylene by General Procedure: Reaction of **3** (0.61 g, 3 mmol) and phenylacetylene (0.61 g, 6 mmol) gave cycloadduct (**6d**) together with isochroman-1,4-dione (**10**, 0.10 g, 20%) and unidentified intractable products.

Cycloadduct (6d): Yield 0.070 g (9%); colorless oil; IR (liquid film) 1705 cm^{-1} (C=O). Found: C, 77.53; H, 5.24%. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07%. Isochromandione (**10**) was characterized by comparison of the IR spectrum with that of an authentic sample.[3]

The $Cu(acac)_2$ Catalyzed Decomposition of 3 in Neat Phenylacetylene (Large Excess): The diazo ketone **3** (0.408 g, 2 mmol) was decomposed at 80 °C in a large excess of phenylacetylene (5 g, 50 mmol) and a catalytic amount of $Cu(acac)_2$. Column chromatography of the reaction mixture gave another cycloadduct (**6e**) and a 1:2 adduct (**11**) together with **6d** (45%) and **10** (8%).

Cycloadduct (6e): Yield 0.070 g (13%); colorless oil; IR (liquid film) 1705 cm^{-1} (C=O). Although the elemental analysis of **6e** did not show a satisfactory result, the structure was confirmed by the similarity of the IR spectrum with that of an isomeric cycloadduct (**6d**). The NMR spectrum also supported the structure.

1:2 Adduct (11): Yield 0.045 g (10%); mp 244—246 °C; IR (KBr) 1710 cm^{-1} (C=O); NMR (in $CDCl_3$) δ 3.53 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 5.27 (s, 1H, methine), 5.38 (d, J=2.4 Hz, 1H, methine), 6.50 (d, J=2.4 Hz, 1H, methine), 7.23 (s, 5H, Ph) and 7.0—8.0 ppm (m, 8H, aromatic). Found: C, 74.19; H, 4.92%. Calcd for $C_{28}H_{22}O_6$: C, 74.00; H, 4.88%.

Decomposition of 3 in the Presence of Methyl Phenylpropiolate by General Procedure: Two products were obtained in the reaction of **3** (0.61 g, 3 mmol) and methyl phenylpropiolate (0.64 g, 4 mmol). The main product was confirmed to be isochromandione (**10**, 0.28 g, 58%).

Cycloadduct (6f): Yield 0.097 g (9%); mp 112—113 °C; IR (KBr) 1710 (C=O), 1640 cm^{-1} (C=C). Found: C, 71.37; H, 4.79%. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80%.

The $Cu(acac)_2$ Catalyzed Decomposition of 3 in Neat Methyl Phenylpropiolate (Large Excess): The diazo ketone (**3**) (0.408 g, 2 mmol) was decomposed in neat methyl phenylpropiolate (1.28 g, 8 mmol) in the presence of a catalytic amount of $Cu(acac)_2$ at 80 °C. Column chromatography of the reaction mixture isolated three products, isochromandione (**10**, 0.022 g, 7%), the cycloadduct (**6f**, 0.261 g, 39%), and an isomeric cycloadduct (**6g**): yield 0.058 g (9%); colorless crystals; mp 124—127 °C; IR (KBr) 1710 (C=O), 1640 cm^{-1} (C=C). Elemental analysis of **6g** did not show a satisfactory result.

Hydrolysis of 6f: The cycloadduct **6f** (0.103 g, 0.3 mmol) was hydrolyzed in EtOH (2 ml) and 40% aqueous NaOH solution (2 ml) at room temperature with vigorous stirring for 5 h. Acidification of the reaction mixture with 3 M HCl after evaporation of EtOH gave colorless crystals (**6h**): yield 0.090 g, (93%); mp 260—262 °C (from EtOH–H_2O); IR (KBr) 3450, 3000, 2500, 1690, 930 (COOH), 1710 (C=O), 1640 cm^{-1} (C=C). Found: C, 70.55; H, 4.32%. Calcd for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38%.

Decarboxylation of 6h: A quinoline solution (10 ml) of **6h** (0.040 g, 0.12 mmol) was heated at 200—210 °C for 5 h with a suspension of copper powder (0.10 g). After cooling the reaction mixture was poured into water (50 ml) and acidified with 3 M HCl in order to dissolve the quinoline. Column chromatography of the ether extract gave 0.010 g (27%) of **6d**, which was identified on the basis of the IR and NMR spectra.

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