Nucleophilic Dechlorocarbomethoxylation of (*E*)-Methyl *β*-Chloro-α-methyl-*β*-(3-bromo-2,4,6-trimethylphenyl)acrylate

Michal Beit Yannai and Zvi Rappoport*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received January 8, 1996

Vinylic substitution of alkyl *β*-halocinnamates by nucleophiles was extensively studied.[1] When the α-position is substituted, e.g., with an α-carboalkoxy or an α-cyano group, the reaction usually proceeds by the addition−elimination route[1f,g] (eq 1), whereas with an α-hydrogen

$$\mathrm{ArC(X){=}C(R)CO_2Me + Nu^-} \rightarrow \mathrm{ArC(Nu){=}C(R)CO_2Me} \quad (1)$$

X = Cl, Br; $\mathrm{Nu^-}$ = SR′, OR′, $\mathrm{F^-}$; R = CN, $\mathrm{CO_2Me}$

$$\mathrm{ArC(X){=}CHCO_2Me + Nu^-} \rightarrow \mathrm{ArC{\equiv}CCO_2Me} \quad (2)$$

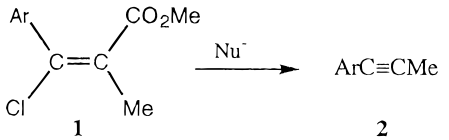
X = Cl; $\mathrm{Nu^-} = \mathrm{R'O^-}$

derivative substitution via addition−elimination[1d] or elimination to the acetylene[1b,e] may take place (eq 2). We have found that when the aryl group is bulky, a different reaction course, i.e., nucleophilic dechlorocarbomethoxylation with formation of an acetylene, takes place.

Results

(*E*)-Methyl α-methyl-*β*-chloro-*β*-(3-bromo-2,4,6-trimethylphenyl)acrylate (**1**) was prepared by a configuration-retaining esterification either with diazomethane or with thionyl chloride and then methanol of the (*E*)-acid, which was prepared in turn according to Adams and Miller.[2] The ester obtained by both methods was identical by ^{1}H NMR and GC/MS.

In an attempted substitution of the vinylic chlorine, the ester was reacted with several oxygen and sulfur nucleophiles. Whereas on reflux of **1** in MeCN for 15.5 h in the absence of a nucleophile **1** was recovered unchanged, with all the nucleophiles a dechlorocarbomethoxylation rather than a substitution process took place with formation of (3-bromo-2,4,6-trimethylphenyl)-methylacetylene (**2**) (eq 3).



(3)

1 **2**

Ar=3-Br-2,4,6-$\mathrm{Me_3C_6H}$

Two thio nucleophiles and three oxygen nucleophiles have been studied:

(a) $\mathrm{MeS^-}$. (i) At a 1:1 [$\mathrm{Nu^-}$]:[**1**] ratio (ca. 0.1 mol/L) after 7 h reflux in MeCN, 12% conversion to **2** was observed, and the rest of the compound was unreacted **1**.

(ii) At a 5:1 [$\mathrm{Nu^-}$]:[**1**] ratio, all the ester had reacted after 6 h reflux in MeCN, giving ca. 90% of **2** and ca. 10% of a compound that by GC/MS displayed isotopomeric molecular peaks at *m*/*z* 388, 390, 392 with intensity distribution consistent with the presence of one chlorine and one bromine atom. The compound was not identified, but by its molecular weight it cannot be an adduct of MeSH to the double bond.

The acetylene was isolated from a large scale experiment.

(b) *p*-$\mathrm{TolS^-}$. (i) With a 1.5:1 [$\mathrm{Nu^-}$]:[**1**] ratio, the reaction is slow, and after 44 h reflux in MeCN only 4% conversion of **1** to **2** was observed. Di-*p*-tolyl disulfide [^{1}H NMR δ ($\mathrm{CDCl_3}$) 2.31 (6H, s, Me), 7.25 (8H, AA′BB′q, J = 8 Hz, Ar-H); mass spectrum *m*/*z* (relative abundance, assignment) 246 (93, M), 123 (B, $\mathrm{TolS^+}$)] is formed in a 4-fold excess over **2**.

(ii) With a 10:1 [$\mathrm{Nu^-}$]:[**1**] ratio, 48 h reflux in MeCN led to 88% conversion. The main product was **2**, but some **1** still remained and di-*p*-tolyl disulfide was also formed. GC/MS showed the formation of three additional compounds (I−III) in very low percentages.

I. Formed in <3% and assigned by its mass spectrum base peak and some fragments as methyl *S*-tolyl thiolcarbonate **3** [*m*/*z* (relative abundance, assignment) 182 (64, M), 152 (4, M − 2Me), 105 (B, PhCO), 77 (50, Ph)]. The most abundant fragment at *m*/*z* 105 is most likely the benzoyl cation $\mathrm{PhCO^+}$, whose formation requires a substantial rearrangement and cleavage. However, an extensive rearrangement is required if the benzoyl fragment arises from any other precursor.

II. A compound whose main fragment is a pair of base peaks with identical intensities at *m*/*z* 225 and 227. Hence, this is bromine-containing, and it is consistent with 3-Br-2,4,6-$\mathrm{Me_3C_6HCO^+}$($\mathrm{ArCO^+}$). However, a parent peak is apparently missing. Other fragments are at *m*/*z* 199, 197 (26, 26, ArCO−2Me), and 117 (27, $\mathrm{ArCO^+H}$ − Br − 2Me). Again, formation of this fragment requires a structural rearrangement.

III. A bromine-containing compound formed in ca. 4%, with the highest *m*/*z* values at 360, 362 (M, 12, 12) whose cleavage pattern [*m*/*z* 233, 237 (31, 31, M − TolS), 158 (B, M − TolS − Br), 143 (44, M − TolS − Br − Me), 128 (26, M − TolS − Br − 2Me) is consistent with structure **4**.

(c) $\mathrm{Nu^-}$ = $\mathrm{PhO^-}$. With a 5-fold excess of nucleophile after 12 h reflux in MeCN 20% of **2** (identified by ^{1}H NMR and GC/MS) and 80% of **1** were observed.

(d) $\mathrm{Nu^-}$ = *i*-$\mathrm{PrO^-}$. With a 5-fold excess of nucleophile, reflux for 70 h in MeCN gave 97% conversion to two products: 57% of the *trans*-esterification product **5** and 40% of the acetylene **2**. The structure of **5** was corroborated by the identity of its spectra with those of an authentic sample prepared from the acyl chloride and 2-propanol. Due to the atropisomerism of **5** resulting from restricted rotation around the Ar−C bond, two isopropyl-Me doublets were observed for this chiral molecule.

(1) (a) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1823. (b) Youssef, A.-H. A.; Abdel-Maksoud, H. M. *J. Org. Chem.* **1975**, *40*, 3227. (c) Youssef, A.-H. A.; Abdel-Reheim, A. G. *Indian J. Chem., Sect. B* **1976**, *14B*, 101. (d) Youssef, A.-H. A.; Sharaf, S. M.; El-Sadany, S. K.; Hamed, A. E. *J. Org. Chem.* **1981**, *46*, 3813. (e) *Indian J. Chem., Sect. B* **1982**, *21B*, 359. (f) Avramovitch, B.; Rappoport, Z. *J. Am. Chem. Soc.* **1988**, *110*, 911; *J. Org. Chem.* **1982**, *47*, 1397. (g) Rappoport, Z.; Gazit, A. *J. Org. Chem.* **1986**, *51*, 4112; *J. Am. Chem. Soc.* **1987**, *109*, 6698.

(2) Adams, R.; Miller, M. W. *J. Am. Chem. Soc.* **1940**, *62*, 53.

S0022-3263(96)00056-4 CCC: $12.00

p-TolSCOOMe **3** ArC(STol-*p*)=CHMe **4**

ArC(Cl)=C(Me)COOPr-*i* **5**

Ar = 3-Br-2,4,6-Me_3C_6H

(e) Nu^- = t-BuO$^-$. With a 4.4-fold excess of the nucleophile, after 18 h reflux in MeCN all precursor **1** had disappeared, but the product was not identified. The GC/MS displayed only one compound with the highest signal at *m*/*z* 123, suggesting the presence of a nitrogen, and signals at *m*/*z* 96 and 83, suggesting the loss of HCN and CH from it. NMR showed several signals, including two Me signals at 2.25 and 2.41 ppm and a ^{1}H singlet at 6.07 ppm. We speculate that cleavage of **1** took part and one of the fragments reacted with the solvent.

Discussion

Decarbalkoxylation of esters, especially malonates and β-keto carboxylates, in water containing aprotic solvents such as DMSO−H_2O was studied extensively by Krapcho and co-workers[3] and by others. The reactions were accelerated by added metal (M) salts, and halides salts and cyanides (MCl, MBr, MI, MCN) were the catalysts used most often. In a mechanistic study of the reaction Krapcho et al.[4] investigated the catalytic efficiency of other salts including NaOAc, Na_3PO_4, Na_2SO_4, and KF. Decarbalkoxylations with NaOEt[5a] and Me_4NOAc[5b] or with amines[6a,b] or a thiolate ion[6c,d] are also known.

Solvent isotope effects suggested that the "uncatalyzed" reaction, i.e., with water as the nucleophile, proceeds by water attack on the ester carbonyl (a $B_{Ac}2$ mechanism) whereas the nucleophilic anions react either by this $B_{Ac}2$ mechanism forming a tetrahedral intermediate[4] or by attack on the alkyl group (a $B_{AL}2$ route).[4,6b] Evidence for the latter route is the isolation of RCN in the KCN-catalyzed reaction of CO_2R esters and the trapping of the carboxylate anion formed from a malonate ester when the reaction is conducted with LiCl/HMPA.[7] However, a concerted loss of RNu and CO_2 initiated by attack on the alkyl group is an alternative route in other systems.[4] It was suggested that in the general case the $B_{Ac}2$ and the $B_{AL}2$ routes are competitive.

The number of decarbalkoxylations of vinylic esters is smaller than in saturated systems,[8] and α,β-dechlorocarbalkoxylation is rare. The first work is that of Ykman and Hall,[9] who were able to substitute the chlorine of ester **6** with KF/crown ether, whereas the analogous

$ClCH=C(CO_2Me)_2$ **6** $Cl_2C=C(CO_2Me)_2$ **7**

$Cl_2C=C(Cl)CO_2Me$ **8**

reaction of ester **7** gave **8** presumably via carbanion **9**. If **9** is formed from **7**, then the dechlorocarbomethoxylation is not concerted. The two options of nucleophilic attack at the Me or the C=O were not distinguished. Formation of **10** via anion analogous to **9** is an overall dechlorocarbomethoxylation, and the same applies to formation of **11a**, **b** from **12a**, **b** with KCl/crown in sulfolane.

$Cl_2C=C^-(CO_2Me)$ **9** $ClC\equiv CCl$ **10**

$XC\equiv CCO_2Me$ **11a**: X = CO_2Me **b**: X = CN

$XC(Cl)=C(CO_2Me)_2$ **12a**: X = CO_2Me **b**: X = CN

Several mechanistic points and questions arise in relation to the observed dechlorocarbomethoxylation. In the catalysis by a thio-nucleophile it is possible that the reaction is initiated by a low conversion to the vinylic substitution product and Cl^-, and the latter serves as the reagent in an autocatalytic dechlorocarbomethoxylation process which is faster than further substitution by the RS^-. We therefore conducted a control experiment in which benzyltrimethylammonium chloride reacted for 7 h in refluxing MeCN with **1**. Since no reaction was observed, this route is excluded.

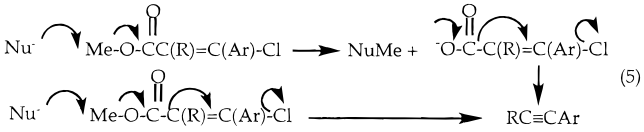
A second question is what is the detailed pathway for the loss of the ester group? Jones and co-workers[10] pyrolytically decomposed methyl β-halovinyl carboxylates, **13** and **14**, which are structurally related to **5**, in the presence or the absence of halide ions (eq 4). Al-

$$RC(X)=CHCO_2Me \longrightarrow MeX + CO_2 \quad (4)$$

13: R = CO_2Me; X = Cl, Br,
14: R = Ph; X = Br

though the main organic product was usually not monitored, **14** gave in $PhNO_2$ without additives both phenylacetylene and α-bromostyrene, whereas with NaBr/crown-6 in MeCN the accelerated reaction gave only phenylacetylene. Hence, at least part of the reaction involves the loss of only the ester group. A similar conclusion is derived from the work of Ykman and Hall.[9]

The two feasible B_{AL}-type routes suggested for the reaction are demonstrated below for **1**. (a) The nucleophile attacks the ester methyl group, generating the carboxylate ion, which by loss of CO_2 generates the vinyl anion which then expels the β-halogen or the loss of the CO_2 and X^- may be concerted, i.e., a Grob-type fragmentation. Indeed, Grob and co-workers obtained acetylenes by heating β-bromocarboxylates[11] (eq 5).



(5)

(3) For a review see: (a) Krapcho, A. P. *Synthesis* **1982**, 805; (b) 893.

(4) Krapcho, A. P.; Weimaster, J. F.; Eldridge J. M.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Stephens, W. B. *J. Org. Chem.* **1978**, *43*, 138.

(5) (a) Thole, F. B.; Thorpe, J. F. *J. Chem. Soc.* **1911**, *99*, 2183, 2187. Ingold, C. K.; Thorpe, J. F. *Ibid.* **1919**, *115*, 143. Cope, A. C.; McElvain, S. M. *J. Am. Chem. Soc.* **1932**, *54*, 4311, 4319. (b) Johnson, W. S.; Harbert, C. A.; Ratcliffe, B. A.; Stipanovich, R. D. *J. Am. Chem. Soc.* **1976**, *98*, 6188. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743.

(6) (a) Huang, B. S.; Parish, E. J.; Miles, D. H. *J. Org. Chem.* **1974**, *39*, 2647. Miles, D. H.; Huang, B. S. *Ibid.* **1976**, *41*, 208. Parish, E. J.; Huang, B. S.; Miles, D. H. *Synth. Commun.* **1975**, *5*, 341. (b) Saunier, Y. M.; Danion-Bougot, R.; Danion, D.; Carrié, R. *Bull. Soc. Chim. Fr.* **1976**, 1963. (c) Keinan, E.; Eren, D. *J. Org. Chem.* **1986**, *51*, 3165. (d) Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1979**, 4459.

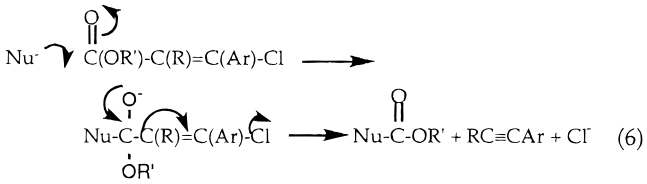
(7) Asaoka, M.; Miyake, K.; Takei, H. *Chem. Lett.* **1975**, 1149.

(8) Venkateswaran, R. V.; Ghosh, V.; Sarkar, A. *Tetrahedron* **1979**, *35*, 553.

(9) Ykman, P.; Hall, H. K., Jr. *Tetrahedron Lett.* **1975**, 2429. See also: Hall, H. K., Jr.; Ykman, P. *Macromolecules* **1977**, *10*, 464.

(10) Jones, G., II; Fantina, M. E.; Pachtman, A. H. *J. Org. Chem.* **1976**, *41*, 329.

A priori, this pathway seems preferable over a (b) B_{AL} route where nucleophilic attack on the ester carbonyl results in expulsion of the CO_2Me group either concertedly with the halide ion (e.g., eq 6) or stepwise with initial formation of the vinyl anion. Our work supplies some



(6)

information concerning this question. First, the reaction with *i*-PrO^- shows clearly that anion exchange, i.e., OMe → OPr-*i*, of the ester takes place, either before or concurrently with acetylene formation. Second, and unfortunate since the compound formed only in a very low yield and was assigned only on its base peak in the mass spectrum, the fragment formed by attack on the carbonyl group with loss of the whole ester group is observed in the reaction with $TolS^-$. The thiolcarbonate ester **3** could be formed only by attack of $TolS^-$ on the ester carbonyl, as in eq 6, followed by cleavage of the C−C═ bond. In contrast, TolSMe, which was not found, is the expected product of eq 5.

Third, the question arises why, in spite of the many reactions of the exclusive vinylic substitution of *β*-halovinylic esters,[1] the dechlorocarbomethoxylation reaction with thionucleophiles and the oxygen (*i*-PrO^-) nucleophiles was not observed so far. We believe that the reason for a reaction at the ester group rather than at the vinylic carbon of the electrophilic vinyl halide is that the approach to the latter is hindered, especially by the bulky substituted mesityl ring. Apparently, the competitive attack on the less hindered carbonyl is faster. This is corroborated by our attempted substitution of **15** with $TolS^-$ and $TolO^-$ anions which gave reaction at the tosylate rather than at the vinylic carbon.[12]

$$MesC(OTs)═C(CO_2Me)_2$$
15

Finally, although the formation of **4** can be ascribed to a substitution−decarbomethoxylation sequence (i), an addition of $TolS^-$ to acetylene **2** (ii) which comprises the "addition" part in the nucleophilic elimination−addition process is also possible. However, reaction of **2** with *p*-$TolS^-$ with or without sonication under the conditions that gave **4** showed no traces of **4,** suggesting that it is formed by route i.

Experimental Section

The salts *p*-TolSNA (Merck) and MeSNa, t-BuOK (Aldrich) were commercial samples. PhONa was prepared according to Elkobaisi et al.[13] and *i*-PrONa according to Seubold.[14] The MeCN was HPLC grade. All the reactions were conducted under argon with oxygen filter. The reactions were conducted with 200 mg of **1** and the appropriate ratio of nucleophile given above in 8−15 mL of MeCN. NMR spectra were recorded with a Bruker AMX-400 pulsed FT spectrometer operating at 400.13 MHz for ^1H and at 100.62 MHz for ^{13}C, and IR spectra were recorded with a Nicolet Impact 400 spectrometer.

(*E*)-Methyl α-Methyl-*β*-chloro-3-bromo-*β*-(2,4,6-trimethylphenyl)acrylate (1). (a) (*E*)-α-Methyl-*β*-chloro-*β*-(3-bromo-2,4,6-trimethylphenyl)acrylic Acid. The acid was prepared according to Adams and Miller[2] in a synthesis which involves a Friedel−Crafts acylation of bromomesitylene with propionic anhydride reported to give bromomesityl ethyl ketone. However, we found that mesitylene and dibromomesitylene are also formed in this reaction, presumably by disproportionation of bromomesitylene under the Friedel−Crafts conditions.[15] The mixture formed was chromatographed on silica with 1:1 CH_2Cl_2:petroleum ether eluent. The first fraction eluted was the known dibromomesitylene, mp 64 °C (lit.[16] mp 64 °C). Anal. Calcd for $C_9H_{10}Br_2$: C, 38.88; H, 3.63. Found: C, 38.52, H, 3.68). The bromomesityl ethyl ketone required for the large scale synthesis was separated from the other compounds by distillation. The fraction boiling at 103 °C at 0.3 mm was nearly pure bromomesityl ethyl ketone, which was used for continuation of the synthesis of the acid.

(b) Ester 1. (i) To a solution of (*E*)-α-methyl-*β*-chloro-*β*-(3-bromo-2,4,6-trimethylphenyl)acrylic acid (1 g, 3.1 mmol) in ether (24 mL) was added a solution of diazomethane in ether (ca. 0.3 g CH_2N_2, prepared from Diazald) at room temperature. After 15 min, AcOH (20 mL) was added to neutralize the unreacted diazomethane, the solution was washed with 10% aqueous $NaHCO_3$ solution, the phases were separated, and the organic phase was washed with water and dried ($CaCl_2$). After evaporation of the ether, the methyl ester was obtained as an oil (400 mg, 39%).

(ii) A solution of the acid (5.56 g, 17.5 mmol) in dry toluene (35 mL) was heated to reflux, and afterwards thionyl chloride (4.5 mL, 62 mmol) was added dropwise. The mixture was refluxed for 2 h, and the IR spectrum showed that the acid absorption at 1688 cm^{-1} was replaced by that of the acyl halide at 1774 cm^{-1}. The solvent and excess $SOCl_2$ were evaporated, toluene (20 mL) was added, and the liquid was further evaporated, leaving a yellow oil. Methanol (25 mL) and pyridine (0.25 mL) were added, and the mixture was refluxed for 3.5 h. IR spectra showed that 1774 cm^{-1} absorption was replaced by that of the ester at 1712 cm^{-1}. The methanol was evaporated, leaving 5.15 g of the crude ester. Chromatography on silica with 80:20 petroleum ether:CH_2Cl_2 as eluent gave 3.5 g (60%) of the pure ester as an oil, which did not form crystals even after standing for a few months. ^1H NMR *δ* ($CDCl_3$): 2.16, 2.23, 2.27, 2.33 (4 × 3H, 4s, Me), 3.49 (3H, s, OMe), 6.94 (1H, s, Ar-H). Mass spectrum *m/z* (relative abundance, assignment): 334, 332, 330 (25, 100, 76, M [$^{37}Cl^{81}Br$, $^{37}Cl^{79}Br/^{35}Cl^{81}Br$, $^{35}Cl\ ^{79}Br$]), 302, 300, 298 [21, 75, 55, M − 2Me − 2H) 297, 295 (8, 8, M − Cl), 267, 265 (3, 9, M − Cl − 2Me), 237, 235 (59, 57, M − Cl − 4Me), 193, 191 (24, 67, M − Br − 4Me), 157 (27, ArC^+═CMe − Br), 141 (32, ArC≡C^+ − Br), 115 (11, $Me_2C_6H_3C$). Anal. Calcd for $C_{14}H_{16}O_2BrCl$: C, 50.43; H, 4.99; Br, 23.05; Cl, 11.09. Found: C, 50.70; H, 4.86; Br, 24.09; Cl, 10.69.

(*E*) Isopropyl α-Methyl-*β*-chloro-*β*-(3-bromo-2,4,6-trimethylphenyl)acrylate (5). To (*E*)-α-methyl-*β*-chloro-*β*-(3-bromo-2,4,6-trimethylphenylacryloyl chloride (1 g, 3 mmol) prepared as described in method ii above were added isopropyl alcohol (20 mL) and pyridine (0.25 mL). The mixture was refluxed for 18 h, after which the only C═O absorption was at 1726 cm^{-1}. The solvent was evaporated, and chromatography of the oil obtained on silica using 4:1 petroleum ether:CH_2Cl_2 eluent gave pure (*E*)-isopropyl α-methyl-*β*-chloro-*β*(3-bromo-2,4,6-trimethylphenyl)acrylate, **5**, as an oil (800 mg, 74%). ^1H NMR *δ* ($CDCl_3$): 0.78 (3H, d, *J* = 6.2 Hz, *i*-PrMe), 0.86 (3H, d, *J* = 6.2 Hz, *i*-PrMe), 2.16, 2.21, 2.34, 2.38 (4 × 3H, 4s, Me), 4.71−4.81 (1H, hep, *i*-PrH), 6.93 (1H, s, ArH). Mass spectrum *m/z* (relative abundance, assignment): 362, 360, 358 (3, 14, 11, M [$^{37}Cl^{81}Br$, $^{37}Cl^{79}Br/^{35}Cl^{81}Br$, $^{35}Cl^{79}Br$]), 302, 300, 298 (6, 17, 14, M − 4Me), 202 (18, M − Cl − Br − *i*-Pr), 194, 192 (9, 24, M − Br − CO_2Pr-*i*), 158 (51, M − Br − Cl − CO_2Pr-*i*), 141 (45, MesC═CH), 115 (23), 43 (B, *i*-Pr^+). Anal. Calcd for $C_{16}H_{20}$-BrClO: C, 53.58; H, 5.34; Br, 22.28; Cl, 9.88. Found: C, 53.84, H, 5.60; Cl, 21.71; Br, 9.46.

(11) Grob, C. A.; Csapilla, J.; Cseh, G. *Helv. Chim. Acta* **1964**, *47*, 1590.
(12) Gazit, A.; Rappoport, Z. Unpublished results.
(13) Elkobaisi, F. M.; Hickinbottom, W. J. *J. Chem. Soc.* **1958**, 2431.
(14) Seubold, F. H., Jr. *J. Org. Chem.* **1956**, *21*, 156.
(15) Adams reported that a similar reaction of acetic anhydride with 3-bromomesitylene gave a poor yield due to "an excessive amount of rearrangement to tribromomesitylene" (Adams, R.; Theobald, C. W. *J. Am. Chem. Soc.* **1943**, *65*, 2383).
(16) Sussenguth, H. *Justus Liebigs Ann. Chem.* **1882**, *215*, 248.

(3-Bromo-2,4,6-trimethylphenyl)methylacetylene (2). A solution of ester **1** (300 mg, 0.9 mmol) and MeSNa (300 mg, 4.3 mmol) in MeCN (15 mL) was refluxed for 9 h under argon. The solvent was evaporated, the remainder was dissolved in CH_2Cl_2, the solution was filtered from the salt residues and then evaporated, and the residue was chromatographed over silica with petroleum ether (40−60 °C) as eluent. The first fraction collected was acetylene **2**, mp 50 °C (60 mg, 28%). ^{1}H NMR δ ($CDCl_3$): 2.15, 2.33, 2.36, 2.56 (4 × 3H, 4s, Me), 6.92 (1H, s, Ar-H). ^{13}C NMR ($CDCl_3$) δ: 4.8 (Me), 77.4 (one C≡C carbon; the other overlaps the solvent signal), 122.8 (C3), 124.4 (C1), 128.8 (C5), 138.7 (C4) 139.6 (C-2,6), (assignment based on additivity scheme). Mass spectrum *m*/*z* (relative abundance, assignment): 238, 236 (93, 97, M [^{81}Br, ^{79}Br]), 223, 221 (4, 4, M − Me), 157 (47, M − Br), 142 (B, M − Br − Me), 115 (26, M − Br − 2Me − C?). Anal. Calcd for $C_{12}H_{13}Br$: C, 60.89; H, 5.77; Br, 33.40. Found: C, 60.78; H, 5.52; Br, 33.40.

Attempted Reaction of 2 with Sodium *p*-Toluenethiolate. A solution of acetylene **2** (20 mg, 0.084 mmol) and sodium *p*-toluenethiolate (60 mg, 0.41 mmol) in MeCN (8 mL) was refluxed with stirring under argon for 17 h. Only **2** and traces of di-*p*-tolyl disulfide were observed. The mixture was sonicated for 4 days at room temperature. TLC analysis during the reaction and NMR and GC/MS of the solid obtained after filtering the mixture and evaporating the solvent showed only **2** and the disulfide and no traces of compound **4**.

Acknowledgment. This work was supported by the U.S.A.−Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which we are indebted.

JO9600565