localization of the negative charge into the oxygens coupled with hydrogen-bonding solvation of this charge. Hydrogen bonding to carbon is notoriously weaker than to more electronegative atoms; it would not be able to compensate for the loss of delocalization and the hydrogen bonding to oxygen and render **5** more stable than **1**.

It should be noted though that exclusion of **5** as the association complex observed in this study does not refute Bordwell's hypothesis that **5** could be an intermediate (nonaccumulating) in the reaction. Saunder's[30] ^{14}C kinetic isotope effect study does, however, argue strongly against **5** as a discrete intermediate.

Experimental Section

Materials. Phenylnitromethane was prepared from benzyl bromide and sodium nitrite by the procedure of Fukuyama et al.[1] Nitromethane and 1-chloro-2,4-dinitrobenzene were commercial products (Aldrich). Acetylacetone was available from a previous study.[11a] The purification of the amines and carboxylic acids has been described in a previous paper.[11a] Me_2SO was stored over 4-A molecular sieves prior to use.

Reaction Solutions. The solutions were prepared essentially as described before.[11a] For the 50% Me_2SO solutions, appropriate amounts of aqueous stock solutions were added to the Me_2SO and the volumetric flasks were topped off with water. For the 70% and 90% Me_2SO solutions, Me_2SO was added to the aqueous phase and the flasks were topped off with Me_2SO. Nitromethane and phenylnitromethane were introduced by injecting a few microliters of concentrated stock solutions in Me_2SO. pH measurements were performed as described previously.[11a]

pK_a^{CH} Measurements. pK_a^{CH} of phenylnitromethane was determined by classical spectrophotometric procedures in all solvents. The same method could be used for nitromethane in water and in 50% Me_2SO. In 70% and 90% Me_2SO, the pK_a values are so high that it was difficult to measure accurate pH values due to sluggish response of the glass electrode. Instead, a method was chosen whereby nitromethane was used as the buffer and phenoxide ion (in 70% Me_2SO) or *p*-chlorophenoxide ion (in 90% Me_2SO) as an indicator. For example, in 90% Me_2SO, an indicator concentration of 8×10^{-5} M *p*-chlorophenol was used with $[CH_3NO_2] + [CH_2{=}NO_2^-] = 0.004$ M. From the known $\epsilon = 3300\ M^{-1}\ cm^{-1}$ of *p*-chlorophenoxide ion at $\lambda_{max} = 313.5$ nm and its known $pK_a = 13.86$[31] in 90% Me_2SO, the pH value of the solution could be deduced for various $[CH_3NO_2]:[CH_2{=}NO_2^-]$ ratios and hence pK_a^{CH} calculated. The procedure in 70% Me_2SO was analogous.

Rate Measurements. All kinetic determinations were performed in a Durrum-Gibson stopped-flow apparatus with computerized data acquisition.[32] For reactions at $pH > pK_a^{CH}$, the nitroalkane was placed in a 10^{-3} M HCl solution of appropriate ionic strength and then mixed in the stopped-flow apparatus with the amine buffer or KOH solution. For reactions at $pH < pK_a^{CH}$, the nitroalkane was placed in a 10^{-3} M KOH solution and then mixed in the stopped-flow apparatus with the carboxylic or amine buffer or HCl solution. Due to gradual decomposition of the basic nitroalkane solution, particularly nitromethane, the stopped-flow experiments were executed immediately after preparing the solutions. In the experiments where formation of the nitronic acid was unimportant, the reactions were monitored at or near λ_{max} of the nitronate ion (for $CH_2{=}NO_2^-$, $\lambda_{max} = 233$ nm (ϵ 8400) in water, 248 nm (ϵ 5900) in 50% Me_2SO, and 258 nm (ϵ 6400) in 90% Me_2SO; for $PhCH{=}NO_2^-$, $\lambda_{max} = 289$ nm (ϵ 21 400) in water, 303 nm (ϵ 20 800) in 50% Me_2SO, and 326 nm (ϵ 22 300) in 90% Me_2SO). In those situations where phenylnitromethane nitronic acid (aci form) formation was extensive, the kinetic experiments were performed at λ_{max} of this latter (286 nm in 90% Me_2SO). This was not possible with nitromethane, though, because λ_{max} of $CH_2{=}NO_2H$ is buried in the Me_2SO absorption, and hence kinetic measurements with strongly acidic buffers could not be carried out.

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Supplementary Material Available: Kinetic data, Tables S1–12 (18 pages). Ordering information is given on any current masthead page.

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(32) Software developed by F. A. Brand.

Notes

A New Synthesis of Pentasubstituted Benzenes by Tandem Dimerization–Ring Opening of 3-Halo-2,5-dialkylthiophene 1,1-Dioxides

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We have recently studied the reactions of a series of 3-halo-2,5-dialkylthiophene 1,1-dioxides with various nucleophiles. We found, for example, that the reaction with secondary amines in toluene offered an excellent stereoselective route to one of the four possible dialkylaminomethyl-substituted halobutadienes.[1]

We have also studied the reaction with benzylthiolate and with various alkoxides.[2] In this connection, we treated 3-bromo-2,5-dimethylthiophene 1,1-dioxide with sodium *tert*-butoxide in *tert*-butyl alcohol. Instead of obtaining the addition products obtained with sodium ethoxide and sodium benzyl oxide, a crystalline compound, mp 63–63.5 °C, analyzed correctly as $C_{12}H_{13}Br$ was isolated. The yield of this product was increased by omitting the *tert*-butoxide and refluxing the *tert*-butyl alcohol solution for a longer period (120 h). The IR spectrum showed a weak band at 2230 cm^{-1}, indicating the presence of a disubstituted acetylene.

Its ^1H and ^{13}C NMR spectra indicated the presence of four nonequivalent methyl groups and one aromatic pro-

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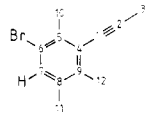
0022-3263/88/1953-3351$01.50/0

Table I. 1-(3-Bromo-2,5,6-trimethylphenyl)propyne (1) INADEQUATE NMR Coupling Constants (Hz)

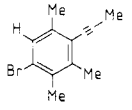


1

	J atom					
atom	2	4	6	8	10	12
1	180.64	90.81				
3	68.60					
5		59.99	66.02		47.92	
7			64.78	57.46		
9		62.26		58.46		45.71
11				44.80		

ton.

Its reaction with butyllithium followed by hydrolysis provided a new compound **3**, with two low-field protons at 6.96 and 6.94 ppm with a coupling constant of 7.9 Hz, characteristic for two benzenic ortho hydrogens, thus indicating that the primary product obtained in 90% yield was either 1-(3-bromo-2,5,6-trimethylphenyl)propyne (**1**) or 1-(4-bromo-2,3,6-trimethylphenyl)propyne (**2**).



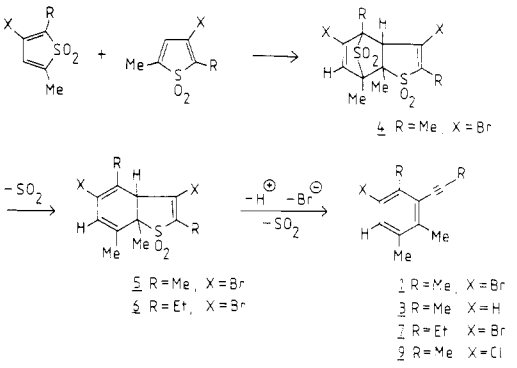
2

The structure was proven to be **1** by analyzing the INADEQUATE NMR spectrum. The $^{13}C-^{13}C$ couplings observed are given in Table I. A proposed reaction path is indicated in Scheme I. The first step is dimerization by cycloaddition to give **4** as an intermediate.[3] This reaction is regiospecific because the 4,5-bond in the dienophilic molecule is more reactive than the 2,3-bond for steric reasons. Furthermore, a dienophile with one electron-withdrawing group and an unsymmetrical diene with a 2-substituent are expected to react in such a way that the two substituents are para-oriented.[4] The intermediate extrudes sulfur dioxide to give 3,5-dibromo-2,4,7,7a-tetramethyl-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**5**). This then loses a proton, and the ring opens with the loss of bromide ion and sulfur dioxide to provide the product **1**.

Aromatization of the benzene ring is of course a strong driving force for the facile ring opening. Similar ring-opening elimination reactions leading to vinylacetylenes have previously been observed in this laboratory in the reaction of 3-bromo- and, especially, 3-chloro-2,5-dimethylthiophene 1,1-dioxides with organolithium compounds.[5,6]

That the reaction occurs in the indicated order was confirmed by the fact that heating of 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide for only 100 h gave a 25% isolated yield of 3,5-dibromo-2,4-diethyl-7,7a-dimethyl-3a,7a-dihydrobenzo[*b*]thiophene 1,1-dioxide (**6**), 50% of 1-(3-bromo-5,6-dimethyl-2-ethylphenyl)-1-butyne (**7**) and unreacted starting material. Heating of **6** in *t*-BuOH for 45 h gave a quantitative yield of **7**. Heating of 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide for 160 h gave **7** in 94% yield.

Scheme I

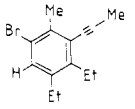


4 R = Me, X = Br

5 R = Me, X = Br
6 R = Et, X = Br

1 R = Me, X = Br
3 R = Me, X = H
7 R = Et, X = Br
9 R = Me, X = Cl

The reaction seems to be quite general. Thus, 3-bromo-5-ethyl-2-methylthiophene 1,1-dioxide furnished 1-(3-bromo-5,6-diethyl-2-methylphenyl)propyne (**8**) in 83% yield.[7] From 3-chloro-2,5-dimethylthiophene 1,1-dioxide, 1-(3-chloro-2,5,6-trimethylphenyl)propyne (**9**) was isolated in 75% yield.



8

Our results thus show that the tandem cycloaddition ring opening of 2,5-dialkylthiophene 1,1-dioxides opens a new short route to unsymmetrically pentasubstituted benzenes. We are continuing our investigation of the scope and limitations of this synthetic path.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 298 spectrometer and were in accordance with the proposed structures. The NMR spectra (^1H, ^{13}C, HETCOR, coupled ^{13}C, selective decoupling for compounds **1**, **3**, **7**, **8**, and **9**, INADEQUATE for compound **1**, ^1H and COSY for compound **6**; $CDCl_3$ as solvent) were recorded on a Varian XL 300 spectrometer. Quantitative gas chromatographic analyses were performed on a Varian 3300 gas chromatograph equipped with a 2-m column of 3% OV 17 on Gaschrom Q, 100–120 mesh, and a flame ionization detector. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatograph–mass spectrometer operating at 70 eV. Elemental microanalyses were performed at Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, West Germany. Column chromatography was carried out with Merck silica gel 60 (230–400 mesh ASTM) and pentane/chloroform (50/50) as eluent.

1-(3-Bromo-2,5,6-trimethylphenyl)propyne (1). A solution of 3-bromo-2,5-dimethylthiophene 1,1-dioxide[5] (22.3 g, 100 mmol) in *t*-BuOH (200 mL) was refluxed for 5 days (120 h). Removal

(3) Similar dimerizations of thiophene 1,1-dioxides have previously been observed: (a) Bailey, W. J.; Cummins, E. W. *J. Am. Chem. Soc.* **1954**, *76*, 1936. (b) Prochazka, M.; Horak, V. *Collect. Czech. Chem. Commun.* **1957**, *24*, 2278. (c) Mahan, J. E. U.S. Patent 2 786 851; 1957; *Chem. Abstr.* **1957**, *51*, 12146i. (d) Backer, H. J.; Melles, J. L. *Proc. K. Ned. Akad. Wet.*, **1951**, *54*, 340; *Chem. Abstr.* **1953**, *47*, 6932b. (e) Prochazka, M.; Horak, V. *Collect. Czech. Chem. Commun.* **1957**, *24*, 1509. (f) Walsh, J. P. *Diss. Abstr. Int.*, B. **1970**, 31, 1846 (with Hatch, L. F.). (g) Wrobel, J. T.; Kabzinska, K. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1974**, *22*, 129. (h) van Tilborg, W. J. M.; Smael, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 132. (i) van Tilborg, W. J. M. *Synth. Commun.* **1976**, *6*, 583. (j) Overberger, C. G.; Whelan, J. M. *J. Org. Chem.* **1961**, *26*, 4328. (k) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 856. (l) Bluestone, H.; Bimber, R.; Berkey, R.; Mandel, Z. *J. Org. Chem.* **1961**, *26*, 346. (m) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 867.

(4) Fleming I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1980; pp 132–140.

(5) Karlsson, J. O.; Gronowitz, S.; Hallberg, A. *Chem. Scr.* **1982**, *20*, 37.

(6) Karlsson, J. O.; Gronowitz, S.; Hallberg, A. *Acta Chem. Scand., Ser. B* **1982**, *36*, 341.

(7) In this particular case we observed that 4% of an isomeric compound was present in the crude material according to a GLC/MS analysis.

Table II. 1-(3-Bromo-2,5,6-trimethylphenyl)propyne (1) Coupled ^{13}C NMR Coupling Constants (Hz) and Chemical Shifts

		J				
atom	^{13}C δ	H3	H7	H10	H11	H12
1	77.7 (q)	4.4				
2	94.1 (q)	10.6				
3	4.4 (q)	131.4				
4	125.3 (br m)[a]					
5	136.5 (qv)		6.4	6.4		
6	121.2 (qv)		5.0	5.4		
7	132.2 (dq)		163.1		5.1	
8	135.1 (qv)				5.4	5.4
9	137.7 (br m)[a]					
10	21.3 (q)			128.0		
11	19.7 (qd)		5.0		126.8	
12	17.5 (q)					126.9

[a] Unresolved.

of the solvent followed by column chromatography afforded 1 (10.65 g, 90%), which crystallized from ethanol, mp 63–63.5 °C: IR 2230 cm^{-1} (C≡C stretch); ^1H NMR ($CDCl_3$) δ 7.26 (s, 1 H,4-H), 2.50 (s, 3 H,2-CH_3), 2.32 (s, 3 H, 6-CH_3), 2.20 (s, 3 H, acetylenic CH_3), 2.16 (s, 3 H, 5-CH_3). For INADEQUATE, see Table I, and the coupled ^{13}C coupling constants and chemical shifts are given in Table II. Mass spectrum, *m/e* 236/238. Anal. Calcd for $C_{12}H_{13}Br$: C, 60.78; H, 5.53; Br, 33.69. Found: C, 60.88, H, 5.55; Br, 33.63.

1-(2,3,6-Trimethylphenyl)propyne (3). A solution of *n*-BuLi in hexane (8.1 mL of 1.50 M, 12 mmol) was added dropwise to a stirred solution of 1-(3-bromo-2,5,6-trimethylphenyl)propyne (1) (1.43 g, 6 mmol) in dry ether (100 mL) at −70 °C under nitrogen. After being stirred for 4 h at 5 °C, the reaction mixture was hydrolyzed with (200 mL) of water. The organic phase was separated, and the aqueous phase was extracted three times with ether (3 × 50 mL). The combined ethereal phase was washed three times with H_2O (3 × 100 mL) and dried over ($MgSO_4$). Removal of the solvent followed by column chromatography afforded the dehalogenated product 3 as an oil (700 mg, 74%): IR 2220 cm^{-1} (C≡C stretch); 1H NMR ($CDCl_3$) δ 6.97 (d, 1 H, 5-H, *J* = 7.9 Hz), 6.93 (d, 1 H, 4-H, *J* = 7.9 Hz), 2.40 (s, 3 H, 6-CH_3), 2.39 (s, 3 H, 2-CH_3), 2.24 (s, 3 H, 3-CH_3), 2.16 (s, 3 H, acetylenic CH_3); mass spectrum, *m/e* 158. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.03; H, 8.91.

3,5-Dibromo-2,4-diethyl-7,7a-dimethyl-3a,7a-dihydrobenzo[*b*]thiophene 1,1-Dioxide (6). A solution of 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide[1] (2.37 g, 10 mmol) in *t*-BuOH (20 mL) was refluxed for 100 h. After removal of the solvent, the residue was dissolved in MeOH (10 mL), and H_2O (100 mL) was added. After standing for 15 h at −20 °C, the product was collected over a glass filter (0.5 g, 25%, mp 142–146 °C): ^1H NMR ($CDCl_3$) δ 6.08 (q, 1 H, 6-H, *J* = 1.5 Hz), 3.66 (s, 1 H, 3a-H), 2.73 (sxt, 1 H, 4-CH_2, *J* = 13.8, 7.5 Hz), 2.57 (q, 2 H, 2-CH_2, *J* = 7.6 Hz), 2.33 (sxt, 1 H, 4-CH_2, *J* = 13.8, 7.5 Hz), 1.99 (d, 3 H, 7-CH_3, *J* = 1.5 Hz), 1.52 (s, 3 H, 7a-CH_3), 1.23 (t, 3 H, 2-CH_3, *J* = 7.6 Hz), 1.64 (t, 3 H, 4-CH_3, *J* = 7.5 Hz); mass spectrum, *m/e* 410/412. Anal. Calcd for $C_{14}H_{18}Br_2O_2S$: C, 41.00; H, 4.42. Found: C, 40.86; H, 4.36.

1-(3-Bromo-5,6-dimethyl-2-ethylphenyl)-1-butyne (7). A solution of 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide[1] (2.37 g, 10 mmol) in *t*-BuOH (20 mL) was refluxed for 160 h. Removal of the solvent followed by column chromatography (Al_2O_3 neutral, pentane) afforded 7 as an oil (1.25 g, 94%): IR 2230 cm^{-1} (C≡C stretch); ^1H NMR ($CDCl_3$) δ 7.25 (s, 1 H, 4-H), 2.97 (q, 2 H, 2-CH_2, *J* = 7.5 Hz), 2.51 (q, 2 H, acetylenic CH_2, *J* = 7.5 Hz), 2.32 (s, 3 H, 5-CH_3), 2.20 (s, 3 H, 6-CH_3), 1.28 (t, 3 H, acetylenic CH_3, *J* = 7.5 Hz), 1.17 (3 H, 2-CH_3, *J* = 7.5 Hz); mass spectrum, *m/e* 264/266. Anal. Calcd for $C_{14}H_{17}Br$: C, 63.41; H, 6.46; Br, 30.13. Found: C, 63.50; H, 6.44; Br, 30.13.

1-(3-Bromo-5,6-diethyl-2-methylphenyl)propyne (8). A solution of 3-bromo-5-ethyl-2-methylthiophene 1,1-dioxide[5] (4.00 g, 17 mmol) in *t*-BuOH (30 mL) was refluxed for 240 h. Removal of the solvent followed by column chromatography afforded 8 as an oil (1.85 g, 83%): IR 2230 cm^{-1} (C≡C stretch); ^1H NMR ($CDCl_3$) δ 7.27 (s, 1 H, 4-H), 2.80 (q, 2 H, 6-CH_2, *J* = 7.5 Hz), 2.59 (q, 2 H, 5-CH_2, *J* = 7.6 Hz), 2.50 (s, 3 H, 2-CH_3), 2.15 (s, 3 H, acetylenic CH_3), 1.19 (t, 3 H, 5-CH_3, *J* = 7.6 Hz), 1.16 (t, 3 H, 6-CH_3, *J* = 7.5 Hz); mass spectrum, *m/e* 264/266. Anal. Calcd for $C_{14}H_{17}Br$: C, 63.41; H, 6.46; Br, 30.13. Found: C, 63.29; H, 6.45; Br, 30.23.

1-(3-Chloro-2,5,6-trimethylphenyl)propyne (9). A solution of 3-chloro-2,5-dimethylthiophene 1,1-dioxide[6] (1.79 g, 10 mmol) in *t*-BuOH (20 mL) was refluxed for 5 days (120 h). Removal of the solvent followed by column chromatography afforded 9 (0.72 g, 75%), which crystallized from ethanol, mp 49–51 °C: IR 2240 cm^{-1} (C≡C stretch); ^1H NMR ($CDCl_3$) δ 7.06 (s, 1 H, 4-H), 2.47 (s, 3 H, 2-CH_3), 2.34 (s, 3 H, 6-CH_3), 2.21 (s, 3 H, 5-CH_3), 2.16 (s, 3 H, acetylenic CH_3); mass spectrum, *m/e* 192/194. Anal. Calcd for $C_{12}H_{13}Cl$: C, 74.80; H, 6.80; Cl, 18.40. Found: C, 74.74; H, 6.78; Cl, 18.38.

Acknowledgment. Grants from the Swedish Natural Sciences Research Council to S.G. and A.H. are gratefully acknowledged.

Registry No. 1, 114532-51-3; 3, 114532-52-4; 6, 114532-53-5; 7, 114532-54-6; 8, 114532-55-7; 9, 114532-56-8; 3-bromo-2,5-dimethylthiophene 1,1-dioxide, 83173-98-2; 3-bromo-2-ethyl-5-methylthiophene 1,1-dioxide, 114532-57-9; 3-bromo-5-ethyl-2-methylthiophene 1,1-dioxide, 83173-99-3; 3-chloro-2,5-dimethylthiophene 1,1-dioxide, 70061-41-5.

Supplementary Material Available: Tables of coupled ^{13}C coupling constants and chemical shifts for compounds 3, 7, 8, and 9 (4 pages). Ordering information is given on any current masthead page.

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The Critical Hydrophobic Interaction Concentration for Aqueous Tetra-*n*-butylammonium Bromide

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In the course of our studies of medium effects on organic reactions in highly aqueous binary mixtures,[1] we recently defined the "critical hydrophobic interaction concentration" (chic)[2] for a hydrophobic cosolvent in aqueous solution. This is the concentration where the hydrophobic hydration shells of the cosolvent start to overlap appreciably, leading to cooperative association to small clusters. On the basis of kinetic[2] and spectroscopic[3] evidence, the chic for *t*-BuOH is 1.4 ± 0.3 m at 25 °C, in reasonable accord with Grunwald's isodelphic/lyodelphic analysis[4] of the solution thermodynamics of *t*-BuOH–H_2O. Since one may view the chic as an extension to small hydrophobic solutes of the concept of the critical micelle concentration (cmc)[5] for surfactant molecules, an endeavor was made to obtain evidence for a chic for *n*-Bu_4NBr. This

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