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Acetylene cyclopropanation by CH_2I_2–Et_3Al reagent

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Abstract

The one-step method for a synthesis of 1,1,2-trialkyl- and 1,1,2,2-tetraalkylsubstituted cyclopropanes from mono- and dialkylsubstituted acetylenes, CH_2I_2 and Et_3Al was developed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Simmons–Smith reaction is known to be suitable and widely used in laboratory practice method for cyclopropanation of olefins and their derivatives [1]. However, with respect to acetylene compounds the method was not developed properly, since terminal acetylenes give products of CH_2 group introduction on terminal C–H bond [2], and disubstituted acetylenes undergo rearrangements [3,4]. Later the modification of the Simmons–Smith reaction with the use of organoaluminium reagents was developed [5], that was found to be sufficiently efficient to olefins, but acetylene reactability was not studied. We have supposed the failures in acetylene cyclopropanation were caused by metal nature, activating CH_2I_2, and thus we have studied the acetylene reactions with CH_2I_2 in the presence of Et_3Al.

2. Results and discussion

The preliminary experiments showed mono- and dialkylsubstituted acetylenes reacted with CH_2I_2, and Et_3Al under mild conditions (20–25 °C) to give 1,1,2-trialkyl and 1,1,2,2-tetraalkylsubstituted cyclopropanes (compound **1**), respectively in average yields (Table 1; Scheme 1).

Mass-spectrometry and element analysis show the presence of cycle or double bond in compounds **1a**–**e**. However, signals of double bond were not observed by NMR spectroscopy. At the same time there are signals in strong field in ^{1}H-NMR spectra (-0.01–0.7 ppm) that evidences the presence of cyclopropane fragment in **1a**–**e**. Moreover, in ^{13}C-NMR spectra signals due to cyclopropane ring carbons show coupling constants $^1J_{CH}$ ca. 155 Hz and those in alkyl groups ca. 125 Hz [6]. The assignments in ^{13}C-NMR spectra were based on the additive scheme [7] and with the use of (Insensitive Nuclei Enhanced by Polarization Transfer) INEPT technique (Fig. 1).

Decyne-5 cyclopropanation proceeds not stereoselectively to give two stereoisomers of **1a** compound in 1:1 ratio. Octyne-4 cyclopropanation proceeds similarly. A reaction of terminal acetylenes (heptyne-1, hexyne-1) with CH_2I_2 and Et_3Al leads to stereoselective formation of trisubstituted cyclopropanes (**1d**,**e**). The above reaction proceeds with octyne-2 to give one stereoisomer in the same way, that evidences a steric control of the reaction stereochemistry. The physical methods used by us did not allow to determine a stereoconfiguration of tri- and tetrasubstituted cyclopropanes.

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Table 1
Acetylene cyclopropanation by CH_2I_2–Et_3Al reagent

Entry	Acetylene	Solvent	Reagent ratio [Alkyne]–CH_2I_2–Et_3Al	Reaction time, h	Product	Yield, %
1	Decyne-5	Hexane	1:2:4	18	**1a**	58
2	Octyne-4	Hexane	1:2:4	18	**1b**	52
3	Octyne-2	Hexane	1:2:4	18	**1c**	55
4	Heptyne-1	Hexane	1:2:3	8	**1d**	43
5	Heptyne-1	Dichloromethane	1:1:1	18	**2d**	46
6	Hexyne-1	Hexane	1:2:3	8	**1e**	49
7	Phenylacetylene	Dichloromethane	1:1:1	18	**2f**	38

A structure of the products was stated to depend on a reagent ratio and a solvent nature. In a ratio of heptyne-1–CH_2I_2–Et_3Al = 1:2:3 trisubstituted cyclopropane **1c** is the main product of the reaction (Entry 4). In equimolar ratio of reagents heptyne-1 gives 1-amyl-1-propylcyclopropane (**2d**) (Entry 5) together with the compound **1d** in sufficient amount (**2d**:**1d** = 5:3 at 60% acetylene conversion degree). The analogous formation of 1-alkyl(phenyl)-1-propylcyclopropanes is observed for the other terminal acetylenes, in the case of phenylacetylene 1-phenyl-1-propylcyclopropane (**2f**) is the main reaction product (Entry 7).

On the basis of experimental data we have proposed a scheme of the reaction course (Scheme 2). A generation of diethyl(iodomethyl)aluminium [8] is the initial step of the reaction, the latter is able to carboaluminate acetylene to give iodocontaining alkenylalane. A subsequent reaction way depends on reagents ratio and an acetylene reactability. Scheme 2 demonstrates a stereoconfiguration of cyclopropane **1** is determinated at the step of Et_2AlI elimination from dialuminium compound, and a formation of either one or two stereoisomers may occur in dependence on a nature of substitutents in initial acetylene.

$$CH_2I_2 + Et_3Al \rightarrow Et_2AlCH_2I + EtI$$

According to Scheme 2, the acetylene carboalumination by diethyl(iodomethyl)aluminium is one of the key steps of the reaction. Cp_2ZrCl_2 is known to be effective acetylene carboalumination catalyst [9]. Under the reaction conditions in the presence of catalytic amounts of Cp_2ZrCl_2 phenyl- and allylcontaining acetylenes react with Et_3Al to give 2,3-disubstituted aluminacyclopent-2-enes, that shows a proceeding of the reaction of acetylene cycloalumination found by us previously [10,11]. However, a reaction of mono- and dialkylsubstituted acetylenes with Et_3Al and CH_2I_2 is not effected by the presence of a catalyst.

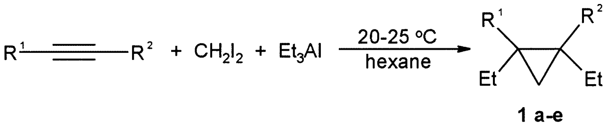
Thus, we have studied for the first time a reaction of cyclopropanation of mono- and disubstituted acetylenes by CH_2I_2–Et_3Al reagent. The effective one-step method for cyclopropanation of mono- and dialkylsubstituted acetylenes to tri- and tetraalkylsubstituted cyclopropanes was developed.

3. Experimental

Commercial 95% Et_3Al (Redkinskii pilot-production plant), starting acetylenes and CH_2I_2 were used.

All reactions were carried out under dry argon atmosphere. Solvents were dried and freshly distilled before use. The reaction products were analyzed using chromatograph 'Carlo Erba' (glass capillary column 'Ultra-1' (Hewlett-Packard), 25 m × 0.2 mm, flame-ionization detector, working temperature 50–170 °C, gas-carrier–helium). Mass spectral measurements were performed on Finnigan 4021 gas chromatograph–mass spectrometer at 70 eV and mass data were tabulated as m/z. ^1H and ^{13}C spectra were recorded as $CDCl_3$ solutions on spectrometers 'JEOL FX-90Q' (22.5 MHz for ^{13}C and 90 MHz for ^1H) and 'Bruker AM-300' (75 MHz for ^{13}C and 300 MHz for ^1H). TMS, C_6D_6 and $CDCl_3$ were used as internal standard. ^{13}C-NMR spectra were recorded on 'JEOL FX-90Q' using complete proton-decoupled mode and with the use of INEPT technique. Partially proton-decoupled mode was used on 'Bruker AM-300' for ^{13}C-NMR. Quoted yields were obtained after distillation.

General procedure for synthesis of 1,2-dialkyl-1,2-diethylcyclopropanes: a 100 ml three-necked-flask equipped with magnetic stirrer was charged with CH_2Cl_2 (50 ml) and Et_3Al (40 mmol) at 0 °C under dry argon atmosphere. Disubstituted acetylene (10 mmol) and CH_2I_2 (20 mmol) consequentially were dropwise added and the reaction mixture was stirred for 15 min at 0 °C. The reaction mixture was allowed to warm to room temperature (r.t.) and was stirred for 18 h. Then the reaction was quenched with 10% water solution of HCl. The layers were separated and the (aq.) layer was extracted with diethyl ether. The combined organic



1 a-e

a: R^1= n-C_4H_9, R^2= n-C_4H_9; **b**: R^1= n-C_3H_7, R^2= n-C_3H_7; **c**: R^1= n-C_5H_{11}, R^2= CH_3; **d**: R^1= n-C_5H_{11}, R^2= H; **e**: R^1= n-C_4H_9, R^2= H

Scheme 1.

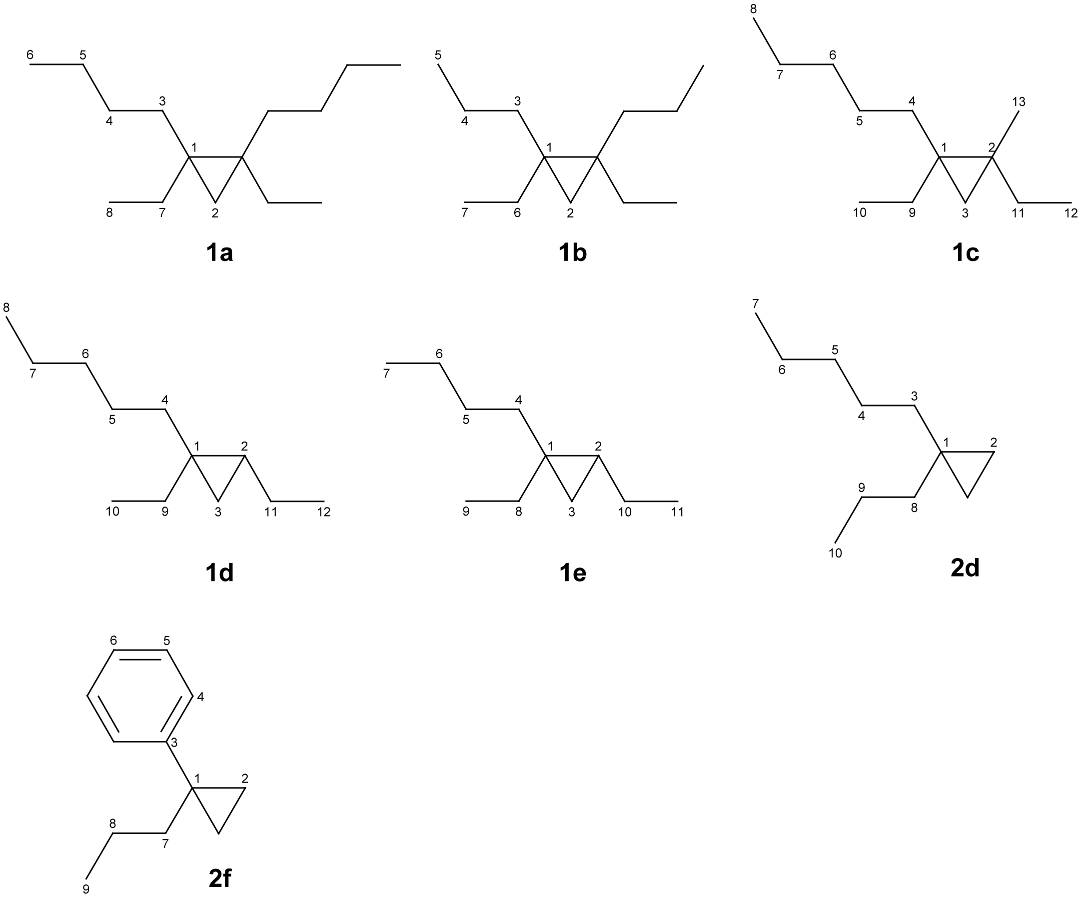


Fig. 1. Indexing of atoms in ^{13}C and ^{1}H-NMR spectral data of **1a**–**e** and **2d**,**f**.

extracts were washed with water (50 ml), sat. aq. NaCl (20 ml), dried over $CaCl_2$ and filtered. After evaporation of solvents the crude product was purified by vacuum distillation.

1,2-Di(*n*-butyl)-1,2-diethylcyclopropane (**1a**). bp. 102 °C/5 Torr. Anal. Found: C, 85.31; H, 14.56. $C_{15}H_{30}$ Calc.: C, 85.63; H, 14.37%. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 30.04 (s, C(1)), 24.27 (t, $^{1}J_{CH} = 155.6$ Hz, C(2)), 30.72 C 30.77 (t, $^{1}J_{CH} = 124.1$ Hz, C(3)), 29.24 (t, $^{1}J_{CH} = 125.4$ Hz, C(4)), 23.30 (t, $^{1}J_{CH} = 125.4$ Hz, C(5)), 14.22 (q, $^{1}J_{CH} = 124.4$ Hz, C(6)), 24.27 (t, $^{1}J_{CH} = 126.1$ Hz, C(7)), 11.18 (q, $^{1}J_{CH} = 125.0$ Hz, C(8)). ^{1}H-NMR ($CDCl_3/C_6D_6$, 300 MHz): δ 0.68–1.10 (m, 14H, C(2)H_2, C(6,8)H_3), 1.17–1.53 (m, 16H, C(3–5,7)H_2). EIMS *m*/*z* (relative intensity): 210 (M^+, 5), 181 (M^+-C_2H_5, 39), 153 (M^+-C_4H_9, 39), 125 (12), 111 (21), 97 (60), 83 (54), 69 (100).

1,2-Di(*n*-propyl)-1,2-diethylcyclopropane (**1b**). bp. 83 °C/10 Torr. Anal. Found: C, 85.79; H, 14.25. $C_{13}H_{26}$ Calc.: C, 85.63; H, 14.37%. ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 30.02 (s, C(1)), 24.43 (t, C(2)), 33.47 C 33.60 (t, C(3)), 20.20 (t, C(4)), 14.74 (t, C(5)), 24.43 (t, C(6)), 11.29 (q, C(7)). ^{1}H-NMR ($CDCl_3/C_6D_6$, 90 MHz): δ 0.73–1.00 (m, 14H, C(2)H_2, C(5,7)H_3), 1.05–1.48 (m, 12H, C(3,4,6)H_2). EIMS *m*/*z* (relative intensity): 182 (M^+, 5), 153 (M^+-C_2H_5, 41), 139(M^+-C_3H_7, 45), 97 (10), 83 (28).

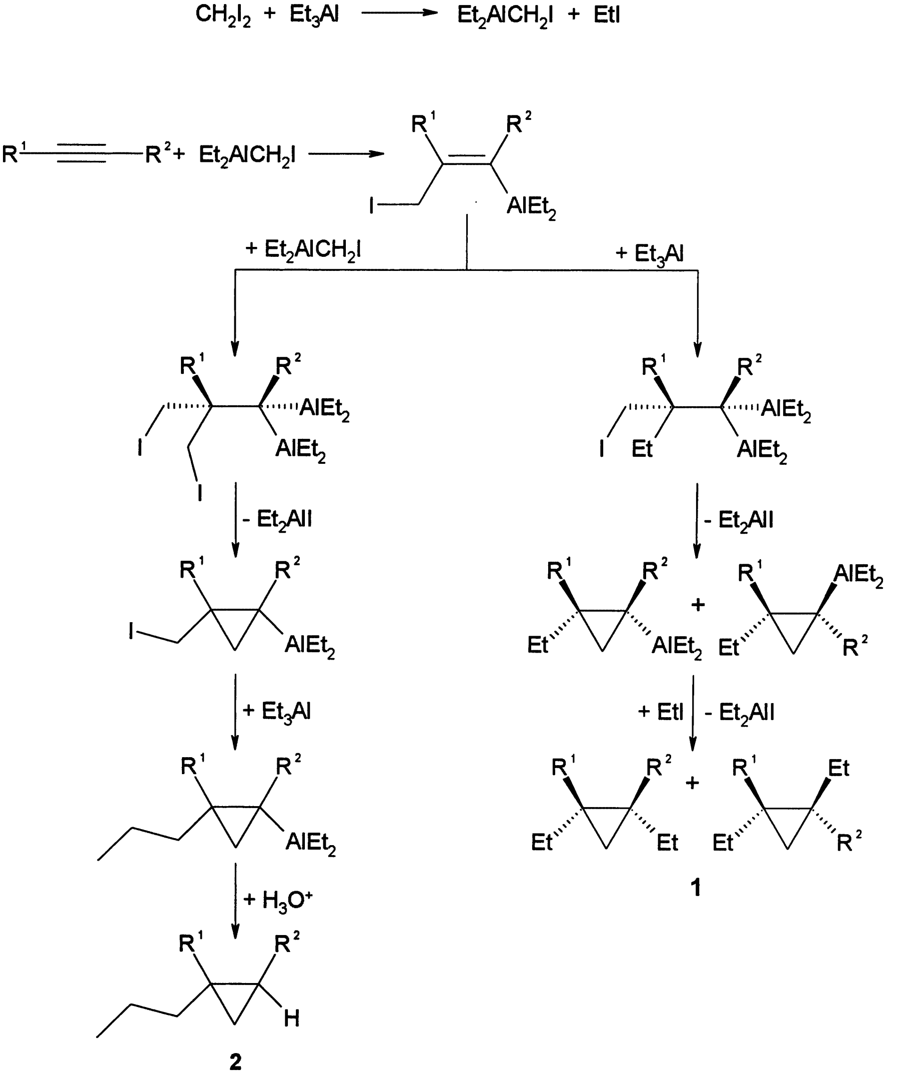
1-(*n*-Amyl)-2-methyl-1,2-diethylcyclopropane (**1c**). bp. 86 °C/12 Torr. Anal. Found: C, 85.47; H, 14.39. $C_{13}H_{26}$ Calc.: C, 85.63; H, 14.37%. ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 29.56 (s, C(1)), 25.73 (s, C(2)), 25.08 (t, C(3)), 29.04 (t, C(4)), 26.90 (t, C(5)), 32.68 (t, C(6)), 22.93 (t, C(7)), 14.22 (q, C(8)), 30.80 (t, C(9)), 11.49 (q, C(10)), 34.38 (t, C(11)), 11.36 (q, C(12)), 18.96 (q, C(13)). ^{1}H-NMR ($CDCl_3/C_6D_6$, 90 MHz): δ −0.07–0.06 (m, 2H, C(3)H_2), 0.61–0.98 (m, 9H, C(8,10,12)H_3), 1.02 (s, 3H, C(13)H_3), 1.06–1.47 (m, 12H, C(4–7,9,11)H_2). EIMS *m*/*z* (relative intensity): 182 (M^+, 5), 153 (M^+-C_2H_5, 23), 111 (M^+-C_5H_{11}, 33), 97 (24), 83 (62), 69 (95), 55 (100).

General procedure for synthesis of 1-alkyl-1,2-diethylcyclopropanes: a 100 ml three-necked-flask equipped with magnetic stirrer was charged with CH_2Cl_2 (50 ml) and Et_3Al (30 mmol) at 0 °C under dry argon atmosphere. Terminal acetylene (10 mmol) and CH_2I_2 (20 mmol) consequentially were dropwise added and the reaction mixture was stirred for 15 min at 0 °C. The reaction mixture was allowed to warm to r.t. and was stirred for 8 h. Then the reaction was quenched with 10% water solution of HCl. The layers were separated and the (aq.) layer was extracted with diethyl ether. The combined organic extracts were washed with water (50 ml), sat. aq. NaCl (20 ml), dried over $CaCl_2$ and filtered. After evaporation of solvents the crude product was purified by vacuum distillation.

1-(*n*-Amyl)-1,2-diethylcyclopropane (**1d**). bp. 75 °C/10 Torr. Anal. Found: C, 85.42; H, 14.23. $C_{12}H_{24}$ Calc.: C, 85.63; H, 14.37%. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 24.82 (s, C(1)), 26.25 (d, $^1J_{CH} = 154.8$ Hz, C(2)), 18.31 (t, $^1J_{CH} = 156.3$ Hz, C(3)), 30.47 (t, $^1J_{CH} = 125.0$ Hz, C(4)), 26.64 (t, $^1J_{CH} = 126.5$ Hz, C(5)), 32.55 (t, $^1J_{CH} = 123.7$ Hz, C(6)), 22.54 (t, $^1J_{CH} = 125.0$ Hz, C(7)), 14.22 (q, $^1J_{CH} = 123.8$ Hz, C(8)), 29.82 (t, $^1J_{CH} = 125.4$ Hz, C(9)), 10.71 (t, $^1J_{CH} = 124.6$ Hz, C(10)), 22.87 (t, $^1J_{CH} = 125.7$ Hz, C(11)), 14.67 (q, $^1J_{CH} = 124.3$ Hz, C(12)). ^{1}H-NMR ($CDCl_3/C_6D_6$, 300 MHz): δ 0.18–0.42 (m, 3H, C(2)H, C(3)H_2), 0.85 (t, $^3J_{CH} = 4.9$ Hz, 6H, C(10,12)H_3), 0.97 (t, $^3J_{CH} = 6.8$ Hz, 3H, C(8)H_3), 1.07–1.50 (m, 12H, C(4–7,9,11)H_2). EIMS *m/z* (relative intensity): 168 (M^+, 4), 139 (M^+-C_2H_5, 3), 126 (3), 112 (11), 97 (M^+-C_5H_{11}, 41), 83 (39), 70 (52), 69 (67), 55 (100).

1-(*n*-Butyl)-1,2-diethylcyclopropane (**1e**). bp. 79 °C/25 Torr. Anal. Found: C, 85.51; H, 14.40. $C_{11}H_{22}$ Calc.: C, 85.63; H, 14.37%. ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 26.14 (s, C(1)), 29.13 (d, C(2)), 18.27 (t, C(3)), 29.46 (t, C(4)), 26.79 (t, C(5)), 23.28 (t, C(6)), 14.18 (q, C(7)), 30.37 (t, C(8)), 10.60 (q, C(9)), 22.44 (t, C(10)), 14.50 (q, C(11)). ^{1}H-NMR ($CDCl_3/C_6D_6$, 90 MHz): δ −0.16–0.35 (m, 3H, C(2)H, C(3)H_2), 0.68–1.02 (m, 9H, C(7,9,11)H_3), 1.14–1.49 (m, 10H, C(4–6,8,10)H_2). EIMS *m/z* (relative intensity): 154 (M^+, 6), 125 (M^+-C_2H_5, 3), 112 (14), 97 (M^+-C_4H_9, 17), 83 (24), 70 (36), 69 (79), 55 (100).

General procedure for synthesis of 1-alkyl(phenyl)-1-propylcyclopropanes: a 100 ml three-necked-flask equipped with magnetic stirrer was charged with CH_2Cl_2 (50 ml) and Et_3Al (10 mmol) at 0 °C under dry



Scheme 2.

argon atmosphere. Terminal acetylene (10 mmol) and CH_2I_2 (10 mmol) consequentially were dropwise added and the reaction mixture was stirred for 15 min at 0 °C. The reaction mixture was allowed to warm to r.t. and was stirred for 18 h. Then the reaction was quenched with 10% water solution of HCl. The layers were separated and the (aq.) layer was extracted with diethyl ether. The combined organic extracts were washed with water (50 ml), sat. aq. NaCl (20 ml), dried over $CaCl_2$ and filtered. After evaporation of solvents the crude product was purified by vacuum distillation.

1-(*n*-Amyl)-1-propylcyclopropane (**2d**). Bp. 68 °C/17 Torr. Anal. Found: C, 85.57; H, 14.21. $C_{11}H_{22}$ Calc.: C, 85.63; H, 14.37%. ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 19.29 (s, C(1)), 12.01 (t, C(2)), 36.13 (t, C(3)), 26.38 (t, C(4)), 32.36 (t, C(5)), 22.87 (t, C(6)), 14.22 (q, C(7)), 38.41 (t, C(8)), 19.87 (t, C(9)), 14.61 (q, C(10)). ^{1}H-NMR ($CDCl_3/C_6D_6$, 90 MHz): δ 0.13 (s, 4H, C(2)H_2), 0.83 (t, $^3J_{CH} = 6.2$ Hz, 6H, C(7,10)H_3), 1.02–1.39 (m, 12H, C(3–6,8,9)H_2). EIMS m/z (relative intensity): 154 (M^+, 1), 126 (2), 125 (2), 112 (6), 98 (19), 84 (24), 70 (67), 69 (68), 55 (100).

1-Phenyl-1-propylcyclopropane (**2f**). Bp. 83 °C/5 Torr. Anal. Found: C, 89.61; H, 9.92. $C_{12}H_{16}$ Calc.: C, 89.94; H, 10.06%. ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 25.79 (s, C(1)), 13.05 (t, C(2)), 145.64 (t, C(3)), 128.08 (t, C(4)), 129.06 (t, C(5)), 125.81 (t, C(6)), 42.83 (t, C(7)), 20.46 (t, C(8)), 14.35 (q, C(9)). ^{1}H-NMR ($CDCl_3$/TMS, 90 MHz): δ 0.60–1.04 (m, 7H, C(2)H_2, C(9)H_3), 1.07–1.66 (m, 4H, C(7,8)H_2), 7.02–7.49 (m, 5H, Ph). EIMS m/z (relative intensity): 160 (M^+, 17), 132 (10), 131 (21), 117 (100), 115 (29), 91 (31).

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