benzene washings were concentrated and cooled to give 150 mg (0.341 mmol, 23%) of a white solid, mp 195–196 °C (benzene). This solid is thought to be 10-phenyl-1,10′-biphenoxazine (**19**): parent peak at *m/e* 440.1461 ($C_{30}H_{20}N_2O_2$ requires *m/e* 440.1520); ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 3 H, aromatic), 7.05 (s, 4 H, aromatic), 6.92–6.32 (m, 10 H, aromatic), 6.19 (d of d, 1 H, *J* = 7.0, 2.0 Hz, H_9), 6.04–5.84 (m, 2 H, $H_{1',9'}$). The IR (Nujol) spectrum did not show an N–H stretch.

Anal. Calcd for $C_{30}H_{20}N_2O_2$ (**19**): C, 81.8; H, 4.55; N, 6.36. Found: C, 81.6; H, 4.65; N, 6.14.

The filtrate was evaporated and chromatographed on silica gel. Elution with 500 mL of 90:10 petroleum ether–benzene gave 55.5 mg (0.214 mmol, 7.2%) of **1**, mp 138–139 °C. Elution with 200 mL of 70:30 petroleum ether–benzene gave 146 mg (0.332 mmol, 22.3%) of a white solid: mp 162–164 °C (benzene); *m/e* (relative intensity) 441 (33), 440 (100), 363 (11), 259 (3), 182 (18); ^{1}H NMR ($CDCl_3$) δ 7.66–7.34 (m, 2 H, *o*-phenyl), 7.06 (s, 3 H, *m,p*-phenyl), 6.92–6.32 (m, 11 H, ring H), 6.26–6.07 (m, 2 H, $H_{1,9}$), 6.02–5.88 (m, 2 H, $H_{1',9'}$). The IR (Nujol) spectrum showed no N–H stretch. This compound is thought to be 10-phenyl-3,10′-biphenoxazine (**20**). Elution with 100 mL of 70:30 petroleum ether–benzene gave 52 mg of a mixture (ThLC) of two compounds, *m/e* 621 and 440. Elution with 250 mL of 50:50 petroleum ether–benzene gave 139 mg (0.224 mmol, 22.5%) of a white solid, mp 181–183 °C, thought to be 10-phenyl-3,10′:7(or 3′),10″-terphenoxazine (**21a** or **21b**). Parent peak at *m/e* 621.1926 ($C_{42}H_{27}N_3O_3$ requires *m/e* 621.2046); ^{1}H NMR ($CDCl_3$) δ 7.80–7.40 (m, 2 H, *o*-phenyl), 7.38 (s, 3 H, *m,p*-phenyl), 7.22–7.04 (m, 2 H, $H_{4,6(or\ 4')}$), 6.98–6.46 (m, 14 H, ring H), 6.46-5.90 (m, 6 H, $H_{1,1',1'',9,9',9''}$).

Half-wave oxidation potentials of 1–4 and 16 were measured by cyclic voltammetry in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. The acetonitrile was Eastman's anhydrous grade and was further dried by being passed through a column of predried alumina. The reference electrode was Ag/Ag^+ (0.1 M) and was calibrated against an SCE electrode. Half-wave potentials were measured at increasing scan rates and leveled off as follows: **1**, 0.36 V; **2**, 0.64 V; **3**, 0.50 V; **4**, 0.46 V; **16**, 0.46 V.[42]

Registry No. **1**, 37832-25-0; $1^{+}\cdot,ClO_4^-$, 67728-02-3; **2**, 71041-09-3; **3**, 71041-10-6; **4**, 71041-11-7; **5**, 71041-12-8; **6**, 71041-13-9; **7**, 71041-14-0; **8**, 71041-15-1; **9**, 71041-16-2; **10**, 6358-23-2; **11**, 20464-44-2; **12**, 6192-43-4; **13**, 71041-17-3; **14**, 71041-18-4; **15**, 71041-19-5; **16**, 71041-20-8; **17**, 71041-21-9; **18**, 71041-22-0; **19**, 71041-23-1; **20**, 71041-24-2; **21a**, 71041-25-3; 1-chloro-2,4-dinitrobenzene, 97-00-7; *o*-aminophenol, 95-55-6; iodobenzene, 591-50-4; 2-chlorophenoxazine, 56821-03-5; phenoxazine, 135-67-1; *p*-bromoiodobenzene, 589-87-7; bromobenzene, 108-86-1; NO_2^-, 14797-65-0; SCN^-, 302-04-5; Br^-, 24959-67-9; Cl^-, 16887-00-6; CH_3OH, 67-56-1; H_2O, 7732-18-5; CN^-, 57-12-5; O_2^-, 11062-77-4; butylamine, 109-73-9; diisopropylamine, 108-18-9; triethylamine, 121-44-8; F^-, 16984-48-8.

(42) We thank Mr. Michael T. Stephenson for making these measurements.

Bizarre Reactions of 2-Butyne during the Addition of Hydrogen Chloride[1]

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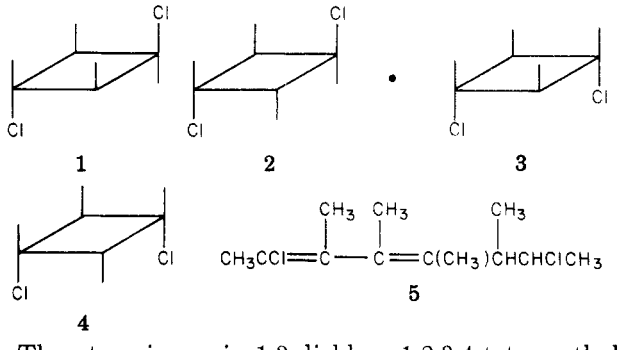
Liquid-phase reactions of anhydrous hydrogen chloride with 2-butyne at ambient temperatures were studied. In addition to the normal reaction products 13 compounds have been identified. They are chlorinated and nonchlorinated cyclic and acyclic dimers and trimers of 2-butyne.

In previous papers we have reported that liquid-phase reactions of anhydrous hydrogen bromide[2,3] and hydrogen chloride [2,4,5] with a series of monoalkylacetylenes resulted partly in 2 + 2 cycloadditions to afford products having four-membered ring structures. By contrast, in the reaction of excess hydrogen chloride with the dialkylacetylene 2-butyne under similar conditions, only 2,2-dichlorobutane was reported as a product.[6]

In continuation of our studies on electrophilically induced cycloaddition reactions, we have now reexamined this reaction with particular attention to the occurrence of nonconventional products.

Results

Reactions of hydrogen chloride with 2-butyne in a relative molar ratio of 5:1 at ambient temperatures gave complete conversions of the substrate within 10 days. GLC analysis of the crude, liquid reaction mixture showed the presence of at least 12 components, of which 11 could be identified. They are 2,2-dichlorobutane (major product, 60–70%), 2-chloro-1-butene,[7] (*Z*)- and (*E*)-2-chloro-2-butene,[7] pentamethylbenzene, hexamethylbenzene, and the hitherto unknown compounds **1**–**5**.[8]



The stereoisomeric 1,3-dichloro-1,2,3,4-tetramethylcyclobutanes **1**–**4** are colorless, crystalline solids. Their stereochemistry was assigned on the basis of the following ^{1}H NMR data (Table I). Isomer **1** exhibited one doublet

(1) Presented by H.S. at the 17th Hauptversammlung der Gesellschaft Deutscher Chemiker, München, 1977.
(2) K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Am. Chem. Soc.*, **87**, 3151 (1965).
(3) K. Griesbaum, W. Seiter, H. Schneider, M. El Abed, and Z. Rehman, *Justus Liebigs Ann. Chem.*, in press.
(4) K. Griesbaum, Z. Rehman, and U.-I. Záhorszky, *Angew. Chem.*, **82** 841 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 273 (1970).
(5) K. Griesbaum and M. El Abed, *Chem. Ber.*, **106**, 2001 (1973).
(6) Belgian Patent 666930 (1965), *Chem. Abstr.*, **65**, 7056e (1965).
(7) These unsaturated adducts may have been partly or totally formed by dehydrohalogenation of 2,2-dichlorobutane during GLC analysis, since they were also detected when pure 2,2-dichlorobutane was analyzed under the same conditions.
(8) The single bonds originating from the cyclobutane rings represent methyl groups.

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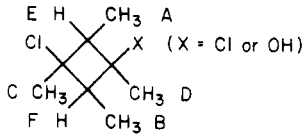
Table I. ^{1}H NMR Data of 1,3-Disubstituted 1,2,3,4-Tetramethylcyclobutanes



compd	solvent	chemical shifts of structural units, δ, ppm[a] A	B	C	D	E	F
1	$CDCl_3$		1.07 d[b]	1.53 s	1.67	2.88 q[b]	
	C_6D_6		0.90	1.27	1.46	2.66	
			Δ −0.17	Δ −0.26	Δ −0.21	Δ −0.22	
2	$CDCl_3$		1.16 d[b]	1.67 s		2.79 q[b]	
	C_6D_6		0.96	1.45 s		2.55	
			Δ −0.20	Δ −0.22		Δ −0.24	
3	$CDCl_3$		1.03 d[b]	1.37 s		3.40 q[b]	
	C_6D_6		0.67	1.03 s		3.49	
			Δ −0.36	Δ −0.34		Δ 0.09	
4	$CDCl_3$	1.31 d[b]	1.05 d[b]	1.57 s		2.36 q[b]	3.26 q[b]
	C_6D_6	1.37	0.72	1.28		2.07	3.30
		Δ 0.06	Δ −0.33	Δ −0.29		Δ −0.29	Δ 0.04
8d	CCl_4		0.95 d[b]	1.33 s	0.97 s	2.81 q[b]	
	C_6D_6		0.69	1.11	0.65	2.78	
			Δ −0.26	Δ −0.22	Δ −0.32	Δ −0.03	

[a] Me_4Si as internal standard. [b] J = 7 Hz.

signal for the methyl groups in the 2- and 4-positions, two singlet signals for the methyl groups in the 1- and 3-positions, and one quartet signal for the methine protons. Isomer **4** on the other hand, exhibited two doulets for the methyl groups in the 2,4-positions, one singlet for the CH_3 groups in 1,3-positions, and two quartets for the methine protons. These spectra could be only reconciled with structures **1** and **4**, respectively. By contrast, the remaining two cyclobutane compounds showed spectra of the same multiplicity (albeit with different chemical shifts of the respective signals), viz. one doublet for the methyl groups in the 2,4-positions, one singlet for the methyl groups in the 1,3-positions, and one quartet for the methine protons. A priori, these spectra were compatible with **2**, **3**, or the fifth possible isomer, 1,3-dichloro-*trans,trans,trans*-1,2,3,4-tetramethylcyclobutane. A distinction between these alternatives was possible by making use of the anisotropy effects[9] of hexadeuterated benzene (Table I). In C_6D_6 (as opposed to $CDCl_3$), all signals in the spectrum of **2** showed an upfield shift in the same order of magnitude (i.e., 0.20–0.24 ppm). This indicates that the molecule has no pronounced dipole moment and hence that the chlorine substituents are in the trans positions. With structure **1** already assigned, the only alternative for a trans isomer was structure **2**. In the spectrum of **3**, on the other hand, only the signals of the methyl groups showed a marked upfield shift of 0.34–0.36 ppm in C_6D_6, while the methine quartet showed a very minute shift (0.09 ppm) in the opposite direction. This is indicative of a dipole moment and hence a cis arrangement of the chlorine substituents in the molecule. Furthermore, in order to experience the same shift in sign and magnitude, all of the four methyl groups had to be arranged on the same side and in the trans position to the chlorine substituents, which is only possible in structure **3**.

Application of this method to isomers **1** and **4** was also in full agreement with their assigned stereochemistry. In the spectrum of **1** all signals showed upfield shifts of the same order of magnitude (0.17–0.26 ppm). By contrast, in the spectrum of **4** the substituents in the trans position to chlorine showed sizeable upfield shifts (0.29–0.33 ppm), whereas the substituents in the cis position to chlorine showed only minute shifts in the opposite direction (Table I).

2,7-Dichloro-3,4,5,6-tetramethylocta-2,4-diene (**5**) is a colorless, viscous liquid. IR, ^{1}H NMR, and mass spectra are in agreement with structure **5**. Spin decoupling experiments showed the coupling constant of the methine protons to be 10 Hz, which proves their vicinal positions. Further structure proof was obtained from ozone degradation in the presence of methanol, which, in an anomalous ozonolysis, afforded methyl acetate and a racemic mixture of (3*R*,4*R*)- and (3*S*,4*S*)-3-methyl-4-chloropentanone (**6**)

$$5 \xrightarrow[CH_3OH]{O_3} 3CH_3COOCH_3 + \underset{\mathbf{6}}{CH_3COCH(CH_3)CHClCH_3}$$

in a molar ratio of 3:1, respectively.[10] On the basis of this finding, **5** could be identified as a racemic mixture of (6*R*,7*R*)- and (6*S*,7*S*)-2,7-dichloro-3,4,5,6-tetramethylocta-2,4-diene. The stereochemistry at the double bonds of **5** could not be assigned.

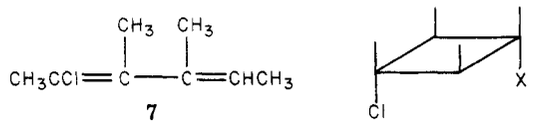
Quantitative GLC and ^{1}H NMR analyses of crude mixtures showed that the nonconventional reaction products were formed in the following approximate selectivities: pentamethylbenzene, 2%; hexamethylbenzene, 2%; 1,3-dichloro-1,2,3,4-tetramethylcyclobutanes (**1**–**4**), 1–2%; and 2,7-dichloro-3,4,5,6-tetramethylocta-2,4-diene (**5**), 15%.

Reactions of hydrogen chloride with 2-butyne in a 1:1 molar ratio at ambient temperatures did not result in complete conversion of 2-butyne within 10 days. GLC analysis of the crude, liquid reaction mixture showed the presence of many components, of which approximately seven were present in more than trace amounts. They are (*Z*)-2-chloro-2-butene as the major product, (*E*)-2-chloro-2-butene, 2,2-dichlorobutane, diene **5**, two stereoisomers of 2-chloro-3,4-dimethylhexa-2,4-diene (**7**), and 1-chloro-*cis,cis,cis*-1,2,3,4-tetramethyl-3-(3-chlorobut-2-en-2-yl)cyclobutane (**8a**).

The two stereoisomers of structure **7** were identified by GC/MS analysis of the crude reaction mixture and by coinjection of the authentic product which was obtained

(9) T. E. Clerk and E. Pretsch, "Kernresonanzspektroskopie", Akademische Verlagsgesellschaft, Frankfurt am Main, 1970, p 135.

(10) H. Schneider and K. Griesbaum, *Tetrahedron Lett.*, 57 (1979).



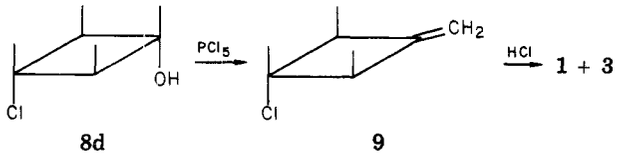
7

8a, X = $CH_3CCl{=}C(CH_3)$-
b, X = CH_3CO-
c, X = CH_3COO-
d, X = HO-

by thermal isomerization of 3-chloro-1,2,3,4-tetramethylcyclobutene.[11] The stereochemistry of the two isomers was not assigned.

Compound **8a** is a colorless liquid which could not be obtained in analytical purity. The structural assignment is based on its IR, ^1H NMR, and mass spectra and on the results of the following reactions. Ozone degradation in methanol produced a mixture of methyl acetate and ketone **8b**. Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid converted **8b** into the ester **8c**, which was subsequently reduced to the alcohol **8d** with lithium aluminum hydride. The stereochemistry of **8d** was again established by ^1H NMR spectroscopy (Table I). In C_6D_6 as opposed to $CDCl_3$ the signal of all methyl groups experienced upfield shifts of 0.22–0.32 ppm, while that of the methine protons showed almost no change in its position.

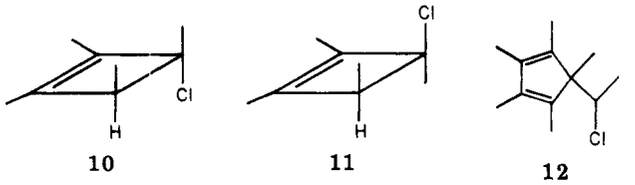
Sequential treatment of **8d** with phosphorus pentachloride and with anhydrous hydrogen chloride gave a mixture of the 1,3-dichloro-1,2,3,4-tetramethylcyclobutanes **1** and **3**. This provides additional proof for the structures assigned to compounds **8a–d** and to the stereochemical arrangement of the methyl groups in the 1-, 2-, and 4-positions of these compounds. The fact that **8d** gives both **1** and **3** does not contradict the assigned structures of **8a–d**, for, when following the reaction of **8d** with PCl_5 by GC/MS and ^1H NMR analysis, it was found that it proceeds via the intermediate formation of 1-chloro-1,2,4-trimethyl-3-methylenecyclobutane (**9**), thus extinguishing the stereochemical identity at the 3-position of the cyclobutane system in **8d**.



8d 9

Quantitative GLC and ^1H NMR analyses of crude reaction mixtures showed that the nonconventional products **7** and **8a** were formed in selectivities of 1 and 5%, respectively.

Reactions of hydrogen chloride with 2-butyne in a relative molar ratio of 1:2 at ambient temperatures gave a liquid reaction product. GLC analysis again showed the presence of many components, of which six were present in more than trace amounts. They are (*Z*)-2-chloro-2-butene, compounds **5** and **8a**, *cis*- (**10**) and *trans*-3-chloro-1,2,3,4-tetramethylcyclobutene (**11**), and 1-(1-chloroethyl)-1,2,3,4,5-pentamethylcyclopentadiene (**12**).



10 11 12

The stereoisomers **10** and **11** were not isolated individually, but as a 60:40 mixture, respectively. Their structures were assigned on the basis of GC/MS and ^1H NMR data. The latter had been published previously;[11] however no definite stereochemical assignment had been made. In the spectra of methyl-substituted 1,3-dihalocyclobutanes (e.g., compound **4**) the signals of the methine and of the methyl protons vicinal to the halo substituent appeared always at lower field positions if they were in the cis configuration to the halo group. Based on this experience, we assign cis geometry (**10**) to the isomer exhibiting its vicinal CH_3 signal at δ 1.03 and its methine signal at δ 3.04, and trans geometry (**11**) to the isomer showing the corresponding signals at δ 1.16 and 2.60, respectively (Table II).

Table II. ^1H NMR Data of 3-Chloro-1,2,3,4-tetramethylcyclobutenes

	chemical shifts of structural units,[a] ppm[b]	
compd	CH_3	H
10	1.03 d[c]	3.04 m
11	1.16 d[c]	2.60 m

[a] The correspondence of the CH_3 and H signals was established by spin-decoupling experiments. Upon irradiation of δ 3.04 (δ 2.60) the doublet at δ 1.03 (δ 1.16) collapsed into a singlet. [b] $CDCl_3$ as solvent, Me_4Si as internal standard. [c] J = 7 Hz.

Compound **12** has been identified by comparison of its IR, ^1H NMR, and MS data with those of an authentic sample. The latter has been obtained by addition of hydrogen chloride to Dewar hexamethylbenzene in a known procedure.[12]

Quantitative GLC analyses of crude reaction mixtures gave the following approximate selectivities for the nonconventional reaction products: compound **5**, 7%; compound **8a**, 8%; compounds **10** + **11**, 22%; and compound **12**, 6%.

Preliminary experiments have shown that the reaction temperature also has a pronounced effect upon the products and their distribution. Thus, by lowering the temperature from 35 to −30 °C, the selectivity for trimeric products was more than doubled. Furthermore, GLC analysis showed the appearance of new components which, according to GC/MS analysis, were composed of three and four molecules of 2-butyne.

It should be mentioned that the quantitative data reported above are average values and that the actual values differed considerably from one experiment to the other. This is not unexpected since the experiments were carried out in nonstirred reactors (sealed glass ampules) in which the conditions (homogeneity, temperature) could not be well adjusted.

Discussion

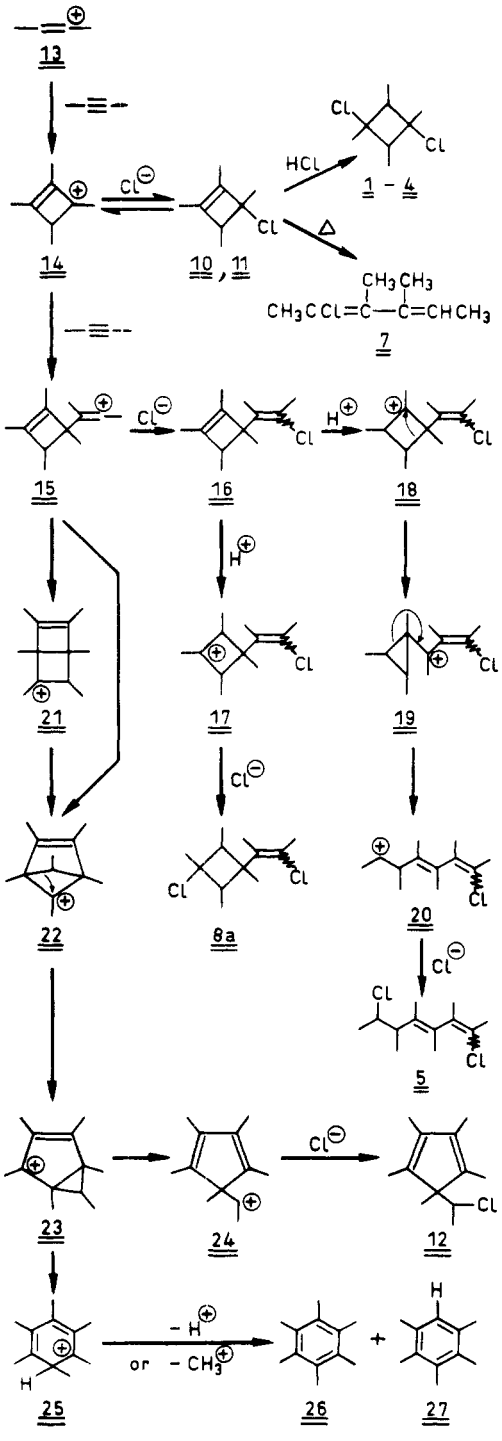
It is evident from the foregoing that the reaction of hydrogen chloride with 2-butyne is considerably more complex than was reported previously[6] and it affords a greater variety of products than we had obtained from the reaction of HCl with any other acetylenic substrate. Nevertheless, all of these products can be plausibly rationalized by the reaction sequences outlined in Scheme I.

The key intermediate is the vinylic cation **13**, which is formed by protonation of 2-butyne. It undergoes a 2 + 2 cycloaddition with 2-butyne to form cation **14**. The latter obviously has a choice of either reacting with chloride ion to form **10** + **11** or alkylating 2-butyne to form cation **15**.

(11) R. Criegee and W. Funke, *Chem. Ber.*, **97**, 2934 (1964).

(12) M. Kunz and W. Lüttke, *Chem. Ber.*, **103**, 315 (1970).

Scheme I



Depending on the HCl concentration, the monochlorides **10** and **11** may be partly or totally converted into the saturated compounds **1**–**4**. Alternatively, they may undergo ring opening to form the dienes **7**. We have not established whether in our case **7** is produced during the reaction or during GLC operations. It is known, however, that **10** and **11** are labile even at relatively low temperatures.[11]

The vinylic cation **15** has again a choice of either reacting with chloride ion to produce **16** or alkylating itself to produce cation **21** or **22**. Compound **16**, in turn, can react with hydrogen chloride at its reactive cyclobutene bond. Depending on the site of protonation, two different cationic intermediates, viz. **17** or **18**, can be formed. Intermediate **17** reacts with chloride ion to form **8a**. Intermediate **18**, on the other hand, may undergo ring contraction to form the more stable allylic cation **19**. Subsequent ring opening of the latter affords the homoallylic cation **20**, which in turn yields **5** upon reaction with chloride ion. Precedents for reactions as in steps **18** → **19**[13] and **19** → **20**[14] are known.

Cation **21** can undergo a sequence of rearrangements via **22** and **23** to eventually afford either **24** or **25**. Reaction of **24** with chloride ion produces **12**, deprotonation of **25** gives hexamethylbenzene (**26**), and demethylation of **25** yields pentamethylbenzene (**27**). The sequences **21** → **12** and **21** → **26** have been formulated previously for the reaction of Dewar hexamethylbenzene with hydrogen chloride.[15] Depending on the reaction conditions (i.e., temperature, HCl concentration, reaction time) either **12** and **26** or monochlorides derived from the cations **22** and **23** were obtained.[15]

Crucial intermediates in reactions of hydrogen halides with acetylenes are obviously cations of type **14**. The extent of the competition of halide ions and of acetylene substrate for cation **14** determines if and to what extent trimerization occurs. In reactions of hydrogen bromide with alkylacetylenes no trimerization products have been detected thus far, not even in the reaction with 2-butyne.[3] This probably reflects the enhanced nucleophilicity of bromide ion over that of chloride ion. In reactions of hydrogen chloride with alkylacetylenes, trimerization has been observed only with propyne.[16] However, the extent of trimerization was less (~10%) than with 2-butyne. This may be a reflection of the enhanced stability of the tetrasubstituted cation **14** over that of the corresponding disubstituted cation which is formed from propyne.[17] Possibly, this greater stability of **14** causes enhanced reversibility of step **14** → **10** + **11**, thus indirectly favoring the alkylating step **14** → **15**.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker WP 60, mass spectra on a Varian MAT 11, and IR spectra with a Beckman Acculab 1 instrument. GLC analyses were carried out on a Varian Aerograph 1400-1 and preparative GLC was carried out on a Perkin-Elmer F-21 instrument.

All reactions of hydrogen chloride with 2-butyne were carried out in thick-walled glass ampules. 2-Butyne was directly introduced, and then the ampule was connected to a vacuum system, cooled with liquid air, and evacuated. Hydrogen chloride was introduced via the vacuum system and condensed into the ampule. Subsequently, the ampule was sealed and placed in a water bath at ambient temperatures. After the reaction, the ampule was again cooled by liquid air, opened, connected to a drying tower, and then allowed to warm up to room temperature, whereby most of the unreacted hydrogen chloride evaporated.

Reactions of HCl with 2-Butyne in a Molar Ratio of 5:1. In a 350-mL ampule 11.8 g (0.33 mol) of HCl and 3.5 g (0.065 mol) of 2-butyne was reacted for 10 days. After evaporation of unreacted HCl there remained 7.0 g of a dark red, mobile liquid which was analyzed by GLC (column 0.3 × 500 cm, 5% Carbowax 20 M on Chromosorb G; 60–160 °C at 2 °C/min; injector temperature 220 °C).

The combined crude products of several reactions (115 g) were distilled. In order to minimize decomposition or rearrangement of sensitive components, distillation was carried out such that the boiling points were kept low by gradually decreasing the pressure. The following fractions were obtained at a bath

(13) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions", Vol. 3, Wiley-Interscience, New York, 1972, p 1332 ff.
(14) W. K. Chwang, P. Knittel, K. M. Kosky, and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 3395 (1977).
(15) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 3197 (1972).
(16) K. Griesbaum, A. Singh, and M. El Abed, *Tetrahedron Lett.*, 1159 (1978).
(17) G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *J. Am. Chem. Soc.*, **97**, 5489 (1975).

temperature of 60 °C: fraction 1, bp 44–43 °C (100–93 mm), 18.0 g; fraction 2, bp 43–20 °C (93–20 mm), 55.0 g; fraction 3, ~20 °C (20–0.01 mm), 2.5 g. Additional distillates were obtained by maintaining the pressure at 0.01 mm and gradually increasing the bath temperature: fraction 4, bath temperature 60–90 °C, 1.5 g; fraction 5, bath temperature 90–120 °C, 1.5 g; fraction 6, bath temperature 120–160 °C, 2.0 g.

Fraction 1 contained mainly 2,2-dichlorobutane and the monoadducts 2-chloro-1-butene as well as (*Z*)- and (*E*)-2-chloro-2-butene. They were identified on the basis of their GLC retention times with the help of authentic samples[5] and by GC/MS analysis. Fraction 2 consisted of 2,2-dichlorobutane. Fraction 3 contained compounds **1–5** and **27**. They were isolated by preparative gas chromatography (column: 0.8 × 450 cm, 5% Carbowax 20 M on Chromosorb G; 100–160 °C at 3 °C/min; injector temperature 170 °C). Fractions 5 and 6 contained hexamethylbenzene (**26**), which precipitated when the fractions were kept in the refrigerator at −20 °C.

1,3-Dichloro-*cis*,*trans*,*trans*-1,2,3,4-tetramethylcyclobutane (1): mp 91–92 °C; ^{1}H NMR see Table I; IR (CCl_4) 2980, 2960, 2930, 2870, 1455, 1445, 1382, 1372, 1150, 1115, 1060, 960, 860 cm^{-1}; MS *m/e* (rel intensities) 117, 119 (15, 5), 90, 92 (87, 28), 83 (52), 81 (18), 55 (100).

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.06; H, 7.79; Cl, 39.15. Found: C, 53.26; H, 7.82; Cl, 38.73.

1,3-Dichloro-*trans*,*cis*,*trans*-1,2,3,4-tetramethylcyclobutane (2): mp 52–55 °C; ^{1}H NMR see Table I; IR (CCl_4) 2980, 2940, 2870, 1460, 1450, 1385, 1170, 1120, 1050, 975, 860 cm^{-1}; MS *m/e* (rel intensities) 117, 119 (9, 4), 90, 92 (100, 36), 83 (44), 81 (15), 55 (100).

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.06, H, 7.79; Cl, 39.15. Found: C, 53.30; H, 7.81; Cl, 38.83.

1,3-Dichloro-*cis*,*cis*,*cis*-1,2,3,4-tetramethylcyclobutane (3): mp 113–115 °C; ^{1}H NMR see Table I; IR (CCl_4) 2985, 2940, 2880, 1465, 1450, 1400, 1380, 1272, 1160, 1100, 1060, 970 cm^{-1}; MS *m/e* (rel intensities) 117, 119 (50, 17), 90, 92 (83, 28), 83 (122), 81 (28), 55 (100).

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.06; H, 7.79; Cl, 39.15. Found: C, 52.64; H, 7.56; Cl, 38.95.

1,3-Dichloro-*trans*,*trans*,*cis*-1,2,3,4-tetramethylcyclobutane (4): mp 67–69 °C; ^{1}H NMR see Table I; IR (CCl_4) 2980, 2940, 2880, 1465, 1453, 1390, 1380, 1237, 1160, 1070, 1037, 980 cm^{-1}; MS *m/e* (rel intensities) 117, 119 (10, 4), 90, 92 (104, 34), 83 (26), 81 (8), 55 (100).

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.06; H, 7.79; Cl, 39.15. Found: C, 53.41; H, 7.77; Cl 39.02.

2,7-Dichloro-3,4,5,6-tetramethylocta-2,4-diene (5): viscous, colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.08 (d, 7 Hz, 3 H), 1.53 (d, 7 Hz, 3 H), 1.68 (m, 3 H), 1.73 (m, 3 H), 1.95 (m, 6 H), 2.60 (m, 7 and 10 Hz, 1 H), 3.87 (m, 7 and 10 Hz, 1 H); IR (neat) 2995, 2950, 2935, 2890, 2870, 1670, 1655, 1465, 1455, 1390, 1382, 1240, 1110, 1070, 960, 720, 680 cm^{-1}; MS *m/e* (rel intensities) 234, 236, 238 (29, 17, 3, M^+), 171, 173 (50, 20), 163 (45).

Anal. Calcd for $C_{12}H_{20}Cl_2$: C, 61.28; H, 8.57; Cl, 30.14. Found: C, 61.46; H, 8.52; Cl 29.98.

Penta- (**27**)[18a] and hexamethylbenzene (**26**)[18b] were identified by comparison of their ^{1}H NMR and MS spectra with literature data.

Reactions of HCl with 2-Butyne in a Molar Ratio of 1:1. In a 350-mL ampule 17.7 g (0.49 mol) of HCl and 24.5 g (0.45 mol) of 2-butyne were reacted for 10 days. After evaporation of unreacted HCl 40 g of a dark red liquid remained. It was analyzed by GLC (column and conditions as above).

GC/MS analysis of the crude reaction product afforded the following MS data for the two components which were assigned structure **7**: *m/e* (rel intensities) 144, 146 (57, 21, M^+), 129, 131 (7, 3), 109 (98), 93 (26), 91 (30), 81 (39), 79 (29), 77 (43), 67 (100). The four isomers of structure **7** which were obtained by the pyrolysis of 3-chloro-1,2,3,4-tetramethylcyclobutene[11] gave the same MS data and two of them had retention times identical with those of the isomers of **7** obtained from 2-butyne.

The combined crude products of several reactions (240 g) were distilled to isolate compound **8a** which, due to its thermal instability, could not be purified by preparative GLC. It was obtained in a small fraction of 1.3 g, contaminated by small amounts of compound **5**.

1-Chloro-*cis*,*cis*,*cis*-1,2,3,4-tetramethyl-3-(3-chlorobut-2-en-2-yl)cyclobutane (8a): colorless liquid; bp 110 °C (0.6–0.2 Torr); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94 (s, 3 H), 1.08 (d, 7 Hz, 6 H), 1.46 (s, 3 H), 1.75 (q, 1.3 Hz, 3 H), 2.08 (q, 1.3 Hz, 3 H), 3.03 (q, 7 Hz, 2 H); MS *m/e* (rel intensities) 234, 236, 238, (9, 6, 1, M^+), 171, 173 (38, 13), 163 (63), 147 (75), 135 (100).

Ozonolysis of 8a. A solution of 1.30 g of **8a** in 10 mL of methanol was ozonized at −78 °C. Distillation afforded 0.3 g of ketone **8b**: bp 70–74 °C (1 mm); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.00 (d, 7 Hz, 6 H), 1.06 (s, 3 H), 1.49 (s, 3 H), 2.08 (s, 3 H), 3.11 (q, 7 Hz, 2 H); IR (neat) 1710 cm^{-1}; MS *m/e* (rel intensities) 188, 190 (1.5, 0.5, M^+), 173, 175 (2, 1), 153 (15), 43 (100).

Baeyer–Villiger Oxidation of 8b. A solution of 0.5 g (2.6 mmol) of **8b**, 1.0 g (5 mmol) of *m*-chloroperbenzoic acid, and 0.5 mL of trifluoroacetic acid in 20 mL of chloroform was warmed to 55 °C for 20 min. It was left standing at room temperature overnight and was then treated with an aqueous solution of 20% sodium bisulfite and 10% potassium hydroxide. Finally, it was washed with water and dried over sodium sulfate and the solvent was evaporated at 30 °C (20 mm). The residue (0.54 g) was a colorless liquid (**8c**): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.06 (d, 7 Hz, 6 H), 1.22 (s, 3 H), 1.36 (s, 3 H), 2.07 (s, 3 H), 3.06 (q, 7 Hz, 2 H); IR (neat) 1735 cm^{-1}; MS *m/e* (rel intensities) 169 (1.4), 43 (100).

$LiAlH_4$ Reduction of 8c. To a suspension of 19 mg (0.5 mmol) of $LiAlH_4$ in 5 mL of ether 50 mg (0.24 mmol) of **8c** was added. The mixture was left at room temperature for 4 h. Then, a mixture of concentrated HCl and ice was added. The organic phase was separated, the aqueous phase was extracted with ether, the extracts were combined with the organic phase and dried over Na_2SO_4, and the ether was removed at 20 mm. The remaining solid residue (30 mg) was sublimated at 100 °C (20 mm) to give 7 mg of **8d**.

3-Chloro-*cis*,*cis*,*cis*-1,2,3,4-tetramethylcyclobutanol (8d): colorless solid, mp 81–83 °C; ^{1}H NMR see Table I; IR (KBr) 3280, 2980, 2940, 2880, 1470, 1460, 1442, 1390, 1382, 1350, 1270, 1210, 1165, 1125, 1108, 1060, 1015, 970, 930, 845, 800, 723, 680 cm^{-1}; MS *m/e* (rel intensities) 126 (20), 111 (81), 83 (94), 55 (100).

Anal. Calcd for $C_8H_{15}OCl$: C, 59.07, H, 9.30; Cl, 21.80. Found: C, 58.90; H, 9.14; Cl 22.08.

Reaction of 8d with PCl_5 and HCl. A mixture of 15 mg (0.09 mmol) of **8d** and 55 mg (0.26 mmol) of PCl_5 in 1 mL of deuterated chloroform was heated to 60 °C for 2 min in an ampule. The product was analyzed to give the following data, consistent with structure **9**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.81 (d, 7 Hz, 6 H), 1.16 (s, 3 H), 3.25 (m, 7 and 2.5 Hz, 2 H), 4.61 (t, 2.5 Hz, 2 H); GC/MS *m/e* 144, 146 (M^+), 109 ($M - Cl)^+$. Then 0.8 mL of anhydrous hydrogen chloride was condensed into the ampule and the sealed ampule was left at room temperature for 3 h. The crude reaction product was washed with water and dried over magnesium sulfate, and the solvent removed at 20 mm. The solid residue was sublimated at 100 °C (20 mm) to give 3 mg (19%) of a 1:3 mixture of **1** and **3**, as shown by ^{1}H NMR and GLC analysis with the help of authenic samples.

Reactions of HCl with 2-Butyne in a Relative Molar Ratio of 1:2. In a 350-mL ampule 8.9 g (0.25 mol) of HCl and 24.5 g (0.45 mol) of 2-butyne was reacted for 10 days. After evaporation of unreacted HCl, 30 g of a dark red, mobile liquid remained. It was analyzed by GLC (column 0.3 × 100 cm, 5% Carbowax 20 M on Chromosorb G, 60–160 °C at 10 °C/min; injector temperature 220 °C) and then distilled to obtain the following fractions: fraction 1, 32 °C (120 mm), 1.7 g; fraction 2, 60 °C (18 mm), 4.8 g; fraction 3, 100 °C (0.2 mm), 2.3 g. The major amount of the distillate (15.8 g) was collected in the cold trap. It consisted of 2-butyne (30%) and (*Z*)-2-chloro-2-butene (70%). Fraction 1 consisted mainly of (*Z*)-2-chloro-2-butene. Fraction 2 consisted of the stereoisomers **10** and **11** and fraction 3 contained a mixture of the trimers **5**, **8a**, and **12** (30%). Compound **12** was isolated by preparative gas chromatography (column 0.8 × 180 cm, 5% Carbowax 20 M on Chromosorb G, 100–160 °C at 5 °C/min; injector temperature 170 °C).

***cis*-(10) and *trans*-3-Chloro-1,2,3,4-tetramethylcyclobutene (11)**:[11] colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si, data obtained at mixture of isomers) **10** δ 1.03 (d, 7 Hz, 3 H), 1.50–1.70

(18) (a) J. G Grasselli, "Atlas of Spectroscopic Data and Physical Constants for Organic Compounds", CRC Press, Cleveland, Ohio, 1973, no. b 1060; (b) *ibid.*, no. b 936.

(overlapping signals, 9 H), 3.04 (m, 1 H), 11 δ 1.16 (d, 7 Hz, 3 H), 1.50–1.70 (overlapping signals, 9 H), 2.60 (m, 1 H); MS *m/e* (rel intensities) 144, 146 (13, 5), 109 (18), 108 (30), 93 (100).

1-(1-Chloroethyl)-1,2,3,4,5-pentamethylcyclopenta-2,4-diene (12): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.07 (d, 6.5 Hz, 3 H), 1.13 (s, 3 H), 1.60–1.90 (overlapping signals, 15 H), 4.15 (q, 6.5 Hz, 1 H); MS *m/e* (rel intensities) 198, 200 (9, 3), 163 (39), 162 (30), 147 (100), 135 (13); IR (neat) 1670, 1660 cm^{-1}. These data were identical with those of an authentic sample, prepared by a known procedure.[12]

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Registry No. 1, 71031-67-9; 2, 71049-88-2; 3, 71049-89-3; 4, 71049-90-6; 5, 71031-68-0; (±)-(*R**,*R**)-6, 70359-35-2; 7, 71031-69-1; 8a, 71031-70-4; 8b, 71031-71-5; 8c, 71031-72-6; 8d, 71031-73-7; 9, 71031-74-8; 10, 71031-75-9; 11, 71031-76-0; 12, 19835-61-1; 26, 87-85-4; 27, 700-12-9; 2-butyne, 503-17-3; 2,2-dichlorobutane, 4279-22-5; 2-chloro-1-butene, 2211-70-3; (*Z*)-2-chloro-2-butene, 2211-69-0; (*E*)-2-chloro-2-butene, 2211-68-9; hydrogen chloride, 7647-01-0.

Gas-Phase Reaction of Benzothiophene with Hydrogen Atoms

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Reaction of benzothiophene with hydrogen atoms was studied at a pressure of 8 torr and at temperatures ranging from 423 to 853 K by using a conventional discharge flow reactor. 1-Thiaindan, dihydro-1-thiaindans, and dihydrobenzothiophenes were the main products at lower temperatures. But at higher temperatures, phenyl vinyl sulfide became the outstanding product. The sharply contrasted reactivity of benzothiophene as compared with that of thiophene was accounted for by a unique 3-position attack by a hydrogen atom and in terms of chemically activated intermediates.

The gas-phase reactions of the thiirane–hydrogen system[1] and 3-thiolene–hydrogen system[2] at room temperature have been shown to form ethylene and butadiene, respectively. A unique one-step abstraction of divalent sulfur by a H atom has been proposed as a plausible mechanism in these instances where the reaction path is highly stabilized by π conjugation. In the thiolane–hydrogen system, on the contrary, the sulfur elimination has been shown to take place through chemically activated butanethiol.[3]

The highly specific desulfurization of thiophene in its reaction with H atoms has been suggested to proceed through the reaction path distinctly different from those of the two typical cases mentioned above. Butadiene, the exclusive product of the system, could be formed via energized 3-thiolene[2] or alternatively via the 1,3-butadienylthio radical.[4]

The present study deals with the gas-phase reaction of the benzothiophene–hydrogen system as an extention of the series and intends specifically to clarify the role of chemically activated intermediates in the course of the sulfur elimination and to relate the possible mechanism with that of the thiophene–hydrogen system.

Experimental Section

The apparatus, full details of which have been described elsewhere,[5] consists of a quartz discharge flow reactor of 350-mm length and 27-mm diameter. The reaction was carried out under a total pressure of 8 torr and at temperatures ranging from 423 to 853 K. The temperature was measured by a chromel–alumel thermocouple placed along the central axis of the reactor and was maintained within ±2 K of the recorded value through the reaction zone.

Table I. Reaction of Benzothiophene

		flow rate, μmol/s				
T, K	*P*, torr	benzothiophene × 10^2	H_2	N_2	reacn time, s	convrsn, %
423	8.0	1.58	37.1	52.1	0.40	7.3
465	8.3	0.61	31.9	51.6	0.39	13.7
568	8.0	1.96	36.6	52.1	0.29	12.3
673	8.3	1.65	36.6	51.6	0.26	12.0
733	8.2	1.06	36.1	51.6	0.23	9.8
785	8.0	0.80	37.3	51.6	0.21	15.9
853	8.0	0.16	37.3	51.6	0.19	9.5

Substrate vapor was introduced along with flowing nitrogen into the reactor from a reservoir immersed in a bath thermostated at temperatures from 353 to 363 K. Products were first collected in an ampule chilled by liquid nitrogen, then dissolved in ether, and finally analyzed by a gas chromatograph equipped with a flame ionization detector. GC peak areas were corrected for detector response. Gaseous products isolated by bulb-to-bulb fractionations were directly introduced into the GC column. A combined GC/MS technique was used for the identification of sulfur compounds.

Commercial reagent grade benzothiophene, having more than 98% purity as analyzed by GC, was used without further purification. Phenyl vinyl sulfide,[6] 1-thiaindan,[7] and *o*-ethyl-

(1) T. Yokota, M. G. Ahmed, I. Safarik, and O. Strausz, *J. Phys. Chem.*, **79**, 1758 (1975).
(2) O. Horie, J. Nishino, and A. Amano, *J. Org. Chem.*, **43**, 2800 (1978).
(3) O. Horie, K. Onuki, and A. Amano, *J. Phys. Chem.*, **81**, 1706 (1977).
(4) O. Horie, N. H. Hanh, and A. Amano, *Chem. Lett.*, 1015 (1975).
(5) O. Horie and N. H. Hanh, *J. Phys. Chem.*, **80**, 1675 (1976).
(6) F. Montanari, *Boll. Sci. Fac. Chim. Ind. Bologna*, **14**, 55 (1956); *Chem. Abstr.*, 57236 (1957).
(7) S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Inst. Pet., Abstr.*, **40**, 76 (1954).

0022-3263/79/1944-3321$01.00/0