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ACETYLENE DIETHERS

DINEOPENTYLOXYETHYNE

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Abstract—Dineopentyloxyethyne has been synthesized from *trans*-2,3-dichloro-1,4-dioxane according to a general procedure already described. In contrast with alkyl neopentyloxyacetylenes, R-C≡C-O-CH_2Bu^t, which only polymerize when are strongly heated (> 150°), dineopentyloxyethyne is a kinetically unstable acetylene diether that polymerizes readily at room temperature. However, the compound has been trapped with $Co_2(CO)_8$ to give either the corresponding hexacarbonyl complex, m.p. 74–75°, or the cyclic trimer, m.p. 205–206°, depending upon the experimental conditions.

Di-t-butoxyethyne is the only stable acetylene diether reported which can be handled at room temperature for some days.[1] However, when it is heated at 70–80°, 2,3,4-tri-t-butoxy-3-cyclobuten-1-one is formed in quantitative yield.[2] This result can be rationalized assuming a thermolytic cleavage leading to isobutene together with an intermediate ketene, which reacts with the parent acetylene, by a [2+2]-cycloaddition, to afford the cyclobutenone as the final reaction product. Detailed investigations, performed with a large number of aliphatic acetylene monoethers,[3] have shown that thermolysis takes place through a concerted process involving an intramolecular H-shift, so that the higher the number of H atoms at the β-position the lower the temperature at which decomposition takes place. Accordingly, it is observed that whereas t-butoxyalkynes, R-C≡C-OBu^t, having nine β-H atoms, decompose very rapidly at 70–80°, the ethoxy derivative, with three β-H atoms, decomposes only at about 120°, and methoxy and neopentyloxyethyne which do not possess β-H atoms, are stable up to 150°, but polymerize when strongly heated (Table 1).[4]

Table 1. Thermal stability of R-C≡C-OR′

R′	Thermal decomposition	Polymerization
$-CH_3$	—	> 150°
$-C_2H_5$	120°	—
$-C(CH_3)_3$	70–80°	—
$-CH_2C(CH_3)_3$	—	> 150°

With the aim of having on our hands an acetylene diether that was both kinetically and thermally stable, in order to use it as a dienophile in thermally induced cycloadditions, we decided to synthesize dineopentyloxyethyne (**1**). For the synthesis we chose the method that involves *trans*-2,3-dichloro-1,4-dioxane (**2**) as the starting material.[1b]

As previously described for other members of the series, *trans*-2,3-dichloro-1,4-dioxane (**2**) was allowed to react, in the presence of solid K_2CO_3, with neopentyl alcohol to give a 60:40 mixture of *cis* and *trans*-2,3-dineopentyloxy-1,4-dioxane (**3**), in 80% yield.

Treatment of this mixture with 2,2-dihydro-2,2,2-trichloro-1,2,3-benzodioxaphosphole (**4**), in methylene dichloride, afforded in 80% yield a 55:45 mixture of *rac* and *meso*-1,2-dichloro-1,2-dienopentyloxyethane (**5**). Notice that, in contrast with all the other examples reported so far,[1b,5] here both acetal alkoxy groups are primary; however, as anticipated, only the cyclic and less hindered one was chemoselectively replaced by the Cl atom.

On the other hand, and in contrast too with other reported examples,[1b] the attack of **4** on **3** occurred in an intermolecular fashion, 1,2-dichloroethane being the only byproduct formed in the reaction.[5] From a general point of view, the course of the cleavage of 2,3-dialkoxy-1,4-dioxanes appears to depend on two factors: (i) the nature of the chlorinating agent (whereas PCl_5 favors the intramolecular attack, phosphole **4** favors the intermolecular one), and (ii) the steric bulk of the alkoxy substituents (the bulkier the substituents the higher the predominance of the intramolecular attack). As the result of these two factors, we have observed that whereas the cleavage of 2,3-di-t-butoxy-1,4-dioxane with PCl_5 occurs exclusively in an intramolecular manner,[5] the attack of **4** on 2,3-dineopentyloxy-1,4-dioxane (**3**) takes place exclusively in an intermolecular way.

Attempts to generate dineopentyloxyethyne (**1**) directly from *rac* and *meso*-1,2-dichloro-1,2-dineopentyloxyethane (**5**) by a double dehydrochlorination (first with $KOBu^t$ in hexane, and then $NaNH_2$ in liq NH_3) failed, the intermediate (*E*)-1-chloro-1,2-dineopentyloxyethene (*E*-**6**)† being recovered together with polymeric material. Better results were obtained performing, before dehydrochlorination, the so-called a "halogen-halogen interchange synthetic operation".[1b] For that, *rac* and *meso*-1,2-dichloro-1,2-dineopentyloxyethane (**5**) was dechlorinated with Mg in THF to give 65% yield of a mixture of (*Z*) and (*E*)-1,2-dineopentyloxyethene (**7**) which was brominated and then dehydrobrominated (first with $KOBu^t$ in pentane at 0° and then with $NaNH_2$ in liq NH_3/pentane). The experimental conditions are very cri-

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†Like the corresponding methoxy, ethoxy and isopropoxy derivatives,[6] 1-halogeno-1,2-dineopentyloxyethenes (**6** and **9**) show great sensitivity to atmospheric oxygen to give neopentyl halogenoneopentyloxyacetates.

tical, but using threefold excess of $NaNH_2$ in liq NH_3, in the presence of pentane as a co-solvent, and a reaction time of 10 min, dineopentyloxyethyne (**1**) was obtained in 46% yield (from **7**) as a pentane solution.

Dienopentyloxyethyne is not so stable as expected: it is even kinetically somewhat less stable than diisopropoxyethyne,[1] probably due to the fact that there are two α-H atoms and the activated triple bond is not so efficiently protected as in the case of di-t-butoxyethyne.[1] However, the product could be detected by NMR spectroscopy ($t_{1/2} \simeq 15$ min, at 37°), and trapped with octacarbonyl dicobalt. In the presence of an excess of reagent the corresponding hexacarbonyl dicobalt complex (**10**), m.p. 74–75°, was isolated in 2.2% yield; catalytic amounts, on the other hand, induces cyclotrimerization to hexaneopentyloxybenzene (**11**), m.p. 205–206°.

In fact, the thermal stability of dineopentyloxyethyne towards polymerization, when compared with the corresponding stability of other acetylene diethers ($Bu^tO{-}C{\equiv}C{-}Bu^t \gg Pr^iO{-}C{\equiv}C{-}OPr^i \simeq Bu^tCH_2O{-}C{\equiv}C{-}OCH_2{-}Bu^t > EtO{-}C{\equiv}C{-}OEt > MeO{-}C{\equiv}C{-}OMe$) correlates well, in a qualitative way, with Charton's ν steric parameters based on effective Van der Waals radii for the corresponding alkoxy groups (Bu^tO:1.22, Pr^iO:0.75, Bu^tCH_2O:0.70, EtO:0.48 and MeO:0.36).[7]

EXPERIMENTAL

M.ps are uncorrected, and were determined on a Kofler microscope, unless otherwise stated. IR spectra were recorded with a Pye Unicam SP1100 spectrometer, and NMR spectra with a Perkin–Elmer spectrometer, model R-24 (the values are given in ppm, δ scale, using TMS as internal reference). MS were recorded with a Hewlett-Packard 5930A mass spectrometer (high resolution with a VG updated MS 902S).

2,3-*Dineopentyloxy*-1,4-*dioxane* 3

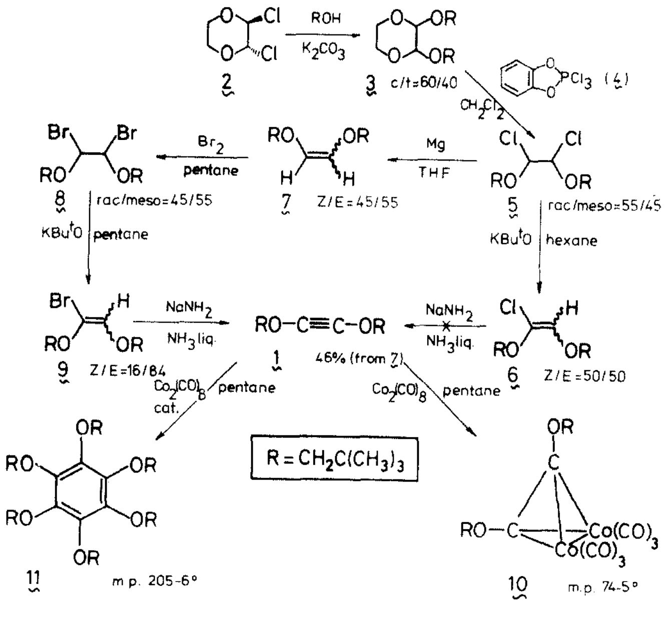
To a 250 ml, 3-necked flask, equipped with mechanical stirring and reflux condenser with $CaCl_2$-tube, 7.85 g (5×10^{-2} mole) *trans*-2,3-dichloro-1,4-dioxane, 44.0 g (5×10^{-1} mole) neopentyl alcohol (Aldrich) and 27.6 g (2×10^{-1} mole) K_2CO_3, freshly activated at 250° for 3 hr, were added. The mixture was stirred and heated at 85° for 20 hr, cooled, added onto 100 ml CH_2Cl_2 in a separatory funnel and treated with a few ml H_2O (just to dissolve the inorganic salts). The organic layer was separated, dried with Na_2SO_4 and solvent removed under vacuum at room temp. Unreacted neopentyl alcohol was distilled off through a 30 cm Vigreux column and residue distilled at 78–80°/0.5 torr, to give 13.0 g (80% yield) of a 60/40 mixture of *cis* and *trans*-2-3-dineopentyloxy-1,4-dioxane. The *trans* isomer partially crystalyzes on standing. Complete isomeric separation can be readily achieved by column chromatography on neutral alumina, eluting with hexane-ether mixtures of increasing polarity.

Trans (less polar isomer), m.p. 60–61°. NMR (CCl_4): 4.22 (s) (2H); 3.96–3.20 (m, AA'BB') (4H); 3.42 (d, J = 9.0 Hz) (2H); 2.97 (d, J = 9.0 Hz) (2H); 0.93 (s) (18H). IR (CCl_4): 2960, 2910, 2875, 1365, 1275, 1150, 1125, 1075, 1055, 1040, 975, 900 and 865 cm^{-1}. (Found: C, 64.36; H, 10.95. Calc. for $C_{14}H_{28}O_4$: C, 64.58; H, 10.84%).

Cis (more polar isomer), m.p. 32–33°. NMR (CCl_4): 4.32 (s) (2H); 3.96–3.20 (m, AA'BB') (4H); 3.37 (d, J = 9.0 Hz) (2H); 2.95 (d, J = 9.0 Hz) (2H); 0.93 (s) (18H). IR (CCl_4): 2960, 2910, 2875, 1485, 1390, 1365, 1350, 1320, 1280, 1255, 1225, 1180, 1090, 1020, 980, 915 and 885 cm^{-1}.

1,2-*Dichloro*-1,2-*dineopentyloxyethane* 5

To a 250 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel with $CaCl_2$-tube, 18.3 g (7.6×10^{-2} mole) **4** and 50 ml CH_2Cl_2 were introduced, the soln cooled with chilly water and a soln of 8.5 g (3.27×10^{-2} mole) 2,3-dineopentyloxy-1,4-dioxane in 20 ml CH_2Cl_2 was added dropwise. The mixture was stirred at room temp for 15 hr, and the solvent removed under vacuum. Hexane (75 ml) was added to the residue and the soln cooled at −15° for some hr. The mother liquid was poured out from crystallized 2-chloro-2,2-dihydro-1,3,2-benzodioxaphosphate, more hexane was added and the whole process repeated four times. The combined organic extracts were cooled at −15° for some hr and the soln was poured out from the crystals once again. In this way, after removing the hexane under vacuum, a mixture of *rac* and *meso*-1,2-dichloro-1,2-dineopentyloxyethane, contaminated with *ca.* 20% of 2-chloro-2,2-dihydro-1,3,2-benzodioxaphosphate, was obtained which was already suitable for the next step. However, analytic material could be prepared by treating the crude product, in 60 ml THF, with 2.4 g (1×10^{-1} mole) of Mg at 40° for 2 hr (under these conditions Mg becomes deactivated and only the by-product is attacked—see below, preparation of 1,2-dineopentyloxyethene **7**). After conventional working-up, 7.5 g (80% yield) of a 55/45 mixture of *rac* and *meso*-1,2-dichloro-1,2-dineopentyloxyethane were obtained. The *meso* isomer partially crystallizes on standing and may be separated by filtration.



Mixture of *rac* and *meso*, NMR (CCl_4): 5.48 (s) (2H) *rac*; 5.42 (s) (2H) *meso*; 3.37 (d, J = 8 Hz) (2H *rac* + 2H *meso*); 3.11 (d, J = 8 Hz) (2H *rac* + 2H *meso*); 0.93 (s) (18H *rac* + 18H *meso*). IR (film): 2980, 2930, 2890, 1490, 1415, 1395, 1375, 1355, 1310, 1230, 1210, 1160, 1125, 1070 and 990 cm^{-1}.

Meso, m.p. 69–71°. NMR (CCl_4): 5.42 (s) (2H); 3.57 (d, J = 8 Hz) (2H); 3.11 (d, J = 8 Hz) (2H); 0.93 (s) (18H). IR (CCl_4): 2930, 2880, 2840, 1465, 1395, 1355, 1290, 1210, 1190, 1135, 970 and 930 cm^{-1}. (Found: C, 53.26; H, 9.11. Calc. for $C_{12}H_{24}Cl_2O_2$: C, 53.14; H, 8.92%).

1-*Chloro*-1,2-*dineopentyloxyethene* **6**

In a 100 ml flask, equipped with magnetic stirring and a Liebig condenser with $CaCl_2$-tube, a soln of *rac* and *meso*-1,2-dichloro-1,2-dineopentyloxyethane (*rac*/*meso* = 55/45), contaminated with 20% 2-chloro-2,2-dihydro-1,3,2-benzodiaxaphosphate, prepared from 2.21 g (8.5×10^{-3} mole) 2,3-dineopentyloxy-1,4-dioxane (see preceeding procedure), was introduced and 1.90 g (1.7×10^{-2} mole) of $KOBu^t$ were slowly added in small portions through the condenser. The mixture was stirred at room temp for 3 hr and then treated with enough H_2O to dissolve all the inorganic salts. The organic layer was separated, dried over Na_2SO_4 and the solvent removed under vacuum. The residue was distilled at 55°/0.05 torr to give 0.95 g (48% overall yield from **3**) of (*Z*) and (*E*)-1-chloro-1,2-dienopentyloxyethene (*Z*/*E* = 50/50).

The *E* isomer could be obtained in an isomerically pure form by selective attack of $NaNH_2$ on the *Z* isomer.

Mixture of *Z* and *E*, NMR (CCl_4): 6.10 (s) (1H) *Z*; 5.60 (s) (1H) *E*; 3.45 (s) (2H) *E*; 3.35 (s) (2H) *Z*; 3.32 (s) (2H *Z* + 2H *E*); 0.93 (s, broad) (18H *Z* + 18H *E*).

E isomer, NMR (CCl_4): 5.60 (s) (1H); 3.45 (s) (2H); 3.32 (s) (2H); 0.96 (s) (9H); 0.92 (s) (9H). IR (film): 2950, 2900, 2860, 1685, 1480, 1400, 1380, 1365, 1325, 1220, 1160, 1090, 1050, 1010 and 810 cm^{-1}. (Found: C, 61.54; H, 10.01; Cl, 15.13. Calc. for $C_{12}H_{23}ClO_2$: C, 61.39; H, 9.87; Cl, 15.10%).

1,2-*Dineopentyloxyethene* **7**

A 250 ml, 3-necked flask, equipped with magnetic stirring, condenser, a pressure-equalized dropping funnel, an inlet tube for N_2 and an immersion thermometer, was carefully dried with an IR lamp under dry N_2, and 2.43 g (1×10^{-1} mole) Mg and 15 ml anh THF were added. The mixture was heated at 50° by means of the IR lamp, and 0.1–0.2 ml 1,2-dibromoethane was added under stirring. Once the reaction ensued, a soln of 7.40 g (2.7×10^{-2} mole) *rac* + *meso*-1,2-dichloro-1,2-dineopentyloxyethane in 50 ml anh THF was added dropwise in a 30 min period, the inside temp being controlled at about 55° by a water bath. After the total addition, further heating for 2 hr was provided, the bath was then removed and stirring continued until the mixture reached room temp. 50 ml ether were added and then a soln of 20 g of NH_4Cl in 50 ml H_2O. The mixture was stirred for a few min and filtered through a sintered glass filter; 50 ml hexane were added to facilitate the separation of the two layers, the organic one washed with 50 ml aq K_2CO_3 and dried over Na_2SO_4.

The solvents were removed *in vacuo* and the residue distilled at high vacuum, the following fractions being collected: (a) 33°/0.15 torr, 3.2 g (*Z*/*E* = 45/55). (b) 30°/0.06 torr, 0.2 g (*Z*/*E* = 19/81). The total yield was 65%, and the *E* isomer crystallized from the second fraction.

Mixture of *Z* and *E*, NMR (CCl_4): 6.13 (s) (2H) *E*; 5.10 (s) (2H) *Z*; 3.30 (s) (4H) *Z*; 3.13 (s) (4H) *E*; 0.92 (s) (18H *Z* + 18H *E*). IR (film): 2960, 2905, 2880, 1480, 1390, 1370, 1225, 1190, 1160, 1130, 1070 and 810 cm^{-1}.

E isomer, m.p. 32–33°. NMR (CCl_4): 6.13 (s) (2H); 3.13 (s) (4H); 0.92 (s) (18H). IR (KBr): 2960, 2910, 2880, 1480, 1370, 1190, 1160, 865 cm^{-1}. (Found: C, 71.69; H, 12.42. Calc. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.07%).

Dineopentyloxyethyne **1**

(a) *Bromination of* 1,2-*dineopentyloxyethene* (**7**→**8**). In a 50 ml flask, equipped with magnetic stirring, a pressure-equalized dropping funnel and a $CaCl_2$-tube, a soln of 2.2 g (1.1×10^{-2} mole) (*Z*) and (*E*)-1,2-dineopentyloxyethene (*Z*/*E* = 45/55), in 35 ml pentane, was introduced. The soln was cooled at 0° and Br_2 added until the color persisted (*ca.* 0.56 ml = 1.1×10^{-2} mole). An aliquot was evaporated to give a mixture of *rac* and *meso*-1,2-dibromo-1,2-dineopentyloxyethane; NMR (CCl_4): 5.96 (s) (2H) *rac*; 5.92 (s) (2H) *meso*; 3.56 (d, J = 10 Hz) (2H *rac* + 2H *meso*); 3.15 (d, J = 10 Hz) (2H *rac* + 2H *meso*); 0.96 (s) (18H *rac* + 18H *meso*). IR (film): 2960, 2920, 2875, 1480, 1390, 1370, 1350, 1300, 1240, 1185, 1165, 1130, 1095, 1060, 1015, 985 and 865 cm^{-1}.

(b) *Dehydrobromination of* 1,2-*dibromo*-1,2-*dineopentyloxyethane* (**8**→**9**). To the above soln, cooled at 0° and under stirring, 1.60 g (1.42×10^{-2} mole) $KOBu^t$ were added in small portions. The mixture was stirred for 90 min at 0° and then treated with enough 5% aq K_2CO_3 soln to dissolve the inorganic salts. The layers were separated and the organic one dried with anh Na_2SO_4/K_2CO_3 and kept under N_2 at low temp.

An aliquot was evaporated to give a 16/84 mixture of (*Z*) and (*E*)-bromo-1,2-dineopentyloxyethene. NMR (CCl_4): 6.21 (s) (1H) *Z*; 5.55 (s) (1H) *E*; 3.30 (s) (2H *Z* + 2H *E*); 3.26 (s) (2H *Z* + 2H *E*); 0.96 (s) (9H) *E*; 0.93 (s) (9H *E* + 18H *Z*).

(c) *Dehydrobromination of* 1-*bromo*-1,2-*dineopentyloxyethene* (**9**→**1**). In a 100 ml, 3-necked flask, equipped with magnetic stirring, an acetone-dry ice condenser, stopped with a KOH-tube, and a pressure-equalized dropping funnel, a suspension of $NaNH_2$ in liq NH_3 was prepared from 0.75 g (3.26×10^{-2} mole) Na and 35 ml liq NH_3. To the stirred suspension, the pentane soln of (*Z*) and (*E*)-1-bromo-1,2-dienopentyloxyethene was added dropwise, the mixture stirred for 10 min and then hydrolyzed with 20 ml iced H_2O. The layers were separated and the organic one washed with 20 ml buffered 0.1M phosphate soln (NaH_2PO_4/Na_2HPO_4) and dried with Na_2SO_4/K_2CO_3 at −78°, under N_2. The dry soln was filtered at low temp, the inorganic salts being thoroughly washed with pentane and dilute with this solvent to the exact volume of 50 ml. This new soln was kept cold, at −78°, and used for further experiments (see below).

An aliquot (5.0 ml) was evaporated under high vacuum at low temp and the residue immediately dissolved in 2 ml CCl_4. Rapid analysis by NMR spectroscopy showed the presence of pure dineopentyloxyethyne: 3.51 (s) (4H) and 0.95 (s) (18H), but the compound underwent rapid polymerization at 37° ($t_{1/2} \simeq 15$ min). After polymerization was complete, the CCl_4 soln was evaporated affording a residue of 0.100 g equivalent to 46% overall yield of dineopentyloxyethyne from 1,2-dineopentyloxyethene.

Hexacarbonyl-μ-(η-*dineopentyloxyethyne*)-*dicobalt*(Co–Co) **10**

In a 80 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, 1.39 g (3.80×10^{-2} mole) $Co_2(CO)_8$ and 10 ml pentane were introduced, under N_2. The mixture was cooled at −78° and 15 ml of the pentane soln of dineopentyloxyethyne (*ca.* 1.50×10^{-3} mole) were added dropwise. The mixture was allowed to warm up to room temp, with continuous stirring, and after 3 hr the solvent removed *in vacuo*. The residue was chromatographed on neutral alumina, eluting with hexane, to give 0.016 g (2.2% yield) of hexacarbonyl-μ-(η-dineopentyloxyethyne)-dicobalt (*Co–Co*), m.p. 74–75°. NMR (CCl_4): 3.38 (s) (4H); 1.03 (s) (18H). IR (CCl_4): 2970, 2940, 2890, 2090, 2050, 2020, 1600, 1370, 1230 and 1190 cm^{-1}. MS (high resolution): 483.9975. Calc. for $C_{18}H_{22}Co_2O_8$: 483.9978. MS: 484 (0.94) ($M^{+\cdot}$), 456 (5.2), 428 (0.47), 369 (0.53), 358 (3.6), 341 (0.82), 286 (6.4), 271 (5.6), 258 (10.3), 244 (16.8), 187 (12.0), 174 (16.8), 146 (14.5), 118 (39.0), 87 (27.5), 71 (100), 57 (48.9%).

Hexaneopentyloxybenzene **11**

In a 50 ml flask, equipped with magnetic stirring and a pressure-equalized dropping funnel, 0.050 g ($1.47 \cdot 10^{-4}$ mole) $Co_2(CO)_8$ were introduced, under N_2. Cooling at −78°, 15 ml of the pentane soln of dineopentyloxyethyne were added dropwise. The mixture was stirred and allowed to warm up to room temp for 15 hr, the solid material filtered off and the solvent removed under vacuum. The residue was chromatographed on neutral alumina, eluting with hexane, to afford 0.013 g (4.3% yield) of hexaneopentyloxybenzene, m.p. 205–206° (sealed capillary). NMR (CCl_4): 3.61 (s) (12H) and 1.02 (s) (54H). IR (KBr): 2980, 2960, 2910, 2870, 1460, 1450, 1400, 1365, 1265, 1050, 1030, 995 and

940 cm^{-1}. (Found: C, 72.37; H, 11.50. Calc. for $C_{36}H_{66}O_6$: C, 72.68; H, 11.18%).

MS: 595 (3.7), 594 ($M^{+\cdot}$) (8.5), 524 (2.7), 454 (2.6), 384 (4.7), 314 (9.0), 244 (11.8), 174 (36.7), 173 (51.1), 71 (100), 57 (14.1%).

REFERENCES

[1a] M. A. Pericàs and F. Serratosa, *Tetrahedron Letters* 4433 (1977); [b] A. Bou, M. A. Pericàs and F. Serratosa, *Tetrahedron* **37**, 1441 (1981).

[2] M. A. Pericàs and F. Serratosa, *Tetrahedron Letters* 4437 (1977).

[3] H. Olsman, *Kon. Ned. Akad. Wetensch. Proc., Ser.* B **69**, 629, 645, 660 and 675 (1966) (*C.A.* **66**, 64994x (1967).

[4] L. Brandsma, H. J. T. Bos and J. F. Arens, in *Chemistry of Acetylenes* (Edited by H. G. Viehe), pp. 808–810. Marcel-Dekker, New York (1969).

[5] M. A. Pericàs and F. Serratosa, *Tetrahedron Letters* 2603 (1978).

[6] M. A. Pericàs and F. Serratosa, *Ibid.* 4969 (1978).

[7] M. Charton, *Progr. Phys. Org. Chem.* **10**, 81 (1973); *J. Org. Chem.* **43**, 3995 (1978).