Promoters for the (Alkyne)hexacarbonyldicobalt-Based Cyclopentenone Synthesis

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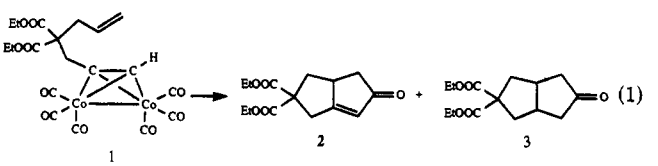
Dimethyl sulfoxide and a variety of other highly polar solvents are shown to promote both inter- and intramolecular cyclopentenone formation from alkenes and (alkyne)hexacarbonyldicobalt complexes. Their use leads to significant changes in both regio- and stereoselectivity when compared to other reaction conditions.

Introduction

Steadily increasing interest in synthetic uses of the formation of cyclopentenones from cobalt complexes of alkynes[1] has led to the development of a variety of modifications designed to improve yields and, if possible, selectivity. Inter alia we and others have employed amine oxides[4-6] and phosphine oxides[6] to promote such reactions. Amine oxides are well-known to oxidize metal-bound CO to CO_2 and can thus be expected to provide free coordination sites for the alkene; the apparent need to use up to 10 equiv of the oxide in order to achieve maximum yields is not understood. Phosphine oxides are poor oxidants and cannot act in the same way; they may substitute CO by a weaker, more easily replaceable ligand. The use of dimethyl sulfoxide as an alternative was tried at Seoul in the hope that it might act similarly to, but more efficiently than, phosphine oxides. It would not be expected to cause the oxidative destruction of the cobalt complexes induced by Me_3NO and might therefore be suitable for catalytic systems. Moreover, optically active sulfoxides might lead to enantioselectivity. Although neither catalysis nor enantioselection has so far been achieved in the presence of sulfoxides, the value of DMSO as a promoter was readily established. Communication of this result to Glasgow led to the testing of other highly polar solvents as promoters, and we here report the combined results of these two investigations.

Results and Discussion

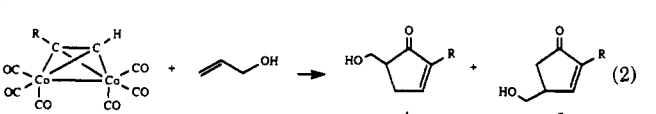
As with Me_3NO as promoter, the use of DMSO was first tried for the intramolecular cyclization (reaction 1) of the



1 2 3

complex 1. Results with the two promoters are compared in Table I: Yields are seen to be similar although DMSO requires significantly higher reaction temperature. Formation of the saturated ketone 3 as a byproduct increases slightly with increasing proportion of DMSO but is avoided by replacing dichloromethane as solvent with benzene. The latter also gives the best total yield, albeit after longer reaction time.

The Me_3NO method[5] had been shown to make possible the use of both allylic and propargylic alcohol components without OH protection (which had previously been found to be necessary under higher temperature conditions[7]). In respect of allylic alcohols the same observation had been made independently (Jan 1991) at Glasgow using the hydrated reagent $Me_3NO \cdot 2H_2O$ under Shambayati, Crowe and Schreiber's conditions.[4] The new results include successful use of unprotected allyl alcohol in the DMSO-promoted reaction 2 even at 60 °C. Remarkably however,



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the changes in solvent (and temperature) lead to major changes in regioselectivity as summarized in Table II. Similar variability has previously been observed by Billington, Farnocchi, and Ganly[8] when reacting (ethyne)-

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(1) "Khand reaction"[2] or "Pauson-Khand reaction".[3]

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(8) Results quoted in ref 2 (Scheme I).

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Table I. Intramolecular Reaction of Allyl(propargyl)malonate (Reaction 1)

promoter	solvent	temp (°C)	time (h)	yield (%) 2	3
Me_3NO	CH_2Cl_2	20	3	90[a]	0
Me_3NO	CH_2Cl_2	0	2	81[a]	2
none	CH_2Cl_2	40	36	25[b]	2
DMSO (1 equiv)[c]	CH_2Cl_2	40	4	85	1
DMSO (2 equiv)	CH_2Cl_2	40	4	84	2
DMSO (3 equiv)	CH_2Cl_2	40	4	83	3
DMSO (3 equiv)	C_6H_6	40	24	92	0
(−)-(Tol)SOMe (3 equiv)	C_6H_6	40	20	90[d]	0
(−)-(Tol)SOMe (1.5 equiv)	C_6H_6	40	24	75[d,e]	0

[a] From ref 5; included here for yield comparison only. The mechanism of Me_3NO and R_2SO promotion is different (cf. footnote *e*). [b] 18% of unreacted cobalt complex was recovered. [c] All sulfoxide-promoted reactions were conducted in air. [d] 0% ee. [e] 95% of the sulfoxide was recovered.

Table II. Reaction of $(RC_2H)Co_2(CO)_6$ with Allyl Alcohol (Reaction 2)

R	promoter	solvent	temp (°C)	time (h)	product ratio 4:5	tot. yield of 4 + 5 (%)
Ph	Me_3NO	CH_2Cl_2/pet.[a]	0	2	2:1	65[b,c]
Ph	DMSO[d]	CH_2Cl_2	40	5	1:2.6	30
Ph	DMSO[d]	C_6H_6	60	24	1:1.2	63
H	$Me_3NO \cdot 2H_2O$	CH_2Cl_2	20	24	3.2:1	74
n-C_5H_{11}	$Me_3NO \cdot 2H_2O$	C_6H_6	20	24	1.9:1	42
n-C_5H_{11}	NMO[e]	CH_2Cl_2	20	24	1.7:1	43

[a] Promoter in CH_2Cl_2 was added to the cobalt complex in light petroleum ether (see Experimental Section). [b] From ref 5. [c] The mixed products have been obtained in up to 85% yield under similar conditions; NMR spectra suggest somewhat greater (2.5–3) ratios of 4:5 in these mixtures; possibly 4 is more likely to be lost by dehydration during chromatographic separation than 5. [d] In air. [e] *N*-methylmorpholine *N*-oxide.

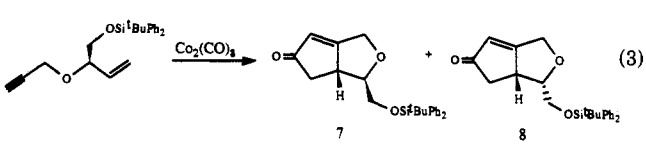
Table III. Cyclization Reaction 3

promoter	solvent	temp (°C)	time (h)	product ratio isomers 7:8	tot. yield of 7 + 8 (%)
silica gel[a]	none	50	3	>20:1[b]	28
none	C_6H_6	80	20	>20:1[b]	8[c]
Me_3NO (4 equiv)	CH_2Cl_2	20	4	4:1	73
DMSO (3 equiv)[d]	CH_2Cl_2	40	12	1.5:1	37
DMSO (3 equiv)[d]	C_6H_6	45	72	5:1	67
DMSO[d]	DMSO	20	120	7:1	54

[a] Adsorbent; solid phase reaction. [b] Isomer 8 was not detected. [c] A complex mixture of products is formed; the starting material appears to be unstable under these conditions. [d] In air.

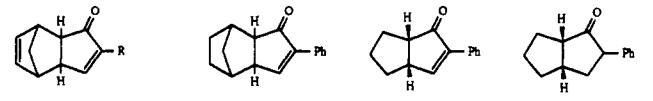
hexacarbonyldicobalt with allyl tetrahydropyranyl ether in benzene, dibutyl ether, and petroleum.

Hardly less striking are the changes in stereoselectivity found in the intramolecular reaction 3 under different



7 8 (3)

conditions (Table III). The formation of relatively minor amounts of endo-isomers of the products **9** and **10** in reactions of norbornadiene, previously noted for the

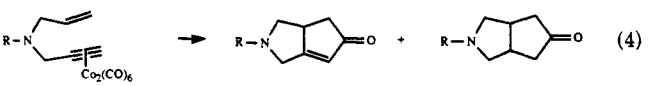


9 R = Ph
10 R = $CH_2CH_2CH_2OH$

11 12 13

Me_3NO method[5] (but not found under thermal conditions[9]), is again found with sulfoxides as promoters (Table IV) but follows no obvious pattern. When DMSO is replaced by (−)-methyl-*p*-tolylsulfoxide, no asymmetric induction is observed (Tables I and IV).

The reaction of cyclopentene with (phenylacetylene)-hexacarbonyldicobalt, which gives a single product, **12**, was then chosen to compare a series of solvent systems and obtain the results in Table V. Ethyl formate and acetate were included because of previous experience of their efficacy in promoting CO replacement from $Cr(CO)_6$.[10] Although all the polar addends tried had a promoting effect, neither these esters nor acetone matched DMSO in the yield attained. Both acetonitrile and methanol on the other hand, while requiring longer reaction times, give comparable or slightly better yields and, in this particular example, somewhat cleaner reactions. As Table V shows, these conclusions relate primarily to dichloromethane solutions of the promoters; when, in place of this, chloroform was used as the major solvent, the product contained variable but substantial amounts of the corresponding saturated ketone, **13** (while in the case of $CH_3CN/CHCl_3$ the combined yield was actually the highest found). That this type of reduction can be dominant, especially under solid-phase conditions, had previously been observed[11] in the case of substrate **14a**. Using Me_3NO-promoted reaction of the related tosylate, **14b**, formation of saturated ketone **16b** had still been significant under argon but was avoided by using an oxygen atmosphere.[5] It is therefore noteworthy that with Me_2SO promotion the (benzyloxy)carbonyl derivative **14c** gave only the cyclopentenone **15c** (eq 4).



14 a R = Ac
b R = Ts
c R = $PhCH_2OCO$

15 16 (4)

Experimental Section

Below are given typical procedures for the reactions collected in Tables I–V, followed by properties of new compounds. Octacarbonyldicobalt (5–10% hexane stabilized) was used as purchased.

Reaction 1 Using DMSO in Benzene (Table I). To a stirred solution of diethyl allyl(propargyl)malonate (0.33 g, 1.4 mmol) in benzene (10 mL) was added octacarbonyldicobalt (0.53 g, 1.55 mmol); after 2 h stirring at room temperature TLC indicated complete consumption of the starting ester. Dimethyl sulfoxide (0.30 mL, 3.0 equiv) was then added and the mixture stirred in air at 40 °C for 1 day. Chromatography of the resulting solution on a short column of silica gel, eluting with hexane/ethyl acetate (1:1), separated metal complexes and DMSO from the product **2**, which was further purified by flash chromatography, eluting

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(10) Hudecek, M.; Gajda, V.; Toma, S. *J. Organomet. Chem.* **1991**, *413*, 155.
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Table IV. Sulfoxide-Promoted Cycloadditions of (Alkyne)hexacarbonyldicobalt with Norbornene (C_7H_{10}) and Norbornadiene (C_7H_8)

alkyne	alkene	promoter[a]	time (h)	product	yield (%)	ratio exo:endo[b]
PhC_2H	C_7H_{10}	DMSO (1.5 equiv)	24	**11**	93	
PhC_2H	C_7H_{10}	(–)-TolSOMe (1.7 equiv)	24	**11**	100[c]	
PhC_2H	C_7H_8	DMSO (1.5 equiv)	48	**9**	94	93:7
PhC_2H	C_7H_8	DMSO (1.5 equiv)[d]	48	**9**	85	94:6
PhC_2H	C_7H_8	(–)-TolSOMe (1.7 equiv)	24	**9**	90[c]	86:14
$HC_2(CH_2)_3OH$	C_7H_8	DMSO (1.5 equiv)	36	**10**	90	94:6

[a] All in C_6H_6 at 40 °C in air (unless otherwise noted). [b] Only exo-isomer was obtained from norbornene. [c] Products obtained using (–)-TsSOMe showed no optical rotation. [d] Under nitrogen.

Table V. Solvent-Promoted Cycloaddition of (Phenylacetylene)hexacarbonyldicobalt with Cyclopentene (in Air)

			yield (%)		
promoter[a]	solvent	time	ketone **12**	ketone **13**[b]	Co complex[c]
DMSO	CH_2Cl_2	9 h	70.5		1.8
AcOEt	CH_2Cl_2	14 h	58.2		13
AcOEt	CH_2Cl_2	6 d	54		
HCOOEt	CH_2Cl_2	4 d	77		22.6
HCOOEt	$CHCl_3$	21 h	71	11.8	16.4
Me_2CO	CH_2Cl_2	6 d	65.3		
Me_2CO	Me_2CO	5 d	63.5	4.4	1.0
MeCN	CH_2Cl_2	48 h	70		~27
MeCN	CH_2Cl_2	7 d	81		2.1
MeCN	$CHCl_3$	16 h	66.8	22	
MeCN[d]	$CHCl_3$	23 h	64	21	
MeCN	ClCH=CHCl	16 h	35		
MeCN	Me_2CO	4 d	61	trace	4
MeCN	MeCN	16 h	51.3		
MeCN	THF	24 h	53		
MeCN	petrol[e]	20 h	46		
MeOH	CH_2Cl_2	3 d	75.4		10.4
MeOH	$CHCl_3$	40 h	29.4	35.5	34.2
MeOH	Et_2O	64 h	68	4.7	8

[a] 10 equiv unless otherwise noted. [b] If detected. [c] Unreacted $(PhC_2H)Co_2(CO)_6$ recovered. [d] 1 equiv. [e] Light petroleum ether, bp 60–72 °C.

with hexane/ethyl acetate (4:1), to give a colorless oil (0.34 g, 92%); no saturated ketone **3** was obtained by this procedure.

Reaction 2 (R = Ph) Using Anhydrous Me_3NO (Table II). Hexacarbonyl(phenylacetylene)dicobalt (0.677/g, 1.75 mmol) and allyl alcohol (1.19 mL, 10 equiv) in light petroleum ether (10 mL) were cooled to 0 °C and placed in a slow stream of oxygen. Trimethylamine *N*-oxide (390 mg, 3 equiv) in dichloromethane (5 mL) was added over 20 min. The reaction mixture was stirred at 0 °C for a further 10 min and then allowed to warm to room temperature and stirred for 1 h. More *N*-oxide (2 equiv) was added all at once and stirring continued for 20 min. Flash chromatography on silica, eluting with chloroform/methanol, permitted separation of 5-(hydroxymethyl)-2-phenylcyclopent-2-en-1-one (**4**, R = Ph) (144 mg) from the 4-hydroxymethyl isomer **5** (R = Ph) (68 mg).

Reaction 3 Using DMSO (Table III). To a stirred solution of ether **6** (0.59 g, 1.6 mmol) in dichloromethane (20 mL) was added octacarbonyldicobalt (0.64 g, 1.87 mmol); after CO evolution ceased the solution was concentrated under reduced pressure, DMSO (6 mL) was added, and the mixture was stirred for 120 h at room temperature. Initial chromatography on a short silica gel column, eluting with hexane/ethyl acetate (1:1), was used to remove metal complexes and DMSO; further chromatography on silica, eluting with hexane/ethyl acetate (5:1), then separated the stereoisomeric ketones **7** (297 mg) and **8** (43 mg) (54% total yield).

DMSO-Promoted Formation of Ketones 9 (Table IV). Octacarbonyldicobalt (0.40 g, 1.17 mmol) was added to a solution of phenylacetylene (0.10 g, 1 mmol) in benzene (7 mL), and the mixture was stirred at room temperature for 1 h. Norbornadiene (0.54 mL, 5 mmol) and DMSO (0.21 mL, 3.0 mmol) were then added, and the mixture was stirred in air at 40 °C for 2 d and then concentrated and chromatographed on a short column of silica gel, eluting with hexane/ethyl acetate (1:1), to separate the products from metal complexes and DMSO. Isomer separation was then achieved by flash chromatography, eluting with hexane/ethyl acetate (40:1).

Methanol-Promoted Synthesis of Ketone 12 (Table V). Octacarbonyldicobalt (0.873 g, 2.55 mmol) was placed under nitrogen in a 100-mL flask fitted with a reflux condenser and magnetic stirrer. Phenylacetylene (0.29 mL, 2.68 mmol) dissolved in dichloromethane (30 mL) was then added, and the mixture was stirred for 30 min to effect complexation. The nitrogen supply was now disconnected, cyclopentene (2.24 mL, 25.5 mmol) and methanol (1.03 mL, 25.5 mmol) were added, and the mixture was refluxed vigorously for 3 d. After filtration through silica, the resultant solution was evaporated to dryness and the residue flash chromatographed on silica. Hexane eluted unreacted hexacarbonyl(phenylacetylene)dicobalt (104 mg, 10.4%) and hexane/ethyl acetate (10:1) then eluted the ketone **12** (381.4 mg, 75.4%) identical with an authentic sample.[6]

Formation of Ketone 15c. To a solution of *N*-((benzyloxy)carbonyl)-*N*-allylpropargylamine (146 mg, 0.637 mmol) in benzene was added octacarbonyldicobalt (250 mg, 5–10% hexane stabilized, 0.73 mmol) in one portion. The mixture was stirred at room temperature for 2 h, and then DMSO (0.13 mL, 3 equiv) was introduced. This mixture was heated at 40 °C for 36 h. The usual workup gave the ketone **15** (105 mg, 64%).

Characteristics of Individual Products. Compound 2. R_f (hexane/ethyl acetate, 3:1): 0.21. IR (film): ν_{max} 1720 (br, s), 1670 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.95 (1 H, t, J = 1.75 Hz), 4.18–4.29 (4H, m), 3.22–3.39 (2H, m), 3.07–3.14 (1H, m), 2.80 (1H, dd, J = 12.7 Hz, 7.5 Hz), 2.64 (1H, dd, J = 18.96 Hz, 6.29 Hz), 2.14 (1H, dd, J = 18.96 Hz, 3.30 Hz), 1.74 (1H, t, J = 12.7 Hz), 1.24–1.31 (6H, m). ^{13}C NMR ($CDCl_3$): δ 209.12, 185.30, 171.12, 170.42, 125.22, 61.85, 61.71, 60.53, 44.75, 44.70, 41.84, 38.61, 34.85, 13.76. MS (m/e): found, 266.1162; calcd for $C_{14}H_{18}O_5$ (M^+), 266.1154.

Compound 3. R_f (hexane/ethyl acetate, 3:1): 0.29. IR (film): ν_{max} 1730 (s) cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 4.21 (2H, q, J = 17.7 Hz), 4.18 (2H, q, J = 17.7 Hz), 1.95–2.80 (10H, m), 1.27 (3H, t, J = 17.7 Hz), 1.24 (3H, t, J = 17.7 Hz). ^{13}C NMR ($CDCl_3$): δ 171.65, 171.55, 61.48, 61.37, 61.34, 43.61, 40.30, 39.12, 13.81. MS (m/e): found, 268.1318; calcd for $C_{14}H_{20}O_5$ (M^+), 268.1311.

5-(Hydroxymethyl)cyclopent-2-en-1-one (4; R = H). This product had NMR peaks in broad agreement with literature values.[12]

4-(Hydroxymethyl)cyclopent-2-en-1-one (5, R = H). ^1H NMR ($CDCl_3$): δ 7.70 (1H, dd, J = 5.7 Hz, 2.5 Hz, H-3), 6.265 (1H, dd, J = 5.7 Hz, 2 Hz, H-2), 3.75 (3H, m, CH_2OH), 3.20 (1H, m, H-4), 2.52 (1H, dd, J = 19 Hz, 6.5 Hz, H-5), 2.18 (1H, dd, J = 19 Hz, 2.3 Hz, H-5′).

5-(Hydroxymethyl)-2-phenylcyclopent-2-en-1-one (4; R = Ph). R_f (hexane/ethyl acetate, 1:1): 0.21. IR (film): ν_{max} 3700–3100 (br), 1690 (s), 1620 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.85 (1H, t, J = 2.9 Hz, H-3), 7.64–7.70 (2H, m) and 7.26–7.43 (3H, m, Ph), 3.98 (1H, dd, J = 10 Hz, 5 Hz) and 3.82 (1H, dd, J = 10 Hz, CH_2OH), 2.4–3.0 (4H, m, $CHCH_2$ and OH). ^{13}C NMR ($CDCl_3$): δ 207.18, 159.02, 142.76, 131.17, 128.36, 128.30, 128.25, 127.00, 126.85, 62.50, 48.30, 29.94. MS (m/e): found, 188.0867; calcd for $C_{12}H_{12}O_2$ (M^+), 188.0837.

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4-(Hydroxymethyl)-2-phenylcyclopent-2-en-1-one (5; R = Ph). R_f (hexane/ethyl acetate, 1:1): 0.15. IR (film): 3600–3100 (br), 1690 (s), 1620 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.79 (1H, d, J = 2.75 Hz, H-3), 7.66–7.72 (2H, m) and 7.26–7.43 (3H, m, Ph), 3.69–3.85 (2H, m, CH_2OH), 3.10–3.22 (1H, m, H-4), 2.72 (1H, dd, J = 18.8 Hz, 6.56 Hz) and 2.38 (1 H, dd, J = 18.8 Hz, 2.44 Hz, H-5), 1.77–1.95 (1H, br, OH). ^{13}C NMR ($CDCl_3$): δ 207.18, 159.69, 143.86, 131.05, 128.44, 128.27, 128.26, 126.99, 126.98, 64.45, 41.01, 39.22. MS (*m/e*): found, 188.0835; calcd for $C_{12}H_{12}O_2$ (M^+), 188.0837.

Ketone 7. R_f (hexane/ethyl acetate, 5:1): 0.13. IR (film): ν_{max} 1710 (s), 1645 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.65–7.70 (4H, m), 7.26–7.45 (6H, m), 6.60 (1H, s), 4.72 (1H, d, J = 15.8 Hz), 4.58 (1H, d, J = 15.8 Hz), 3.89 (1H, dd, J = 10.0 Hz, 4.34 Hz), 3.85 (1H, dd, J = 10.0 Hz, 5.17 Hz), 3.54–3.60 (1H, m), 3.17 (1H, br), 2.59 (1H, dd, J = 17.9 Hz, 6.42 Hz), 2.17 (1H, dd, J = 17.9 Hz, 3.43 Hz), 1.07 (9H, s). ^{13}C NMR ($CDCl_3$): δ 209.26, 184.19, 133.56, 135.51, 133.04, 129.82, 127.75, 124.59, 83.08, 66.05, 64.79, 47.65, 39.49, 26.76, 19.21. MS (*m/e*): found, 335.1099; calcd for $C_{20}H_{19}O_3Si$ ($M^+ - C_4H_9$), 335.1098.

Compound 8. R_f (hexane/ethyl acetate, 5:1): 0.06. IR (film): ν_{max} 1710 (s), 1650 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 7.64–7.72 (4H, m), 7.15–7.24 (6H, m), 5.65 (1H, s), 4.26 (1H, d, J = 15 Hz), 4.10 (1H, d, J = 15 Hz), 3.54 (1H, dd, J = 11.42 Hz, 4.54 Hz), 3.24 (1H, dd, J = 11.42 Hz, 2.44 Hz), 2.67–2.74 (1H, m), 2.36 (1H, dd, J = 17.37 Hz, 4.27 Hz), 2.22 (1H, dd, J = 17.37 Hz, 6.56 Hz), 1.02 (9H, s). ^{13}C NMR (C_6D_6): δ 207.72, 183.17, 135.88, 133.15, 133.09, 130.17, 130.07, 128.17, 128.14, 122.75, 77.80, 66.01, 64.59, 47.05, 38.59, 26.72, 19.04. MS (*m/e*): found, 335.1097; calcd for $C_{20}H_{19}O_3Si$ ($M^+ - C_4H_9$), 335.1098.

Compound 15 (Mixture of Two Rotamers). R_f (hexane/ethyl acetate, 1:1) 0.3. IR (film): 1700 (br, s), 1650 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.28–7.38 (5H, m), 6.10 (0.5H, s), 6.07 (0.5H, s), 5.17 (2H, s), 4.08–4.41 (3H, m), 3.28 (1H, br), 2.89–2.97 (1H, m), 2.60–2.70 (1H, m), 2.13–2.23 (1H, m). ^{13}C NMR ($CDCl_3$): δ 207.49, 207.45, 179.54, 179.03, 153.90, 153.93, 127.86, 127.42, 127.22, 125.09, 125.04, 66.36, 49.93, 46.02, 45.75, 43.22, 42.51, 39.61, 39.56, 39.55. MS (*m/e*): found, 257.1093; calcd for $C_{15}H_{15}NO_3$ (M^+), 257.1052.

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