

Formation of Heterocyclic Compounds from 1,3-Diazabuta-1,3-diene Derivatives

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N-Trimethylsilyl(diphenylmethylene)amine gives quantitatively various open-chain 1,3-diazabutadienes (V) by coupling with benzimidoyl chlorides. The 1,3-diazabutadienes react with isocyanates, diphenylketen, diketen (4-methyleneoxetan-2-one), and dimethyl acetylenedicarboxylate to give the 3,4-dihydro-1,3,5-triazin-2(1*H*)-ones (VI), the azetidinone (VIII), the dihydro-1,3-oxazinones (XII), and the pyrimidinone (XIV), respectively.

1,4-CYCLOADDITION reactions of heteradienes would be expected to be applicable to the synthesis of heterocyclic compounds containing two or more heteroatoms. Although many examples of dienes containing two nitrogen atoms are reported^{1,2} there are few reports of the 1,3-di-

azabuta-1,3-diene (N=C-N=C) system.³ One clear case of cycloaddition of the N=C-N=C linkage, in the formamidine derivatives (I), is reported, in which one C=N bond is part of a heterocyclic ring.⁴

We have reported that the 1 : 1 insertion product (II),

¹ M. Lora-Tamayo and J. L. Soto, '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 179.

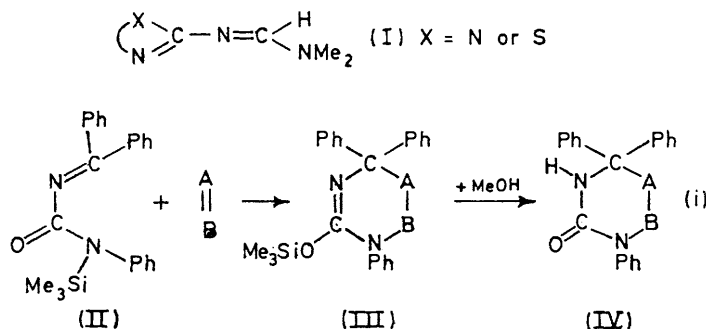
² W. Bartman, *Chem. Ber.*, 1967, **100**, 2938.

³ C. Grundmann, G. Weisse, and S. Seide, *Annalen*, 1952, **577**, 77.

⁴ R. Richter and H. Ulrich, *Chem. Ber.*, 1970, **103**, 3525.

obtained in the reaction of *N*-trimethylsilyl(diphenylmethylene)amine with phenyl isocyanate, behaves as a synthetic equivalent of the N=C-N=C system in that its reaction with the dienophile A=B gave the formal 1,4-cycloaddition product (III).^{5,6} In this paper a simplified method for preparing 1,3-diazabutadienes and their

butadienes (V) with 1 equiv. of isocyanate in benzene, the dihydrotriazinones (VI) were obtained in good yield as a result of [4 + 2] cycloaddition. The presence of an excess of isocyanate did not give any 2 : 1 cycloadduct, such as has been reported.² The 1,3,5-triazinone structure (VI) was confirmed by the i.r. spectrum (C=O and



cycloadditions to give four- or six-membered heterocycles, depending on the dienophiles, are described.

RESULTS AND DISCUSSION

Preparation of 1,3-Diazabutadienes.—The reaction of *N*-trimethylsilyl(diphenylmethylene)amine with 1 equiv. of benzimidoyl chloride in benzene gave quantitatively

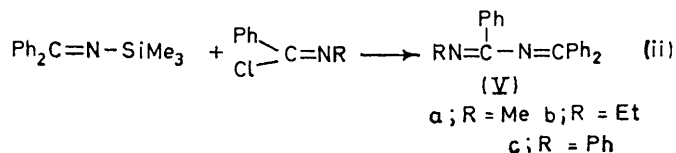
C=N stretching bands at 1 672—1 700 and 1 630—1 642 cm^{-1} , respectively). A 1 : 1 cycloadduct of the 1,3-diazetidione type from [2 + 2] addition of isocyanate with either C=N bond would show a C=O stretching band above 1 750 cm^{-1} . On the other hand, triazinone derivatives obtained from the reactions of isocyanates with 2 equiv. of imine have C=O stretching bands at *ca.* 1 670

TABLE I
Results of [4 + 2] cycloadditions

Product	R	R'	Conditions	Yields (%)	Recryst. solvents	M.p. (°C)	τ (CDCl ₃)	$\nu_{\text{max.}}$ /cm ⁻¹ (KBr)
(VIa)	Me	Ph	C ₆ H ₆ , reflux, 34 h	90	MeOH	188—190	6.98 (3 H, s)	1 686 (C:O), 1 640 (C:N)
(VIb)	Et	Ph	C ₆ H ₆ , reflux, 30 h	100	EtOH	193.5—195	9.37 (3 H, t) 6.36 (2 H, q)	1 672 (C:O), 1 630 (C:N)
(VIc)	Ph	Ph	C ₆ H ₆ , reflux, 25 h	85	MeOH	199—201		1 692 (C:O), 1 641 (C:N)
(VI d)	Me	Me	C ₆ H ₆ , 95 °C, ^a 180 h	68	MeOH	182.5—183.5	7.25 (3 H, s) 7.06 (3 H, s)	1 688 (C:O), 1 640 (C:N)
(VIe)	Ph	Me	CH ₂ Cl ₂ , 45 °C, ^a 173 h	78	MeOH	213.5—215	7.21 (3 H, s)	1 700 (C:O), 1 642 (C:N)

^a In a sealed tube.

the benzimidine derivatives (V), with elimination of trimethylsilyl chloride. The same products (Va and c) were obtained from the reaction of diphenylmethyleneamine with benzimidoyl chloride in the presence of triethylamine or 1,8-diazabicyclo[5.4.0]undec-7-ene as acceptor of the hydrogen chloride generated. However use of *N*-trimethylsilyl(diphenylmethylene)amine has the following advantages: (a) no need for a hydrogen chloride acceptor; (b) isolation of (V) from the reaction

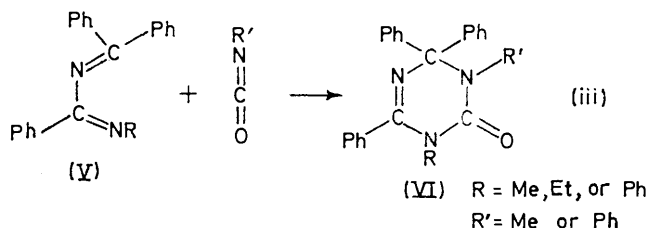


mixture before carrying out cycloadditions is unnecessary; and (c) the yield is higher.

[4 + 2] Cycloaddition.—In the reactions of the diaza-

⁵ I. Matsuda, K. Itoh, and Y. Ishii, *J.C.S. Perkin I*, 1972, 678.

cm^{-1} .⁷ Although compounds (V) behaved as a hetero-1,3-diene toward isocyanates, they were less reactive than



the analogues (I) because of the absence of the electron-donating dimethylamino-group. This suggests that the first step in the cyclization is nucleophilic attack of the terminal imino-nitrogen atom at the central isocyanate carbon atom. The results are summarized in Table I.

[2 + 2] Cycloaddition.—The reaction of compound

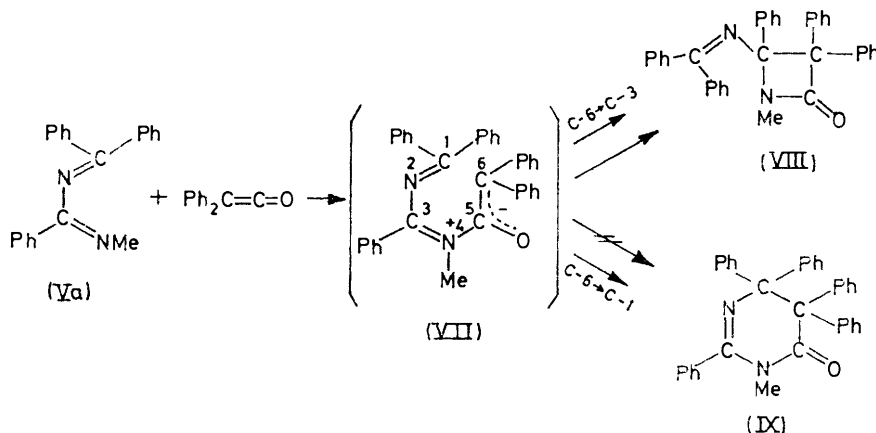
⁶ I. Matsuda, S. Yamamoto, and Y. Ishii, preceding paper.

⁷ J. P. Chupp and E. R. Weiss, *J. Org. Chem.*, 1967, **33**, 2357.

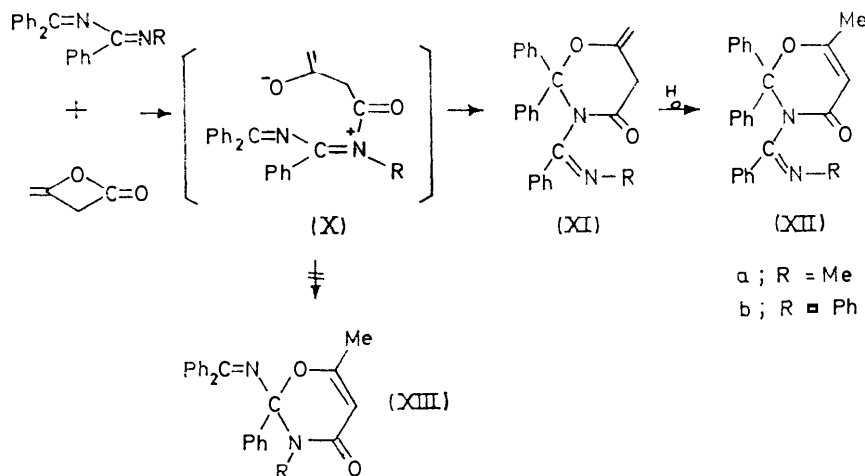
(Va) with 1 equiv. of diphenylketen proceeded smoothly at room temperature to give the azetidinone (VIII) quantitatively. The i.r. spectrum showed the presence of a β -lactam ($\nu_{\text{C=O}}$ 1746 cm^{-1}) and a C=N double bond (1648 cm^{-1}). The unusual high-field proton resonance of the *N*-methyl protons (τ 8.39) could be caused by the diamagnetic anisotropy of the phenyl rings in the diphenylmethyleneamino-group. The formation of the dihydropyrimidinone (IX) would be expected by analogy

excludes the possibility of the 1,3-oxazinone structure (XIII) which might be expected to be formed through the zwitterionic intermediate (X). The appearance of the ions $M^+ - (\text{MeN}=\text{CPh} + \text{H})$ (m/e 263) and $263 - \text{NCO}$ (m/e 221) indicates the presence of a pendant *N*-methylbenzimidoyl group.

The reaction path may be deduced from the structure of the product. Initial nucleophilic attack of the terminal nitrogen atom of (V) on the carbonyl carbon atom



SCHEME 1



SCHEME 2

with the reactions with isocyanates. The difference between the reactions may be explained by steric factors: nucleophilic attack of C-6 at C-1 to form (IX) would be inhibited by the four phenyl substituents.

Reactions of Diketen (4-Methyleneoxetan-2-one).—A different type of heterocyclic compound, a 1,3-oxazinone (XII), was obtained in the reaction of the heteradienes (V) with 1 equiv. of diketen. The n.m.r. spectra of (XIIa and b) showed C-methyl (τ 8.51 and 8.46) and vinyl proton (τ 5.32 and 5.17) signals consistent with the assigned structure.^{8,9} The mass spectrum of (XIIa)

of diketen to give the zwitterionic intermediate (X) is presumably followed by cyclization involving attack at the carbonyl carbon atom of (X) (Scheme 2). The reaction resembles that of the urea (II) with diketen, which is initiated by nucleophilic attack of the amino-nitrogen atom of the urea on the carbonyl carbon atom of diketen.⁶

Reaction of the Heteradiene (Vc) with Dimethyl Acetylenedicarboxylate.—The reaction of (Vc) with 1 equiv. of dimethyl acetylenedicarboxylate was carried out in ethanol with the aim of effecting a pyrimidine synthesis by a [4 + 2] cycloaddition. Two products, the pyrimi-

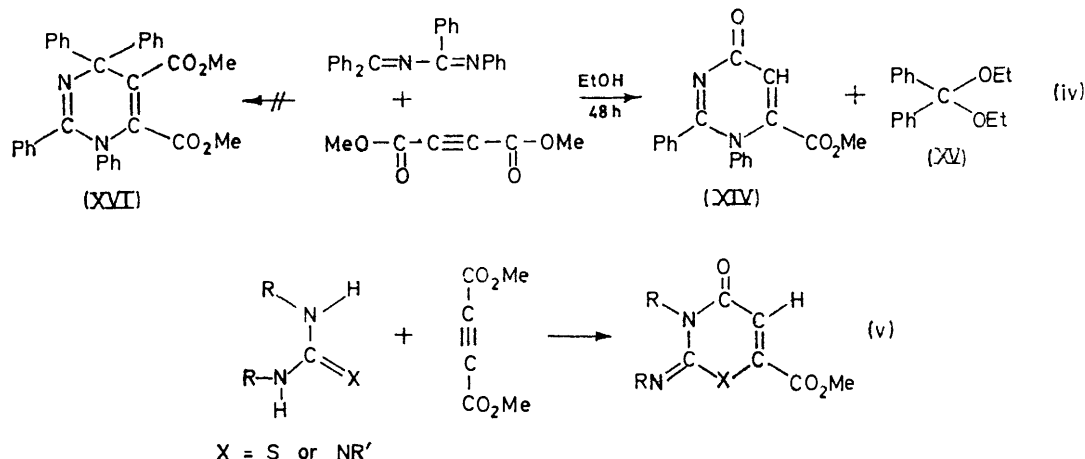
⁸ T. Kato and H. Sakamoto, *Yakugaku Zasshi*, 1967, **87**, 1322.

⁹ H. Suzuki, I. Matsuda, K. Itoh, and Y. Ishii, *Bull. Chem. Soc. Japan*, 1974, **47**, 2736.

dinone (XIV) and benzophenone diethyl acetal (XV), were obtained, but not the expected pyrimidine (XVI). The structure of (XIV) was determined by elemental analysis and i.r., n.m.r., and mass spectral data. The

EXPERIMENTAL

I.r., n.m.r., u.v., and mass spectra were recorded with JASCA IR-403G and IR-S, JEOL C-60HL, Hitachi 124, and JEOL JMS-01SG instruments, respectively. *N*-Trimethyl-



presence of an *O*-methyl group (τ 6.40), a vinyl proton (τ 3.37), and two phenyl groups (τ ca. 2.83) was confirmed by the n.m.r. spectrum. Elemental analysis suggested the formula $C_{18}H_{14}N_2O_3$, consistent with the molecular ion peak at m/e 306. Other diagnostic fragment ions were $M^+ - PhCN$ (m/e 203) $203 - CO$ (m/e 175), and $175 - OMe$ (m/e 144). The acetal (XV) was identified by comparison (i.r. and n.m.r. spectra) with an authentic sample. The formation of both products involves, formally, a novel [3 + 3] cyclization with elimination of a diphenylmethylene and

silyl(diphenylmethylene)amine⁵ and diphenylketen¹² were prepared according to the literature. All reactions were carried out under nitrogen. Analyses are summarized in Table 2.

Preparation of 1,3-Diazabutadienes.—(i) *N*-Diphenylmethylene-*N'*-methylbenzimidine (Va). A solution of *N*-methylbenzimidoyl chloride (0.38 g, 2.47 mmol) and *N*-trimethylsilyl(diphenylmethylene)amine (0.63 g, 2.47 mmol) in benzene (4 ml) was heated for 24 h under reflux. The mixture was evaporated under reduced pressure and the residue was washed with diethyl ether. The amidine (Va) was filtered off (0.74 g, quantitative) and gave pale yellow

TABLE 2
Analyses

Compd.	Formula	Found (%)			Reqd. (%)		
		C	H	N	C	H	N
(Va)	$C_{21}H_{18}N_2$	84.4	6.15	9.4	84.55	6.1	9.4
(Vb)	$C_{22}H_{20}N_2$	84.7	6.65	8.85	84.6	6.45	8.95
(Vc)	$C_{26}H_{20}N_2$	86.9	5.8	7.85	86.65	5.6	7.75
(VIa)	$C_{26}H_{23}N_3O$	80.45	5.7	10.05	80.55	5.55	10.05
(VIb)	$C_{29}H_{25}N_3O$	80.95	6.05	9.65	80.7	5.85	9.75
(VIc)	$C_{33}H_{25}N_3O$	82.55	5.4	8.75	82.65	5.25	8.75
(VIId)	$C_{23}H_{21}N_3O$	77.75	5.7	11.85	77.7	5.95	11.8
(VIe)	$C_{26}H_{23}N_3O$	80.7	5.45	10.05	80.55	5.55	10.05
(VIII)	$C_{35}H_{28}N_2O$	85.45	6.0	5.55	85.35	5.75	5.75
(XIIa)	$C_{25}H_{22}N_2O_2$	78.4	5.6	7.5	78.5	5.8	7.3
(XIIb)	$C_{30}H_{24}N_2O_2$	80.7	5.75	6.25	81.05	5.45	6.3
(XIV)	$C_{18}H_{14}N_2O_3$	70.8	4.8	9.05	70.6	4.6	9.15

a methoxy-group. Similar elimination of a methoxy-group from dimethyl acetylenedicarboxylate to give cyclic compounds has been reported in the condensation of thiourea and guanidine derivatives with dimethyl acetylenedicarboxylate [reactions (v)].^{10,11} The reaction (iv) thus has good precedent.

¹⁰ J. W. Lown and J. C. N. Ma, *Canad. J. Chem.*, 1967, **45**, 939.

¹¹ J. W. Lown and J. C. N. Ma, *Canad. J. Chem.*, 1967, **45**, 953.

needles on recrystallization from ethanol-*n*-hexane (3 : 1), m.p. 135–136 °C, ν_{max} (KBr) 1 627s and 1 614s cm^{-1} (C:N), τ (CDCl₃) 7.20 (3 H, s, NMe) and 2.3–2.8 (15 H, m, 3 Ph).

When a solution of diphenylmethylenamine (1.36 g, 7.48 mmol), *N*-methylbenzimidoyl chloride (1.13 g, 7.35 mmol), and triethylamine (1.41 g, 15.4 mmol) was refluxed for 5 h, crude (Va) (1.64 g, 73%) was also obtained after the removal of triethylamine hydrochloride and evaporation.

¹² E. C. Taylor, A. McKillop, and G. H. Hawks, *Org. Synth.*, 1972, **52**, 36.

(ii) *N-Diphenylmethylene-N'-ethylbenzamidine* (Vb). Similarly compound (Vb) was obtained quantitatively from *N*-ethylbenzimidoyl chloride (1.03 g, 6.12 mmol) and *N*-trimethylsilyl(diphenylmethylene)amine (1.65 g, 6.50 mmol) in benzene (5 ml), as pale yellow *needles*, m.p. 126.5—127.5 °C (from 90% aqueous ethanol), ν_{\max} (KBr) 1 623s and 1 606s cm^{-1} (C:N), τ (CDCl₃) 8.85 (3 H, t, Me, *J* 7.0 Hz), 6.81 (2 H, q, CH₂, *J* 7.0 Hz), and 2.3—2.9 (15 H, m, 3 Ph).

(iii) *N-Diphenylmethylene-N'-phenylbenzamidine* (Vc). Compound (Vc) was obtained quantitatively by the same treatment from *N*-phenylbenzimidoyl chloride (0.37 g, 1.71 mmol) and *N*-trimethylsilyl(diphenylmethylene)amine (0.46 g, 1.79 mmol) in benzene (5 ml), as yellow *needles*, m.p. 142—143 °C (from ethanol), ν_{\max} (KBr) 1 625s and 1 609s cm^{-1} (C:N).

When a solution of diphenylmethyleneamine (2.66 g, 14.7 mmol), *N*-phenylbenzimidoyl chloride (2.75 g, 12.8 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.11 g, 15.3 mmol) in benzene was refluxed for 3 h, crude (Vc) (2.78 g, 60%) was also obtained (after removal of DBU hydrochloride and evaporation).

[4 + 2] *Cycloadditions*.—A typical procedure is described for the heteradiene (Va). Results and reaction conditions are summarized in Table 1. A solution of (Va) (1.36 g, 4.56 mmol) and phenyl isocyanate (0.59 g, 5.01 mmol) in benzene (5 ml) was heated under reflux. After 36 h the benzene was evaporated off under reduced pressure and the residue was washed with diethyl ether. Crude 3,4-dihydro-1-methyl-3,4,4,6-tetraphenyl-1,3,5-triazin-2(1H)-one (VIa) was filtered off (1.71 g, 90%); it crystallized from methanol as a white powder.

Reaction of Diphenylketen with the Heteradiene (Va).—A solution of *N*-methylbenzimidoyl chloride (0.42 g, 2.32 mmol) and *N*-trimethylsilyl(diphenylmethylene)amine (0.62 g, 2.45 mmol) in benzene (3 ml) was heated for 20 h under reflux. Methylene chloride (4 ml) and diphenylketen (0.38 g, 2.00 mmol) were added, and the mixture was kept for 24 h at room temperature. The solvent was evaporated off under reduced pressure and the residue was washed with ether. Recrystallization from chloroform-*n*-hexane (1 : 2) gave prisms of 4-diphenylmethyleneamino-1-methyl-3,3,4-triphenylazetidin-2-one (VIII) (82%), m.p. 156—157 °C, λ_{\max} (EtOH) 250 nm (log ϵ 4.93), ν_{\max} (KBr) 1 746s (C:O) and

1 648m cm^{-1} (C:N), τ (CDCl₃) 8.39 (3 H, s, NMe) and 2.3—3.2 (25 H, m, 5 Ph).

Reactions of Diketen with the Heteradienes (V).—(i) 2,3-Dihydro-6-methyl-3-(*N*-methylbenzimidoyl)-2,2-diphenyl-1,3-oxazin-4-one (XIIa). A solution of *N*-methylbenzimidoyl chloride (0.41 g, 2.66 mmol) and *N*-trimethylsilyl(diphenylmethylene)amine (0.69 g, 2.72 mmol) in benzene was refluxed for 20 h. After evaporation, the residue was dissolved in methylene chloride (2 ml) and diketen (0.19 g, 2.32 mmol) was added. The mixture was heated for 19 h at 90—100 °C in a sealed tube. Evaporation, washing with diethyl ether, and recrystallization from methylene chloride-hexane gave the *oxazinone* (0.58 g, 65%) as white needles m.p. 261—262 °C, ν_{\max} (KBr) 1 710s and 1 686s (C:O) and 1 640s cm^{-1} (C:N), τ (CDCl₃) 8.51 (3 H, s, CMe), 7.15 (3 H, s, C=CH), and 2.3—2.8 (15 H, m, 3 Ph).

(ii) 2,3-Dihydro-6-methyl-2,2-diphenyl-3-(*N*-phenylbenzimidoyl)-1,3-oxazin-4-one (XIIb). An analogous procedure with diketen (0.13 g, 1.54 mmol) and (Vc) [obtained *in situ* from *N*-phenylbenzimidoyl chloride (0.74 g, 2.18 mmol) and *N*-trimethylsilyl(diphenylmethylene)amine (0.56 g, 2.22 mmol) in benzene], gave the *oxazinone* (XIIb) (0.39 g, 57%) as white needles, m.p. 170—172 °C (from ethanol), ν_{\max} (KBr) 1 706s and 1 700s (C:O) and 1 648s cm^{-1} (C:N), τ (CDCl₃) 8.46 (3 H, s, CMe), 5.17 (1 H, s, C=CH), and 2.3—3.2 (20 H, m, 4 Ph).

Reaction of Dimethyl Acetylenedicarboxylate with the Heteradiene (Vb).—An ethanolic solution (20 ml) of (Vb) (0.25 g, 0.69 mmol) and dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was heated for 48 h under reflux. The ethanol was evaporated off under reduced pressure. The residue was washed with diethyl ether and the product was filtered off and recrystallized from benzene-*n*-hexane (1 : 2) to give pale yellow *needles* (49%), m.p. 162—163 °C, ν_{\max} (KBr) 1 752s and 1 656s cm^{-1} (C:O), τ (CDCl₃) 6.40 (3 H, s, OMe), 3.37 (1 H, s, C=CH), and 2.7—3.1 (20 H, m, 4 Ph). Benzophenone diethyl acetal (0.09 g, 53%) was obtained from the filtrate by evaporation and washing the residue with 50% aqueous ethanol, as white needles, m.p. 51—52 °C (from 2 : 1 ethanol-water), τ (CDCl₃) 8.86 (6 H, t, CMe), 6.75 (4 H, q, OCH₂), and 2.4—2.9 (10 H, m, 2 Ph).

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