3229

Diphenylacetylene and the LICKOR Superbase: *o*,*o*'-Dimetalation and Reaction with Electrophiles. A Convenient Synthesis of o, o'-Disubstituted Diphenylacetylenes[†]

Janusz Kowalik* and Laren M. Tolbert

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, U.S.A.

janusz.kowalik@chemistry.gatech.edu

Received October 30, 2000

The renaissance of acetylene chemistry in recent years can be attributed in great part to research in the area of materials chemistry.^{1,2} Breakthroughs in palladiumcatalyzed cross-coupling reactions involving acetylenes opened the doors to a plethora of exotic structures, interesting for their theoretical ramifications on, for example, the limits to aromaticity ³ and for their practical synthetic utility as well. In this context, the chemistry of diphenylacetylene and its derivatives continues to attract significant interest, as they constitute intermediate or final components of many of the technologically important structures. Nevertheless, only a handful of convenient synthetic methods are available for the preparation of substituted derivatives of diphenylacetylene. For example, one of the most versatile derivatives of diphenylacetylene, o,o'-diiododiphenylacetylene (2b), is produced by halogen exchange of o, o'-dibromodiphenylacetylene,⁴ which is itself obtained through a tedious multistep process.⁵ Our direct approach is to employ the easily available diphenylacetylene, which upon double ortho-metalation, followed by reaction with electrophilic agents, should result in a symmetrical double substitution. To our knowledge, there is no report in the literature about such a direct ortho-functionalization of diphenylacetylene without affecting the acetylene unit. It is known that diphenylacetylene reacts with n-butyllithium in THF to form an addition product, 1-lithio-2-butylstil-

bene, which undergoes further ring ortho-lithiation⁶ if the reaction is carried out in hexane in the presence of TMEDA. An elegant reinvestigation by Schleyer et al.⁷ provided the spectroscopic and crystallographic proof of structure. In contrast to n-butyllithium, the LICKOR (Lochmann–Schlosser) superbase (n-butyllithium/ t-BuOK)⁸ does not affect the triple bond in lithium phenylacetylide, producing ortho-metalated material in high yields and regioselectivity.⁹ It has been shown that the ortho-directing and activating effects of the lithium acetylide group are analogous although somewhat weaker in strength to those of OCH₃, CH₂NMe₂, SLi, sulfonyl, and silyl or amido groups.^{9c,10} The nature of the resulting dianion is not known but is assumed to involve coordination of the potassium with the aromatic ring. The structure of that species might be as complex as that of the LICKOR superbase itself.¹¹

Addition of diphenylacetylene to a preformed¹² LICKOR superbase (made of equimolar amounts of potassium tert-butoxide and n-butyllithium) in THF/ hexane at -78 °C produces o, o'-dimetallodiphenylacetylene 1, which reacts smoothly with various electrophiles including methyl iodide, chlorotrimethylsilane, chlorodiphenylphosphine, methyl disulfide, and chlorotri-*n*-butyltin, providing corresponding *o*,*o*'-disubstituted derivatives 2 in reasonable isolated yields (47-86%) (Scheme 1) (Table 1).

In the case of iodine as an electrophile it is found that much better results can be obtained when the original o, o'-dipotassiodiphenylacetylene (1) is converted

(8) (a) Lochmann, L.; Pospíšil, J.; Lím, D. Tetrahedron Lett. 1966, 257.
(b) Schlosser, M. J. Organomet. Chem. 1967, 8, 9.
(9) (a) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. J. Chem. Soc.,

^{*} Fax: (404) 894-7452.

[†] Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday.

⁽¹⁾ Modern Acetylene Chemistry; Stang, P. J., Diederich, F., Eds.; VCH Publishers: New York, 1995.

⁽²⁾ For an excellent review, see: (a) Haley, M. M. Synlett 1998, 7, 557. (b) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. J. Am. Chem. Soc. 2000, 122, 3015. Diederich, F.; Rubin, Y. Angew. Chem., Int. Ed. Engl. 1992, 31, 1101. (c) Katayama, N.; Czarnecki, M. A.; Satoh, M.; Watanabe, T.; Ozaki, Y. *Appl. Spectrosc.* **1997**, *51*, 487. (d) Taniike, K.; Katayama, N.; Sato, T.; Ozaki, Y.; Czarnecki, M. A.; Satoh, M.; Watanabe, T.; Yasuda, A. *Mikrochim. Acta* **1997**, *14*, 581. (e) Sarala, S.; Roy, A.; Madhusudana, N. V.; Nguyen, H. T.; Destrade, C.; Cluzeau, P. Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A 1995, 261, 1. (f) Cluzeau, P.; Nguyen, H. T.; Destrade, C.; Isaert, N.; Barois, P.; Babeau, A. Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **1995**, 260, 69. (g) Godt, A.; Cryst. Liq. Cryst. Sci. Technol., Sect. A 1995, 260, 69. (g) Godt, A.;
Fréchet, J. M.; Beecher, J. E.; Willand, C. Macromol. Chem. Phys. 1995, 196, 133. (h) Juang, T. M.; Chen, Y. N.; Lung, S. H.; Lu, Y. H.; Hsu, C. S. Liq. Cryst. 1993, 15, 529. (i) Morichere, D.; Chollet, P. A.; Fleming, W.; (j) Jurich, M.; Smith, B. A.; Swalen, J. D. J. Opt. Soc. Am. B 1993, 10, 1894. (k) Wu, S. T.; Hsu, C. S.; Chen, Y. N.; Wang, S. R.; Lung, S. H. Opt. Eng. 1993, 32, 1792.
(3) Wan, W. B.; Kimball, D. B.; Haley, M. M. Tetrahedron Lett. 1998, 6795

^{6795.}

^{(4) (}a) Dierks, R.; Vollhardt, K. P. C. J. Am. Chem. Soc. 1986, 108, 3150. (b) Whitlock, B. J.; Whitlock, H. W. J. Org. Chem. 1972, 37, 3559. (5) (a) Letzinger, R. L.; Nazy, J. R.; J. Am. Chem. Soc. 1959, 81, 3013. (b) Diercks, R.; Vollhardt, K. P. C. Angew. Chem. 1986, 98, 268.

^{(6) (}a) Mulvaney, J. E.; Garlund, Z. G.; Garlund, S. L. J. Am. Chem. Soc. **1963**, *85*, 3897. (b) Mulvaney, J. E.; Garlund, Z. G.; Garlund, S. L.; Newton, D. J. J. Am. Chem. Soc. **1966**, *88*, 476. (c) Mulvaney, J. L.; Hewon, D. J. J. Org. Chem. 1968, 33, 3286. (d) Mulvaney, J. E.;
 Newton, D. J. J. Org. Chem. 1969, 34, 1936.
 (7) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. J. Am. Chem.

Soc. 1988, 110, 6033

Chem. Commun. 1981, 366. (b) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. Tetrahedron Lett. 1981, 2495. (c) Brandsma, L.; Hommes, H.; Verkruijsse, H. D.; deJong, R. L. P. Recl. Trav. Chim. Pays-Bas 1985, 104, 226.

⁽¹⁰⁾ For a review, see: (a) Schlosser, M.; Faigl, F.; Franzini, L.; Geneste, H.; Katsoulos, G.; Zhong, G. *Pure Appl. Chem.* **1994**, *66*, 1439. (b) Chadwick, S. T.; Rennels, R. A.; Rutheford, J. L.; Collum, D. B. J. Am. Chem. Soc. 2000, 122, 8640 and references therein. (c) For a review on CIPE effects, see: Beak, P.; Meyers, A. I. Acc. Chem. Res. **1986**, *19*, 356. (d) Snieckus, V. Bull. Chem. Soc. Fr. **1988**, *1*, 67. (e) Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. J. Am. Chem. Soc. 1989, 111, 658. (f) Figuly, G. D.; Loop, C. K.; Martin, J. C. J. Am. Chem. Soc. 1989, 111, 654. (g) Gais, H.-J.; Vollhardt, J. Tetrahedron Lett. 1988, 1529. (h) Tamao, K.; Yao, H.; Tsutsumi, Y.; Abe, H.; Hayashi, T.; Ito, Y. Tetrahedron Lett. 1990, 2925. (i) Jayasuriya, K.; Iyer, S. Int. J. Quantum Chem. 1988, 34, 199.

⁽¹¹⁾ For a recent review on reaction of organolithium compounds with alkali metal alkoxides and reactions of "superbases", see: (a) Lochmann, L. Eur. J. Inorg. Chem. 2000, 115. Schlosser, M. Pure Appl. Chem. 1988, 60, 1627. (b) Kremer, T.; Harder, S.; Junge, M.; Schleyer, P. v. R. Organometallics 1996, 15, 585. (c) den Besten, R.; Lakin, M. T.; Veldman, N.; Spek, A. L.; Brandsma, L. J. Organomet. Chem. 1996, 514, 191. (d) Harder, S.; Streitwieser, A. Angew. Chem., Int. Ed. Engl. 1993, 32, 1066. (e) Lochmann, L.; Jakubov, A.; Brandsma, L. Collect. Czech. Chem. Commun. 1993, 58, 1445. (f) Bauer, W.: Lochmann, L. J. Am. Chem. Soc. 1992, 114, 7482.

⁽¹²⁾ It was found that changing the procedure to a potentially more convenient one, in situ formation of the LICKOR superbase with diphenylacetylene present in the reaction mixture followed by quenching with chlorotrimethylsilane, produced a complex mixture of at least nine compounds with the yield of the desired o, o'-disubstitution not exceeding 30% (by gas chromatography, uncorrected).

Scheme 1



 $\begin{array}{l} \mathsf{R}\text{= SiMe_3 (2a); CH_3 (2c); CH_3S (2d); Ph_2P (2e); n-Bu_3Sn (2f)} \\ \mathsf{X}\text{= Cl (2a, 2e, 2f); $1(2c); CH_3S (2d)} \end{array}$

Table 1. Reaction of o, o'-Dimetallodiphenylacetylene with Electrophiles



R= SiMe₃ (**2a**); I (**2b**); CH₃ (**2c**); CH₃S (**2d**); Ph₂P (**2e**); n-Bu₃Sn (**2f**)

| entry | electrophile | reaction product | yield (%) |
|-------|------------------------------------|------------------|-----------|
| 1 | TMSCl | 2a | 63 |
| 2 | I_2 | 2b | 52^{a} |
| 3 | CH ₃ I | 2 c | 86 |
| 4 | CH ₃ S-SCH ₃ | 2d | 59 |
| 5 | Ph ₂ PCl | 2e | 47 |
| 6 | (n-Bu) ₃ SnCl | 2f | 62 |

^a via Grignard reagent (Method A).

to a much less basic Grignard reagent by adding 2 equiv of magnesium bromide etherate, relative to diphenylacetylene, before addition of iodine (Method A). ^{9b} Presumably, the initially formed **1**, a very strong base, is capable of eliminating hydrogen iodide from the monoor diiodinated diphenylacetylene, leading to a very reactive benzyne derivatives and thus depleting the yield of the desired o, o'-diiododiphenylacetylene. We have also found that the most convenient preparation of this compound includes a two-step process, where the readily available o, o'-bis(trimethylsilyl)diphenylacetylene (**2a**), obtained in 63% yield, is allowed to react with iodine chloride in methylene chloride to give the target structure in 74% isolated yield, after crystallization (Method B) (Scheme 2).

The observed preference for the o, o'-dimetalation reaction can be explained by analogy with the double lithiation of biphenyl¹³ or diphenyl ether.¹⁴ According to the calculational studies of Schleyer et al., the o, o'-dilithiated derivatives of both exist as symmetrically doubly bridged structures,^{13a,b} a result that was confirmed by an X-ray crystal structure.^{13c,d} However, in this case steric constraints prevent such bridging, and the role of potassium needs to be acknowledged. As has been shown in the case of trityl alkali metal structures, the location (and binding) of potassium and rubidium cations is dramatically difScheme 2 ICi / CH₂Cl₂, rt, 8h

2a

ferent from the way the other first group metals coordinate the anion.^{15a} In the case of potassium, the crystal structure reveals monomeric species with η^{6} -coordination of the metal ion and a single THF molecule in the coordination sphere. In contrast, tolyl and diphenylmethyl anions coordinate potassium and rubidium ions with the formation of the polymeric entities, with no involvement of the solvent.^{15b,c} In all of these complexes chelating triamine (PMDTA) completes the coordination sphere of the metal ion.

Activation of an ortho position by an adjacent acetylene function is precedented.⁹ The Hammett σ_p value for the acetylene moiety at 0.23^{16} classifies it as modestly electron-withdrawing. The first metalation in the ortho position may provide an additional activation of the ortho position in the other phenyl ring by facilitating formation of a bimetallic complex through, perhaps, the intervention of the triple bond as a σ -donor. Such a synergistic effect should actually facilitate the second metalation step and explain the observed preference for o, o'-dimetalation of diphenylacetylene. P. v. R. Schleyer has suggested a similar explanation,¹⁷ "The metalation cluster complexes with the triple bond and this 'activates' the ortho CH bonds in the immediate vicinity."

In summary, the reaction of diphenylacetylene with the LICKOR superbase (*n*-BuLi/KO*t*-Bu) produces the corresponding *o*,*o*'-dimetalated species with high regiose-lectivity. Subsequent substitution with halogen-, carbon-, sulfur-, silicon-, tin-, and phosphorus-centered electrophiles results in moderate-to-good yields of *o*,*o*'-disubstituted diphenylacetylenes.

Experimental Section

General Methods. ¹H and ¹³C NMR spectra were recorded on a Gemini 300 spectrometer at 300 MHz and 75 MHz, respectively, using tetramethylsilane (TMS) as an internal standard. The solvent was CDCl3 unless noted otherwise. Chemical shifts (ppm) are reported relative to TMS for ¹H and ^{13}C NMR spectra and 85% H_3PO_4 for ^{31}P NMR spectra (external capillary). Mass spectra were measured on a VG Instruments 70 SE system. FTIR (KBr pellet) spectra were recorded on a Nicolet 60SXR. Melting points were determined on Electrothermal melting point apparatus and are uncorrected. TLC analyses were performed using Analtech silica gel GF TLC plates; Rf values are reported for a n-hexane (95+%)/acetone (5:1) solvent system. THF and hexane were distilled under argon over sodium/ benzophenone and lithium aluminum hydride, respectively. All other reagents were used as received. All experiments were performed on a vacuum line in an argon atmosphere.

General Procedure. Bis(2-trimethylsilylphenyl)acetylene (2a). A solution of potassium *tert*-butoxide (1.20 g, 10.7 mmol) in THF/hexane (18/15 mL) was cooled to -78 °C, and while stirred, a 2.5 M hexane solution of *n*-butyllithium (3.5 mL, 8.5 mmol) was added dropwise via syringe over 15 min, resulting in a yellow solution. Stirring at -78 °C was continued for 20 min, followed by dropwise addition of diphenylacetylene (0.70 g, 3.93 mmol) dissolved in THF (3.5 mL) over 10 min. The reaction was continued at -75 °C for 40 min, followed by 1.5 h

^{(13) (}a) Kos, A. J.; Schleyer, P. v. R. J. Am. Chem. Soc. 1980, 102, 7928. (b) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. J. Organomet. Chem. 1982, 228, 107. (c) Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. J. Chem. Soc., Chem. Commun. 1982, 1184. (d) Ref 7d in ref 14. (14) Schleyer, P. v. R. Pure Appl. Chem. 1984, 56, 151.

^{(15) (}a) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R.; Pieper, U.; Stalke, D.; *Organometallics* **1993**, *12*, 1193. (b) Hoffmann, D.; Bauer, W.; Hampel, F.; Hommes, N. J.; Schleyer, P. v. R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528. (c) Refs 34 and 40 in ref 15a.

⁽¹⁶⁾ Landgrebe, J. A.; Rynbrandt, R. H. J. Org. Chem. 1966, 31, 2585.

⁽¹⁷⁾ Schleyer, P. v. R. private communication.

at -25 °C. The initially red solution changed to very deep burgundy. The temperature of the reaction mixture was lowered to -43 °C, and chlorotrimethylsilane (1.5 mL) was added via syringe over 2 min. Stirring was continued at $-40\ ^\circ C$ for 30 min, and then the cooling bath was changed to ice and the reaction mixture was allowed to reach room temperature (5 h). The color of the reaction mixture changed to blue, blue-green, greenyellow, and finally light yellow. Solvents were removed in vacuo, ether (80 mL) was added, and the mixture was washed with saturated aqueous citric acid solution and water. The ether extracts were dried (MgSO₄) and filtered, and the solvent was removed in vacuo to give an oil (1.00 g), which solidified upon standing. Crystallization from hexane yielded 0.80 g (63%) of colorless crystalline product, mp 72–74 °C, R_f 0.91. ¹H NMR δ 7.55 + 7.54 (d + d, J = 7.5 Hz, 2H); 7.40-7.29 (m, 2 H); 0.43 (s, 18 H). $^{13}\mathrm{C}$ NMR δ 142.54, 134.25, 132.06, 129.04, 128.84, 127.57, 93.72, -1.19. EIMS 322(49.49), 307(32.16), 291(8.52), 247(6.47), 233(57.42), 191(12.49), 129(10.02), 73(100), 59(30.83). IR (ν_{max} , cm⁻¹) 3069, 3050, 2951, 2896, 1581, 1466, 1243, 1128, 1076, 855, 838, 781, 751, 721, 691, 676, 621, 559, 451. Anal. Calcd for C20H26Si2: C, 74.46; H, 8.12. Found: C, 74.17; H, 8.11.

Bis(2-iodophenyl)acetylene (2b). Method A. The initially formed **1** was converted to the corresponding Grignard reagent by the addition of 2 equiv of magnesium bromide etherate, relative to diphenylacetylene, followed by the reaction with iodine and the workup as above. Yield 52%, mp 98–100 °C, R_f 0.77. ¹H NMR δ 7.88 (dd, J = 7.6 Hz, 0.4 Hz, 2H); 7.61 (dd, J = 7.6 Hz, 1.6 Hz, 2H); 7.33 (dt, J = 7.6 Hz, 0.4 Hz, 2H); 7.02 (dt, J = 7.6 Hz, 1.6 Hz, 2H); 7.33 (dt, J = 7.6 Hz, 0.4 Hz, 2H); 7.02 (dt, J = 7.6 Hz, 1.6 Hz, 2H). ¹³C NMR δ 138.69, 132.89, 129.58, 129.42, 127.70, 100.45, 94.65. EIMS 430(100), 303(11.02), 215-(3.39), 176(84.39), 150(14.87), 127(2.81), 126(4.64), 88(19.19). IR-($ν_{max}$, cm⁻¹) 1474, 1428, 1413, 1012, 750, 728, 649, 552, 434. Anal. Calcd for C₁₄H₈I₂: C, 39.10; H, 1.88; I, 59.02. Found: C, 38.37; H, 1.83; I, 59.88.

Bis(2-iodophenyl)acetylene (2b). Method B. A 1.0 M solution of iodine chloride in methylene chloride (5.8 mL, 5.80 mmol) was added to a stirred solution of **2a** (0.91 g, 2.82 mmol) in methylene chloride (25 mL), and the reaction mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo, hexane was added, and the crystalline product was filtered to give 0.90 g of a pale yellow material. Upon cooling of the mother liqueur, another 0.20 g of crystalline material was recovered. Recrystallization from 95% ethanol yielded 0.90 g (74%) material, identical with that obtained using direct iodination of o, o'-bis(bromomagnesio)diphenylacetylene.

Bis(2-methylphenyl)acetylene (2c). Yield 86%, oil.¹⁸ ¹H NMR δ 7.52 (d, J = 7.2 Hz, 2H); 7.27–7.15 (m, 6H); 2.53(s, 6H).

 ^{13}C NMR δ 140.17, 132.06, 129.65, 128.37, 125.75, 123.49, 92.34, 20.72. EIMS 206(100), 205(74.98), 204(17.11), 203(17.88), 202-(17.39), 191(40.04), 178(39.75), 165(17.68), 115(14.56).

Bis(2-methylthiophenyl)acetylene (2d). Yield 59%, mp 122–124 °C, R_f 0.57. ¹H NMR δ 7.54 (dd, J = 7.6 Hz, 1.3 Hz, 2H); 7.30 (dt, J = 7.5 Hz, 1.4 Hz, 2H); 7.18 (dd, J = 7.9 Hz, 1.3 Hz, 2H); 7.11 (dt, J = 7.5 Hz, 1.3 Hz, 2H). ¹³C NMR δ 141.59, 132.59, 128.84, 124.23, 121.38, 93.15, 15.24; EIMS 270(5.37), 255(50.86), 240(100), 222(10.54), 221(19.58), 176(2.08); IR(ν_{max} , cm⁻¹) 1583, 1471, 1433, 1278, 1244, 1074, 1035, 954, 752, 718, 680, 563, 519, 446. Anal. Calcd for C₁₆H₁₄S₂: C, 71.07; H, 5.22; S, 23.71. Found: C, 71.09; H, 5.17; S, 23.62.

Bis(2-diphenylphosphinylphenyl)acetylene (2e). Yield 47%, mp 167–169 °C(dec); R_f 0.59. ¹H NMR (acetone- d_6) δ 7.41–7.38 (m, 12H); 7.33–7.23 (m, 12H); 7.19–7.15 (m, 2H); 6.79–6.75 (m, 2H); ¹³C NMR (acetone- d_6) δ 140.11 (d, $J_{CP} = 12.6$ Hz), 136.56 (d, $J_{CP} = 11.5$ Hz), 134.06 (d, $J_{CP} = 20.3$ Hz), 132.38 (d, $J_{CP} = 20.6$ Hz), 128.66, 128.45 (d, $J_{CP} = 7.3$ Hz), 128.11 (d, $J_{CP} = 9.1$ Hz), 127.85 (d, $J_{CP} = 20.6$ Hz), 90.09; ³¹P NMR δ –8.5. CIMS 547(84.54), 471(100); EIMS 546(19.19), 469(100), 392(14.46), 357(2.01), 313(9.73), 283(19.62), 273(15.62), 252(7.01), 183(10.91); IR(ν_{max} , cm⁻¹) 3068, 3054, 3026, 3010, 3001, 1581, 1486, 1434, 1305, 1180, 1158, 1120, 1090, 1068, 1026, 998, 758, 745, 731, 694, 585, 544, 527, 492, 474, 411. Anal. Calcd for C₃₈H₂₈P₂: C, 83.50; H, 5.16. Found: C, 82.86; H, 5.31.

Bis(2-tri-*n***-butylstannylphenyl)acetylene (2f).** Yield 62%, oil, purified by column chromatography on silica gel, elution with hexanes, R_f 0.94. ¹H NMR δ 7.53–7.47 (m, 4H), 7.33–7.24 (m, 4H), 1.68–1.42 (m, 12H), 1.29 (sextet, J = 7.2 Hz, 12H), 1.21–1.01 (m, 12H), 0.83 (t, J = 7.2 Hz, 18H); ¹³C NMR δ 146.40, 136.55, 131.78, 131.20, 128.11, 127.46, 91.98, 29.03, 27.21, 13.44, 9.81; EIMS 699(6.1), 643(60.4), 585(5.0), 529(4.1), 473(1.6), 411 (18.1), 353(26.5), 291(100), 235(41.2), 179(42.9); IR (neat, ν_{max} , cm⁻¹) 3052, 2956, 2930, 2871, 2863, 1484, 1434, 1418, 1376, 1340, 1292, 1284, 1248, 1181, 1150, 1109, 1072, 980, 879, 845, 758, 718, 890, 887, 850, 597, 558, 507; Anal. Calcd for C₃₈H₆₂-Sn₂: C, 60.35; H, 8.26. Found: C, 60.44; H, 8.29.

Acknowledgment. The financial support from the U.S. Department of Energy is gratefully acknowledged. We thank Professors Lambert Brandsma and Paul von Ragué Schleyer for valuable discussions.

JO001533T

⁽¹⁸⁾ Reported mp 28.7 °C (from ethanol, Coops, J.; Hojitink, G. J.; Kramer, T. J. E.; Faber, A. C. *Recl. Trav. Chim. Pays-Bas* **1953**, *72*, 781). According to the GC analysis our sample contained ca. 10% of the monomethylated derivative, not separable by column chromatography or distillation.