these measurements are subject to rather large errors, particularly at high values of [enolate]/[LiX], certain trends are immediately obvious. The rates of the forward reaction (A,B → X,Y) are relatively insensitive to changes in absolute concentrations, provided [enolate]/[LiX] is maintained constant, but they are sensitive to this ratio. In contrast, the back reaction (X,Y → A,B) is insensitive to both these factors. These observations are consistent with the mechanism given below, in which the exchange of magnetization between the two sites is effected through the intermediacy of a free enolate ion. The data in Table IV can be analyzed in terms of this mechanism in a manner which follows closely that developed by Williams and Brown[18] for exchange of ^{7}Li and ^{1}H between $(CH_3Li)_4$ and $Li_2Zn(CH_3)_4$. We note that the data refer to 25° at which temperature only the "high temperature" form of the halide free enolate is present.

$$\underset{\mathrm{C}}{\mathrm{Li_5(enolate_4^*\ Cl)}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{A}}{\mathrm{Li_5(enolate_3^*\ Cl)^+}} + \underset{\mathrm{E}}{\mathrm{enolate^{*-}}}$$

$$\underset{\mathrm{E}}{\mathrm{enolate^{*-}}} + \underset{\mathrm{D}}{\mathrm{Li}_n\mathrm{(enolate)}_n} \xrightarrow{k_2} \underset{\mathrm{D^*}}{\mathrm{Li}_n\mathrm{(enolate^*)(enolate)}_{n-1}} + \mathrm{enolate}$$

Employing the steady state assumption for E

$$\begin{aligned} \mathrm{d(E)/d}t &= k_1\mathrm{(C)} - k_{-1}\mathrm{(A)(E)} - k_2\mathrm{(E)(D)} \\ &= k_1\mathrm{(C)} - k_{-1}\mathrm{(E)}^2 - k_2\mathrm{(E)(D)} = 0 \\ \mathrm{(E)} &= k_1\mathrm{(C)}/[k_{-1}\mathrm{(E)} + k_2\mathrm{(D)}] \\ \mathrm{d(D^*)/d}t &= k_2\mathrm{(E)(D)} = k_1k_2\mathrm{(C)(D)}/[k_{-1}\mathrm{(E)} + k_2\mathrm{(D)}] \end{aligned}$$

If $k_{-1}\mathrm{(E)} \ll k_2\mathrm{(D)}$

$$\mathrm{d(D^*)/d}t = k_1\mathrm{(C)}$$

If (T) is the total enolate concentration in all forms

$$\mathrm{(C)} = p_\mathrm{X}\mathrm{(T)}/4,\ \mathrm{(D)} = p_\mathrm{A}\mathrm{(T)}/n$$

$$1/\tau_{\mathrm{A,B}} = (1/n\mathrm{(D)})(\mathrm{d(D^*)/d}t) = k_1\mathrm{(C)}/n\mathrm{(D)} = k_1p_\mathrm{X}/4p_\mathrm{A} \quad (1)$$

$$1/\tau_{\mathrm{X,Y}} = (1/4\mathrm{(C)})(\mathrm{d(D^*)/d}t) = k_1/4 \quad (2)$$

The data in Table IV can be used to test eq 1 and 2. For the chloride system $1/\tau_{\mathrm{A,B}}$ correlates well (r = 0.993) with $p_\mathrm{X}/p_\mathrm{A}$ and leads to k_1 = 71 ± 4 sec^{-1}. $1/\tau_{\mathrm{X,Y}}$ is reasonably constant and corresponds to k_1 = 91 ± 14 sec^{-1}. For bromide systems the corresponding values are 46.4 ± 3.6 and 60 ± 8 sec^{-1}. In both cases a small upward trend in $1/\tau_{\mathrm{X,Y}}$ with increasing halide concentration is apparent and similar trends are seen in the somewhat analogous systems studied by Williams and Brown.[18] It is possible that this is the result of increasing ionic strength, and certainly the values of k_1 calculated from $1/\tau_{\mathrm{X,Y}}$ and $1/\tau_{\mathrm{A,B}}$ are in better agreement at low halide concentrations.

The free energies of activation for dissociation of an enolate ion from these complexes are of the order of 15–16 kcal mol^{-1}, most of which is attributable to the enthalpies of activation. Effects of this magnitude are clearly capable of influencing the reactions of enolate ions in the presence of halide ions, a possibility which we are currently investigating.

(18) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4132, 4140 (1966).

Use of Thieno[2,3-*b*]thiophene in the Synthesis of Heterohelicenes by Double Photocyclizations

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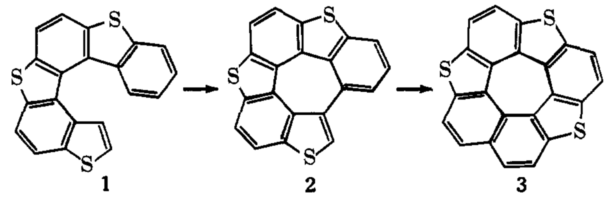
Contribution from the Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands. *Received October 2, 1972*

Abstract: Five new heterohexahelicenes were prepared. Two new elements in heterohelicene synthesis have been introduced: (a) double photocyclizations and (b) the use of thieno[2,3-*b*]thiophene (**4**) as a building block for helicenes. In the nmr spectrum of one of the helicenes (**6**) "through-space coupling" is observed. The unusual spectral properties of helicenes containing the thiophthene moiety are discussed.

Ever since the discovery and preparation of hexahelicene,[1] this compound has fascinated many chemists. Groen and Wynberg developed the chemistry and determined the absolute configuration of the heterohelicenes.[2] Recently we reported the first synthesis of a [7]heterocirculene **3**.[3] We wish to draw attention to the fact that with the preparation of this circulene **3** use has been made for the first time of the unique structural properties of the helicenes in the preparatively useful synthesis of other interesting com-



1 **2** **3** (1)

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(1) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

(2) (a) H. Wynberg and M. B. Groen, *ibid.*, **90**, 5339 (1968); **92**, 6664 (1970); (b) *Chem. Commun.*, 964 (1969); (c) M. B. Groen, H. Schadenberg, and H. Wynberg, *J. Org. Chem.*, **36**, 2797 (1971); (d) M. B. Groen and H. Wynberg, *J. Amer. Chem. Soc.*, **93**, 2968 (1971); (e) M. B. Groen, G. Stulen, G. J. Visser, and H. Wynberg, *ibid.*, **92**, 7218 (1970).

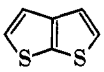
(3) J. H. Dopper and H. Wynberg, *Tetrahedron Lett.*, 763 (1972).

Table I. Preparation of Alkenes and Helicenes

Alkene	From	Yield, %	Mp, °C	By irradiation	Helicene	Yield, %	Mp, °C
15	**13** + **11**	75	244–246		**6**	69	210–211.5
16	**14** + **11**	78	245.5–246.5		**7**	60	220–222
19	**17** + **12**	95	325–327		**8**	51	279–280
20	**18** + **12**	91	329–332		**9**	50	289–291.5
25	**27** + **29**	23	277–279[a]		**10**	50	240–241
25	**17** + **28**	57	279–280[a]				

[a] Probably corresponding to the trans–trans isomer.

pounds.[4] Thus a completely new dimension to the role that heterohelicenes[5,6] have played in chemistry has been added by the synthesis of **3** from **1** (eq 1). This use of helicenes as starting materials for the synthesis of circulenes (and possibly other aromatics) has prompted us to study alternate routes for the preparation of the former. Simultaneously, five novel helicenes, embodying a new heteroaromatic moiety, were prepared. The alternate routes make use of (a) double photocyclizations, a method which has been shown to be eminently useful in the synthesis of benzohelicenes by Martin,[7ab] but unsuitable in heterohelicene synthesis until now;[2c] and (b) thieno[2,3-*b*]thiophene (**4**)[8] as a building block for helicenes.



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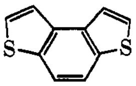

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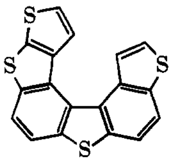

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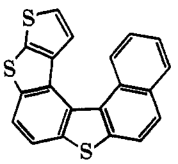

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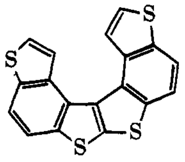

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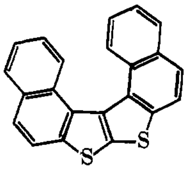

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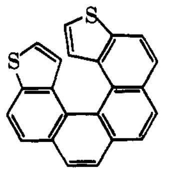

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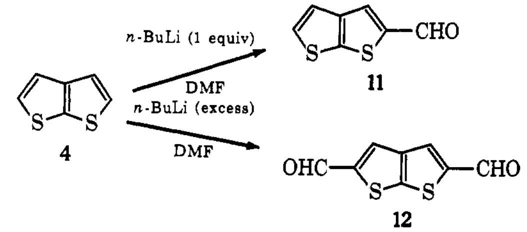
One of the great advantages in the irradiation of 1,2-di(hetaryl)ethenes over that of 1,2-diarylethenes is that cyclizations in the former can occur only in one way.[2c,9] From a synthetic point of view this unique cyclization is the principal reason for using benzodithiophene **5** as a central structural unit. In our present synthesis this principle is illustrated by using **4** as one of the main building blocks for the helicenes **6**, **7**, **8**, and **9**. Thiophthene **4** was found to have distinct advantages in the synthesis of heterohelicenes. A large-scale preparation[10] of **4** as well as convenient synthesis (in about 50% yields) of **11** and **12** by mono- and dilithiation reactions of **4**, followed by formylation with DMF, could be realized[11ab] (eq 2).

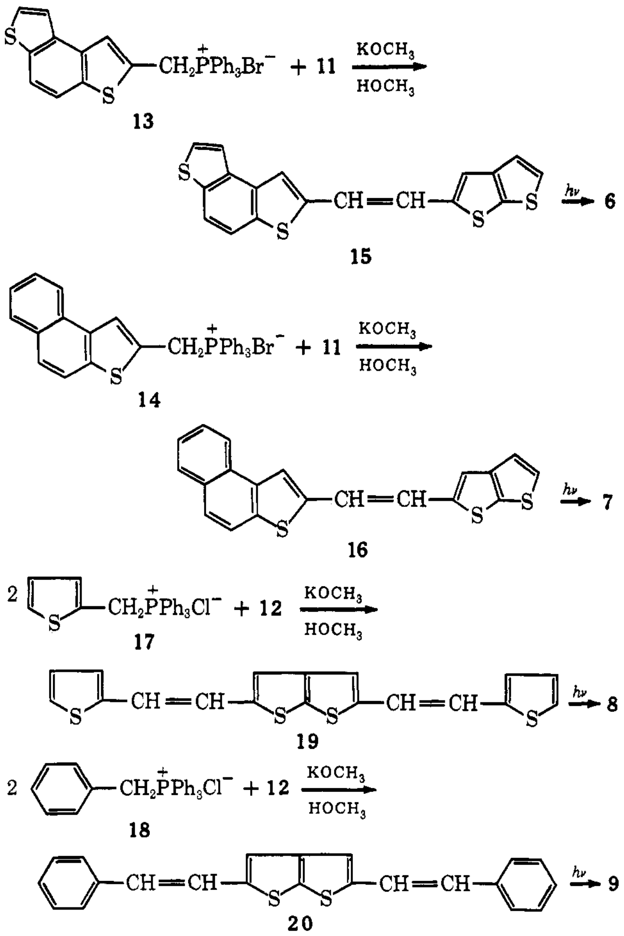


(2)

Results

Wittig reactions between **11** and the phosphonium salts **13** and **14** gave the alkenes **15** and **16** in good yields. Double Wittig reactions between **12** and the phosphonium salts **17** and **18** furnished the alkenes **19** and **20** in excellent yields (Table I, Scheme I).

Scheme I



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(4) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5788 (1968). This author reported tlc evidence for the formation of traces of coronene upon pyrolysis of hexahelicene at 485°.

(5) We wish to stress, that the role of thiophene in these studies has been pivotal. For a general review see: H. Wynberg, *Accounts Chem. Res.*, **4**, 65 (1971).

(6) We have not been able to complete the [7]circulene[3] synthesis using hexahelicene: J. H. Dopper, unpublished results in this laboratory.

(7) (a) R. H. Martin, M. J. Marchant, and M. Baes, *Helv. Chim. Acta*, **54**, 358 (1971); (b) R. H. Martin, G. Morren, and J. J. Schurter, *Tetrahedron Lett.*, 3683 (1969).

(8) In this publication the name thiophthene refers to the thieno-[2,3-*b*]thiophene isomer **4**.

(9) R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

(10) S. Gronowitz and B. Persson, *Acta Chem. Scand.*, **21**, 812 (1967).

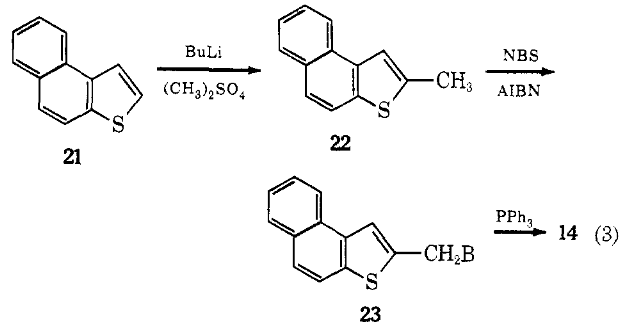
(11) (a) A. Bugge, *ibid.*, **25**, 27 (1971); (b) *ibid.*, **22**, 63 (1968).

Table II. Mass Spectra of the Heterohelicenes **6–10**, **30**, and **31**[a]

Helicene	M^+	$M - H^+$	$M - 2H^+$	$M - CH_3^+$	$M - C_2H_4^+$	$M - H_2S^+$	$M - CHS^+$	$M - CH_3S^+$	$M - C_2H_2S_2^+$	M^{2+}	$(M - 2H)^{2+}$
6	100	55	45				10	5	8	20	35
7	100	60	50	10		10	10	7		35	50
8	100	49	49			<5	14	10		28	42
9	100	60	55	20		5	<5	<5		25	40
10	100	42	28	14		14	8	10		21	30
30	100	11	5.5	<5	17	13	<5	10		20	<5
31	100	5	5	<5	<5	24	<5	15		25	<5

[a] All intensities are relative to that of the molecular ion (100%).

The phosphonium salt **13** was prepared as described.[12] Using essentially this procedure, **14** was prepared (eq 3). The compound **22**, mp 88–90°, had been prepared earlier.[9] The last step in the synthesis is the well-described[2,5] photocyclization reaction. No information was available prior to our experiments on the behavior of thiophthene under photocyclization conditions. However, no rearrangements[5] occurred and the expected products (**6**, **7**, **8**, and **9**) were formed in good yields.

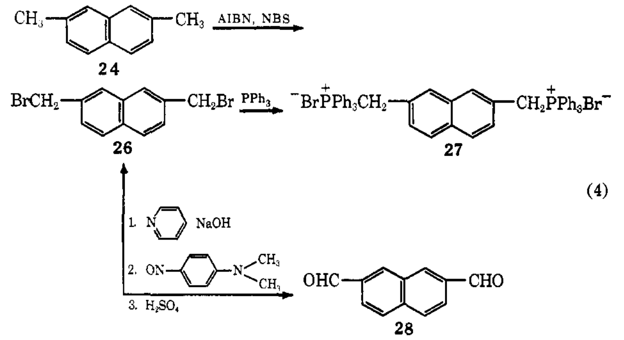


(3)

The preparation of **25**, apparently straightforward, deserves special comment. Martin[7a] has shown that the reaction of 2,7-dimethylnaphthalene (**24**)[13ab] with benzylideneaniline, an example of the "Siegrist reaction,"[14] proceeds in good yield to form the hexahelicene precursor. All our attempts to prepare **25** by this reaction, using thienylideneaniline failed,[15] and we were forced to use a double Wittig reaction. Both routes indicated in eq 5a and 5b were successful, with (5b) superior.

Discussion

Spectral comparison between the photocyclized compounds **6–10** and previously prepared helicenes[2c] provided conclusive evidence that the assigned helical structures were correct. However, the hexahelicenes prepared in this study have an additional interesting structural feature in common. If the assigned structures **6**, **7**, **8**, **9**, and **10** are correct, intramolecular hydrogen abstraction, leading to a new aryl–aryl bond, must be feasible. In this respect these helicenes differ from the so far prepared heteropenta- and -heptahelicenes.[2c]



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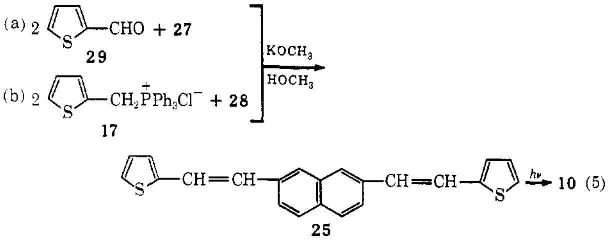
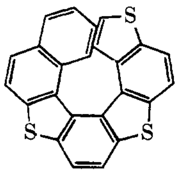


(5)

In addition to chemical evidence for this possible loss of hydrogen, mass spectral data were convincing. Thus in Table II the hexahelicenes **6–10** have a M − 2 H peak 10–15 times as intense as that in the heptahelicenes **30** and **31**.[2c] We ascribe this peak to the fragment remaining after loss of the two hydrogen atoms from the molecular ion of **10** (eq 6).



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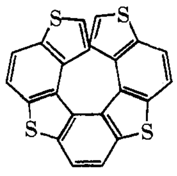

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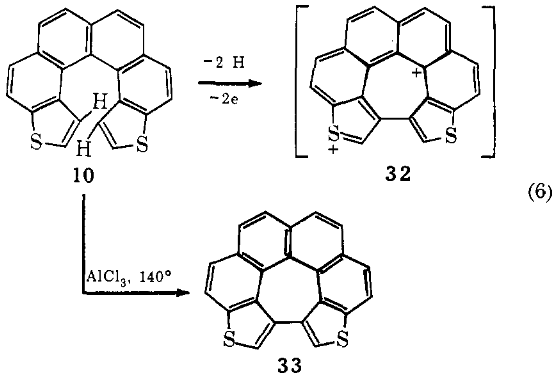

(6)

An additional interesting feature in the mass spectra of these helicenes is the high intensity peak of the double

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(12) P. G. Lehman and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **90**, 1113 (1971).

(13) (a) W. Baker, J. F. W. Mc. Omie, and W. K. Warburton, *J. Chem. Soc.*, 2991 (1952). (b) The synthesis of **24** was completed in this laboratory by Mr. E. P. Schudde using a slightly different method.

(14) A. E. Siegrist, P. Liechti, A. R. Meijer, and K. Weber, *Helv. Chim. Acta*, **52**, 2521 (1969).

(15) This work has been carried out by Mr. K. Lammertsma of this laboratory.

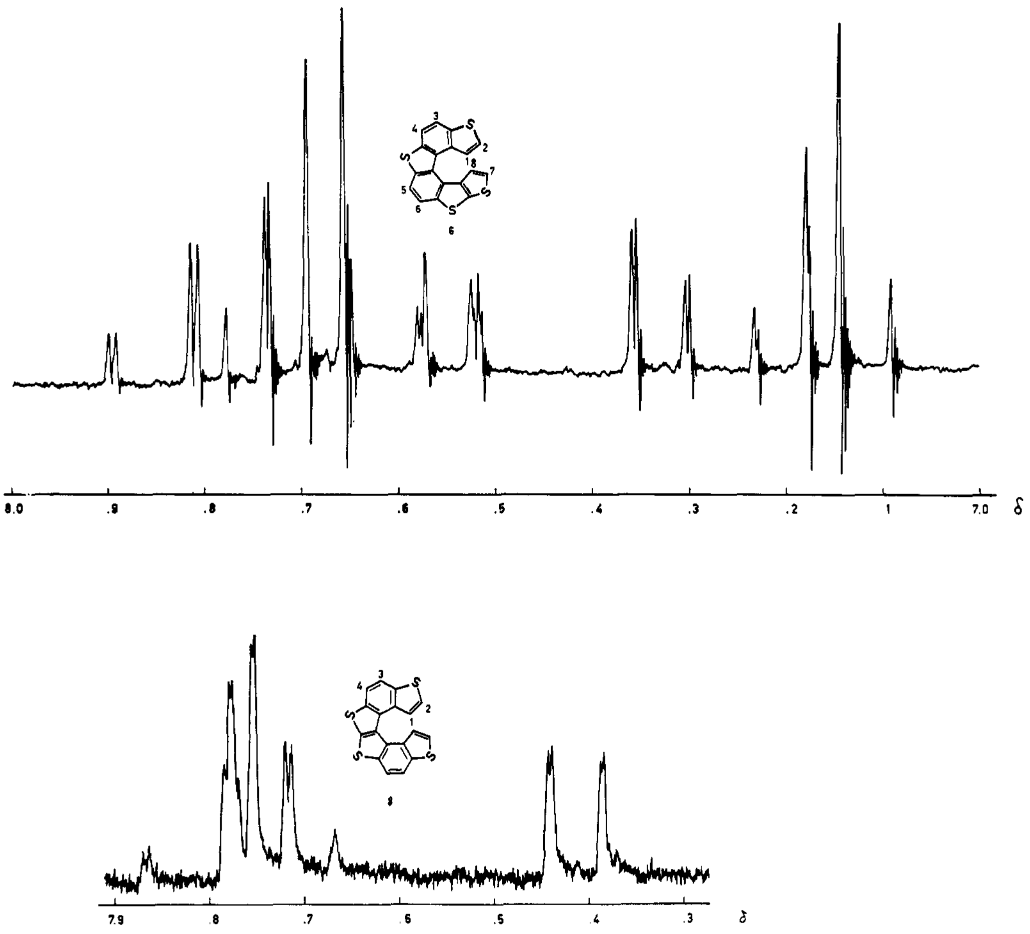
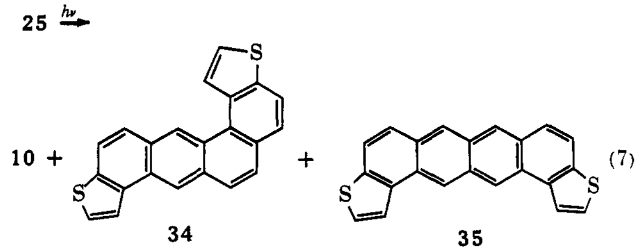


Figure 1. 100-MHz nmr spectra of 6 and 8 in CS_2.

charged ions to which we now assign the dehydrohelicene structure **32**. Hückel stabilized resonance may be responsible for this phenomenon.

A Scholl-type reaction[16,17] using $AlCl_3$ at 140° indeed converts all of these helicenes, except **9**, to the corresponding *de*-hydrohelicenes[3,18] in excellent yields (*e.g.*, **33**). This oxidative intramolecular bond formation is further proof for the helicene structure.

Photocyclization of **25** can give in principle three isomeric products, **10**, **34**, and **35** (eq 7). From the reaction mixture only one product is isolated (tlc, nmr), and from molecular models it is evident that only **10** can undergo this intramolecular hydrogen abstraction.



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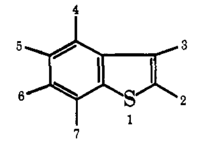
Nmr Spectra.[19] The 100-MHz nmr spectra of **6** and **8** were carefully studied using indor techniques and are shown in Figure 1. The results are worked out in Table III.

Table III. Nmr Data of 6 and 8

6				8			
	δ, ppm		Hz		δ, ppm		Hz
H_1	7.55	$J_{1,2}$	5.50	H_1	7.74	$J_{1,2}$	5.6
H_2	7.32	$J_{1,3}$	0.76	H_2	7.40	$J_{3,4}$	9.0
H_3	7.85	$J_{1,8}$	0.30	H_3	7.83	$J_{1,3}$	0.7
H_4	7.71	$J_{2,4}$	0.44	H_4	7.71	$J_{2,4}$	0.4
H_5	7.63	$J_{3,4}$	8.50				
H_6	7.73	$J_{5,6}$	8.36				
H_7	7.11	$J_{7,8}$	4.34				
H_8	7.20						

The positions of protons 2 and 7 in helicene **6** were assigned unambiguously by double lithiation and deuteration. The doublets centered at δ 7.32 and 7.11 ppm disappear almost competely, while the doublets centered at δ 7.55 and 7.20 collapse to signals having small coupling constants. Assignment of H_1 is confirmed by analogy to the benzo[*b*]thiophene system **36**,



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(16) For a review, see G. A. Olah, "Friedel Crafts and Related Reactions," Vol. 2, Wiley, New York, N. Y., 1964, pp 979–1047.

(17) M. Zander and W. H. Franke, *Chem. Ber.*, **102**, 2728 (1969).

(18) J. H. Dopper and H. Wynberg, publication in preparation.

(19) For a detailed analysis of the nmr spectrum of the benzohelicenes, see R. H. Martin, N. Defay, A. P. Figeys, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbeke, and J. J. Schurter, *Tetrahedron*, **25**, 4985 (1969).

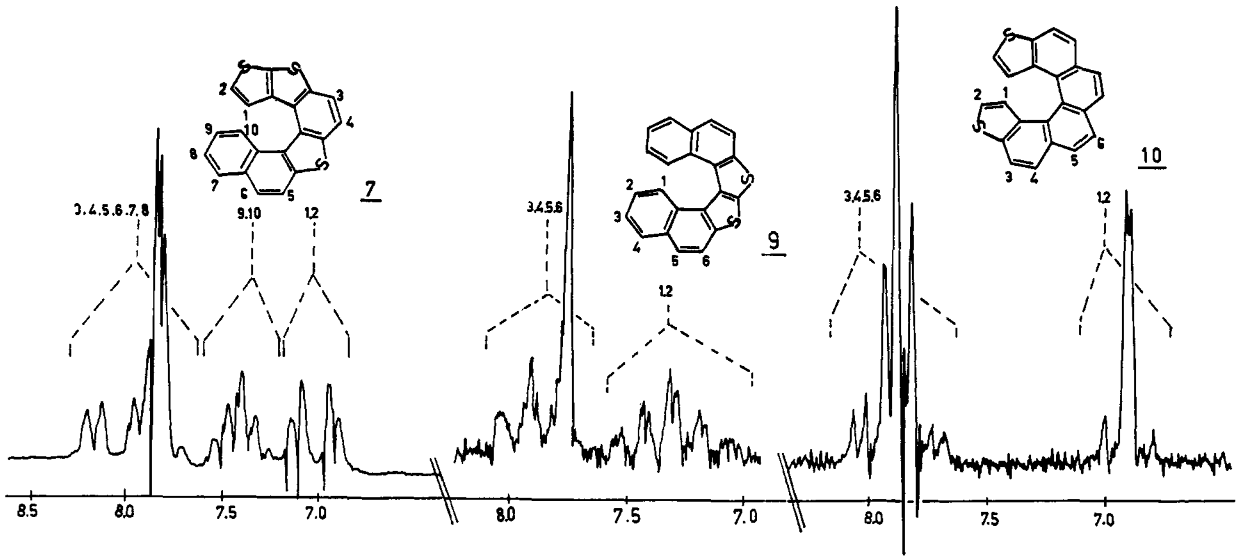

Figure 2. Nmr spectra of **7**, **9**, and **10** in CS_2.

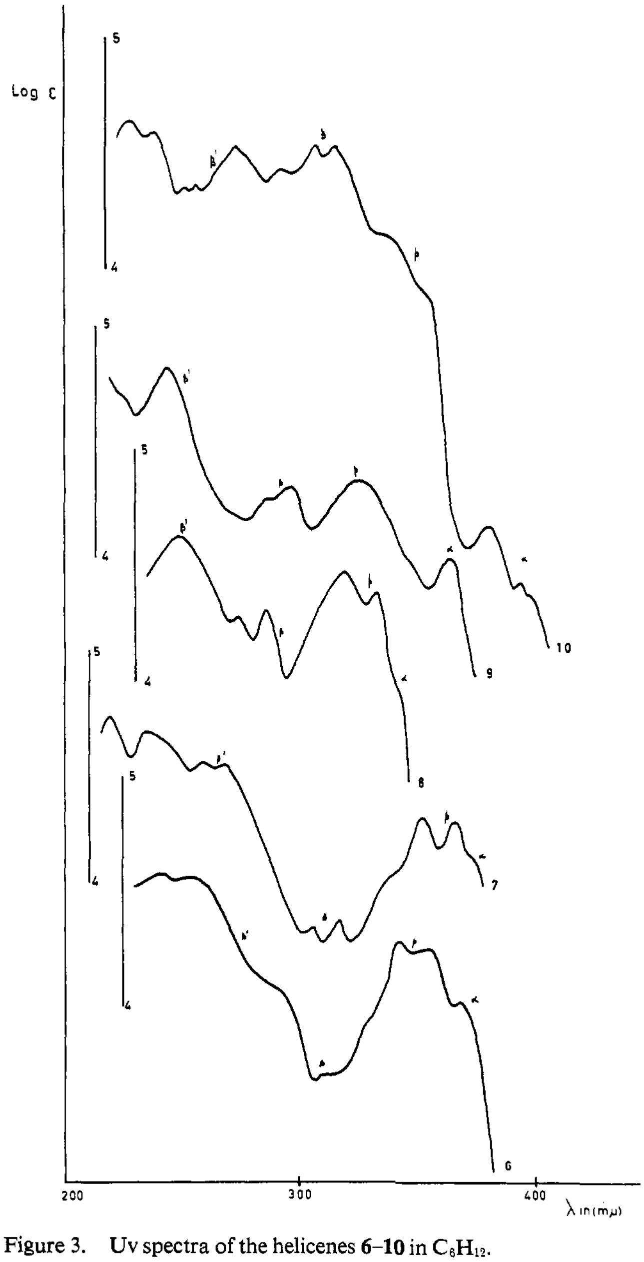

Figure 3. Uv spectra of the helicenes **6–10** in C_6H_{12}.

which exhibits long-range so-called "zig-zag" coupling,[20ab] between the protons H_8 and H_7 with a coupling constant $J_{8,7}$ of 0.5–0.6 Hz. In compound **6** one observes coupling of an identical nature of protons H_1 and H_3 and of protons H_2 and H_4. On the basis of the known position of H_1, assignment can be made for all of the remaining protons. The AB spectra of the terminal thiophene rings show additional splitting. Double resonance experiments established that, in addition to the "zig-zag" coupling, long-range coupling between H_1 and H_8 is operative. To our knowledge this is one of the rare examples of observed long-range coupling between the termini of a hexahelicene system.[21ab,22] The protons of helicene **8** are assigned on the same basis. The 100-MHz spectrum of **7** and the 60-MHz spectra of **9** and **10** are shown in Figure 2.

Uv Spectra. The uv spectra of the helicenes **6–10** are shown in Figure 3. A comparison between the uv spectra of the heterohelicenes[2d] with those of the benzohelicenes[1,23] indicates that the longest wavelength band (α band)[24] is found at a shorter wavelength (*ca.* 30 mμ), while the second and third band (p and β band, respectively) differ very little in their position. The intensity of the α band is much higher and that of the third band much lower. The synthesis of these new hexahelicenes made it possible to study the influence of the thiophthene moiety on the uv spectra. A comparison of the uv spectra of **6–9** with those of **37** and **38** shows that incorporation of thiophthene in hexahelicenes results in a blue shift of all of the absorption bands.

The shift for the α band is 10–30 mμ depending on the place of the thiophthene moiety in the molecule. As can be seen from the spectra, the effect is the largest when **4** is in the middle of the molecule. In this respect the effect on the spectra of helicenes of the incorpora-

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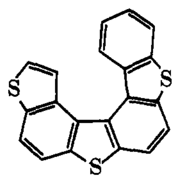
(20) (a) E. V. Blackburn, T. J. Cholerton, and C. J. Timmons, *J. Chem. Soc., Perkin Trans. 2*, 101 (1972); (b) J. A. Elridge and R. G. Foster, *J. Chem. Soc.*, 981 (1964).

(21) (a) K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta, Part A*, **23**, 1689 (1967); (b) M. S. Newman, R. G, Mentzer, and G. Slomp, *J. Amer. Chem. Soc.*, **85**, 4018 (1963).

(22) K. D. Bartle and D. W. Jones, *J. Chem. Soc. A*, 437 (1969).

(23) O. E. Weigang, J. A. Turner, and P. A. Trouard, *J. Chem. Phys.*, **45**, 1126 (1966).

(24) For an explanation of this nomenclature, see E. Clar, "Polycyclic Hydrocarbons," Academic Press, London, 1964.



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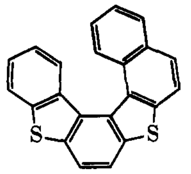

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tion of thiophthene **4** is essentially different from the incorporation of two or more thiophene moieties which are separated from one another by benzene rings. We see here a rather startling phenomenon: an aromatic ring can be fused to an aromatic system without causing a red shift in the uv. This behavior of a thiophthene is in sharp contrast to the behavior of thiophene itself. For the latter structural unit v. Reijendam and Janssen[25] have amply demonstrated that its conjugative properties are equal to or greater than that of a benzene ring. The uv spectrum of **10** does not possess typical heterohelicene features.[26] Remarkable is the place of the low intensity (log $\epsilon < 3$) α band which appears at longer wavelength (390–400 mμ) than that of the corresponding heterohelicenes **37** and **38**. This feature is typical for benzohelicenes, and therefore the uv spectrum of **10** can best be compared with that of hexahelicene.[1]

Experimental Section

All reagents were purified where necessary by standard methods. For column chromatography neutral alumina (Merck A_1) or silica gel (BDH) was used. Melting points (corrected) up to 300° were determined on a Mettler FP_1 microscope and between 300 and 350° (uncorrected) on a Reichert hot-stage apparatus. Uv spectra were measured on a Zeiss PMQ 11 or recorded with a Beckman DB-G grating spectrophotometer. Nmr spectra were obtained with a Varian A60D or a Varian XL-100-15 instrument, using tetramethylsilane as an internal standard. Mass spectra were obtained with a AEI MS 902 instrument. Photolyses were carried out with a Hanau Q-700 unfiltered medium-pressure lamp equipped with a quartz jacket. Elemental analyses were carried out by the microanalytical department of this laboratory under the supervision of Mr. W. M. Hazenberg.

Thieno[2,3-*b*]thiophene-2-carboxaldehyde (11). To a solution of 1.5 g (10.7 mmol) of **4** in 10 ml of dry ether at 25° under nitrogen, a solution of 5.1 ml of *n*-butyllithium (2.1 *N* in hexane) was added dropwise. The color changed to orange. The solution was heated under reflux for 30 min and after cooling 0.8 g (10.8 mmol) of DMF in 20 ml of dry ether was added. After extraction, the ether layer was washed with water and $NaHCO_3$ solution. After drying ($MgSO_4$) and evaporation of the ether, the oil was chromatographed over silica gel using benzene as a solvent. Besides some starting material, 0.9 g (5.35 mmol) of **11** (50%), mp 45.5–47° (from ethanol), was isolated (lit.[11] mp 45–46°).

Thieno[2,3-*b*]thiophene-2,5-dicarboxaldehyde (12). To a solution of 500 mg (3.6 mmol) of **4** in 50 ml of dry ether at 25° under nitrogen a solution of 7.2 ml of *n*-butyllithium (2.0 *N* in hexane) was added dropwise. The color changed to bright yellow and the dilithium salt precipitated. The solution was heated under reflux for 25 min and 5 g (70 mmol) of DMF in 10 ml of dry ether was added slowly. After 30 min the mixture was poured into 40 ml of cold diluted HCl solution. The yellow dialdehyde precipitated directly, was removed by filtration, and was washed with water, ether, and methanol. After sublimation (140°, 0.1 mm) 325 mg (49%) of **12**, mp 181.5–183.5°, was obtained: ir (KBr) 2843, 1658, 1504, 1229, 1132, 1090, 861, 731, 631, and 596 cm^{-1}; nmr ($CDCl_3$) 7.95 (s, 2 H), 9.95 (s, 2 H). *Anal.* Calcd for $C_8H_4O_2S_2$: C, 48.96; H, 2.06; S, 32.67. Found: C, 49.0; H, 2.1; S, 32.7.

2-Methylnaphtho[2,1-*b*]thiophene (22). Naphtho[2,1-*b*]thiophene (1 g, 5.45 mmol) was lithiated and methylated as was described for the synthesis of 2-methylbenzo[*b*]thiophene.[27] The yield of **22** was 0.93 g (86%), mp 88–89.5°, lit.[9] 88–90°.

2-Triphenylphosphoniomethylnaphtho[2,1-*b*]thiophene Bromide (14). The bromide **23** was prepared from **22** (577 mg, 2.91 mmol), as was described for the synthesis of **13**.[12] After recrystallization from hexane, 639 mg (79%) of 2-bromomethylnaphtho[2,1-*b*]thiophene (**23**) was obtained, mp 110–130° dec. The corresponding phosphonium salt **14** was obtained from **23** in 81% yield, mp 298–300° (from methanol–ether).

1-[2-Thieno[2,3-*b*]thienyl]-2-[2-benzo[1,2-*b*:4,3-*b*′]dithienyl]ethene (15). Thieno[2,3-*b*]thiophene-2-carboxaldehyde (**11**) (100 mg, 0.6 mmol) and 2-triphenylphosphoniomethylbenzo[1,2-*b*:4,3-*b*′]dithiophene bromide (**13**) (325 mg, 0.6 mmol) were dissolved in 10 ml of anhydrous methanol. With external cooling and stirring, a solution of potassium *tert*-butoxide (100 mg, 0.9 mmol) in dry methanol (5 ml) was added dropwise. The solution was stirred at 20° for 30 min and heated to reflux for 10 min to complete the reaction. After cooling, the bright yellow product was removed by filtration and washed with methanol and ether. The alkene **15** (160 mg, 75%) was obtained. The analytical sample sublimed (230°, 0.1 mm) as minute yellow prisms, mp 244–246°. *Anal.* Calcd for $C_{18}H_{10}S_4$: C, 60.98; H, 2.84; S, 36.18. Found: C, 60.7; H, 2.8; S, 36.0. Uv (benzene): λ max (log ϵ) 404 (4.20), 383 (4.36), 364 (4.31), 300 (4.13). The alkenes **16**, **19**, **20**, and **25** were prepared according to a procedure analogous to that for the preparation of **15**.

1-[2-Thieno[2,3-*b*]thienyl]-2-[2-naphtho[2,1-*b*]thienyl]ethene (16). The compound **16** was prepared from thieno[2,3-*b*]thiophene-2-carboxyaldehyde (**11**) (803 mg, 4.8 mmol) and 2-triphenylphosphoniomethylnaphtho[2,1-*b*]thiophene bromide (**14**) (2.82 g, 5.0 mmol).

Analytical pure **16** (mp 245.5–246.5°) was obtained in 78% yield. *Anal.* Calcd for $C_{20}H_{12}S_3$: C, 68.93; H, 3.48; S, 27.60. Found: C, 68.9; H, 3.5; S, 27.6. Uv in benzene: λ max (log ϵ) 364 (4.24), 383 (4.25), 405 (4.20).

2,5-Di[β-(2-thienyl)vinyl]thieno[2,3-*b*]thiophene (19). The compound **19** was prepared from thieno[2,3-*b*]thiophene-2,5-dicarboxaldehyde (**12**) (500 mg, 2.5 mmol) and 2-thenyltriphenylphosphonium chloride (**17**) (2.015 g, 5.1 mmol). The yield of analytical pure **19** (mp 325–327°) was 857 mg (95%). *Anal.* Calcd for $C_{18}S_4H_{12}$: C, 60.63; H, 3.40; S, 35.98. Found: C, 60.3; H, 3.4; S, 36.0. Uv in benzene: λ max (log ϵ) 336 (s) (4.48), 352 (s) (4.53), 368 (4.58).

2,5-Di[β-styryl]thieno[2,3-*b*]thiophene (20). The compound **20** was prepared from thieno[2,3-*b*]thiophene-2,5-dicarboxaldehyde (**12**) (200 mg, 1.02 mmol) and benzyltriphenylphosphonium chloride (**18**) (786 mg, 2.04 mmol). The yield of analytically pure **20** (mp 329–332) was 325 mg (91%). *Anal.* Calcd for $C_{22}H_{16}S_2$: C, 76.71; H, 4.67; S, 18.62. Found: C, 76.7; H, 4.7; S, 18.6. Uv in benzene: λ max (log ϵ) 319 (4.53), 332 (4.52), 358 (4.52).

2,7-Dimethylnaphthalene[13] (24), 2,7-dibromomethylnaphthalene[28a] (26), and 2,7-naphthalenedicarboxaldehyde[28b] (28) were prepared by literature procedures.

2,7-Naphthyldimethyltriphenylphosphonium bromide (27) was prepared from **26** (2 g, 6.3 mmol) and triphenylphosphine (3.3 g, 12.6 mmol). The yield of **27** (mp > 350°) was 4.7 g (89%).

2,7-Di[β-(2-thienyl)vinyl]naphthalene (25). The compound **25** was prepared according to eq 4 and 5a and 5b. By eq 5a: from 2-thiophenealdehyde (**29**) (200 mg, 1.8 mmol) and 2,7-naphthyldimethyltriphenylphosphonium bromide (**27**) (3.3 g, 12.6 mmol). The yield of analytical pure **25** (mp 277–279°) was 70 mg (23%). By eq 5b: from 2,7-naphthalenedicarboxaldehyde (**28**) (200 mg, 1.09 mmol) and 2-thienyltriphenylphosphonium chloride (**17**) (860 mg, 2.18 mmol). The yield of analytical pure **25** (mp 279–280°) was 213 mg (57%), mixture melting point of **25** obtained by eq 5a and 5b 277–280°. *Anal.* Calcd for $C_{22}H_{16}S_2$: C, 76.70; H, 4.68; S, 18.62. Found: C, 76.3; H, 4.7; S, 18.1. Expected for $C_{22}H_{16}S_2$, M = 344.478; found by mass spectrometry, M = 344. Uv in benzene: λ max (log ϵ) 395 (s) (2.76), 356.5 (s) (4.49), 343 (4.54), 330 (s) (4.43); ir (KBr) sharp peaks at 949, 836, 797, and 782 cm^{-1}.

[1]-Benzothieno[4,5-*d*]thieno[3,2-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene (6). A solution of **15** (340 mg, 0.97 mmol) in 550 ml of benzene, to which 10 mg of iodine was added, was irradiated with a Q-700 lamp

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for 4 hr. The solution was concentrated and chromatographed over alumina with benzene. Evaporation of the solvent left an almost colorless material, which was recrystallized from methylcyclohexane. The yield of **6**, mp 210–211.5°, was 231 mg (69%). *Anal.* Calcd for $C_{18}H_8S_4$: C, 61.33; H, 2.29; S, 36.38. Found: C, 61.4; H, 2.5; S, 36.0.

The helicenes **7**, **8**, **9**, and **10** were prepared according to a procedure identical with that of the preparation of **6**.

Naphtho[1,2-*d*]thieno[3,2-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene (7). The helicene **7** was prepared by irradiation for 1.5 hr of a suspension of **16** (420 mg, 1.2 mmol) in 550 ml of benzene to which 10 mg of iodine was added. The yield of **7**, mp 220–222°, was 249 mg (60%). *Anal.* Calcd for $C_{20}H_{10}S_3$: C, 69.23; H, 2.91; S, 27.76. Found: C, 69.3; H, 3.0; S, 27.8.

Dithieno[3,2-*e*:3′,2′-*e*′][1]benzothieno[2,3-*b*][1]benzothiophene (8). The helicene **8** was prepared by irradiation for 1 hr of a suspension of **19** (50 mg, 0.14 mmol) in 550 ml of benzene to which 5 mg of iodine was added. The yield of **8**, mp 279–280°, was 25 mg (51%). *Anal.* Calcd for $C_{18}H_8S_4$: C, 61.33; H, 2.29; S, 36.38. Found: C, 61.4; H, 2.3; S, 36.1.

Dibenzo[*e*:*e*′][1]benzothieno[2,3-*b*][1]benzothiophene (9). The helicene **9** was prepared by irradiation for 1.5 hr of a suspension of **20** (100 mg, 0.29 mmol) in 550 ml of benzene to which 5 mg of iodine was added. The yield of **9**, mp 289–291.5°, was 50 mg (50%). *Anal.* Calcd for $C_{22}H_{12}S_2$: C, 77.60; H, 3.56; S, 18.83. Found: C, 77.6; H, 3.7; S, 18.8.

Naphtho[2′,1′-*b*′]thieno[4,′5′-*f*]naphtho[2,1-*b*]thiophene (10). The helicene **10** was prepared by irradiation for 2 hr of a suspension of **25** (300 mg, 0.87 mmol) in 550 ml of benzene to which 20 mg of iodine was added. The yield of **10**, mp 240–241°, was 146 mg (50%). *Anal.* Calcd for $C_{22}H_{12}S_2$: C, 77.60, H, 3.56; S, 18.83. Found: C, 77.7; H, 3.7; S, 18.8.

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Stable Carbocations. CXLII.[1] 1-Acenaphthenium Ions

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Abstract: The 1-acenaphthenium ion **1a** and several of its substituted derivatives were directly observed in superacid solutions and were characterized by proton and carbon-13 nuclear magnetic resonance spectroscopy. Spectroscopic data show that positive charge is heavily delocalized into one of the naphthalene rings indicating the classical nature of these ions. The intramolecular degenerate 1,2-hydrogen shift in 1,2-dimethyl- and 1-methyl-2-ethyl-1-acenaphthenium ions was studied by pmr spectroscopy. The parent 1-acenaphthenium ion and 1,2,2-trimethyl-1-acenaphthenium ions undergo no 1,2-hydrogen shift or methyl shift in the temperature range studied.

In a study of acid-catalyzed polymerization, Gandini and Plesch[3] claimed on the basis of ultraviolet spectral data that they observed the secondary carbenium ion **1a** when acenaphthylene was treated with concentrated sulfuric acid. Young,[4] however, in an extension to their work concluded that the species observed by Gandini and Plesch was not the 1-acenaphthenium ion but more likely a dimeric cation.

We wish to report the first unambiguous preparation of the 1-acenaphthenium ion and show from proton and carbon-13 nmr spectral data that it is a secondary nonequilibrating carbenium ion in the temperature range −90 to 40°. This contrasts with the results for a number of other arylcarbenium ions[5] which undergo fast intramolecular 1,2-hydrogen and 1,2-methyl shifts in a similar temperature range. Fast intramolecular 1,2-hydrogen shifts have been found to occur in substituted arenium ions,[6] and recently in the parent benzenium ion.[7] The rates of such processes appear to vary over a wide range. 1,2-Methyl shifts in benzenium ions have been found to be very slow processes in comparison to the 1,2-hydrogen shifts.[6a,b,8] In superacid media and some other acid systems,[6b,8] equilibrations in acyclic and alicyclic carbenium ions[9,10] which occur *via* 1,2-hydrogen or methyl shifts have also been examined by nuclear magnetic resonance. In most cases, the intramolecular hydrogen or methyl shift is fast and strongly dependent on the structure of the carbenium (or arenium) ion. Rates and activation parameters for the 9,10-methyl shift in 9,10,10-trimethylphenanthrenium ion have recently been determined by means of nmr spectroscopy.[11] In this system, the rate of the 1,2-methyl shift is nearly as fast as the 1,2-hydrogen shift in methylbenzenium ions. Furthermore, the relative migratory tendencies of aryl groups in the

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