Cope Interconversions of the 9-Methoxy-*endo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dienyl Cation and its [4.3.0.$0^{2,5}$]Tautomer. Evidence of Enhanced Ionic Stability by Delocalization of Neighbouring σ Bonds

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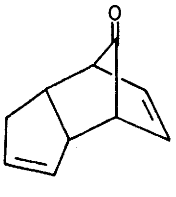
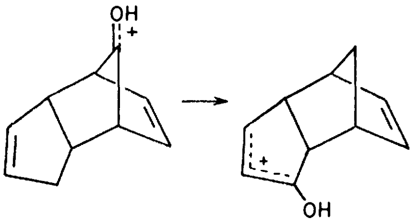
Dissolution of 9-chloro-9-methoxy-*endo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (7b, c) in liquid SO_2 gives rise to a dissociation equilibrium which involves the rearranged 7-methoxy-*endo*-tricyclo[4.3.0.$0^{2,5}$]nona-3,9-dienyl cation (11). This allylic ion was formed quantitatively by dissolution of (7b, c) in FSO_3H–SO_2 or $AlCl_3$–CH_2Cl_2. Its structure was established by ^1H and ^{13}C n.m.r. spectroscopy. Quenching of the ionic solutions with methanol afforded the starting acetal (7a). In contrast, reaction of (11) with pyridine produced its corresponding pyridinium salt (17a). Ionization of (7b, c) under short-life conditions, *i.e.* reaction with pyridine in CH_2Cl_2, proceeds without skeletal rerrangement. The structure of the reaction products of the reference compounds (8)—(10) appeared to be independent of the conditions used. In all cases the unrearranged structures were observed. The ready skeletal rearrangement of (7b, c) under acidic conditions is ascribed to the involvement of a homoaromatic Cope transition state. From the enhanced reaction rate of (7b, c) relative to (8b, c)—(10b, c) it is concluded that the σ bond involved in the Cope rearrangement provides stabilization of the incipient cation in (7). This kind of stabilization is also present in the rearranged cation (11), as indicated by its enhanced stability relative to the corresponding allylic ion (3) and by comparison of their ^1H and ^{13}C n.m.r. data.

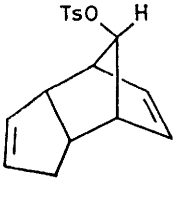
FACILE rearrangements and fluxional behaviour of organic structures has often been encountered if an aromatic (six-electron) Cope transition state is involved. These processes are still more facilitated by the introduction of conjugating electron-deficient centres. For instance, the bicyclopentadien-8-one (1) undergoes relatively rapid Cope rearrangements, whereas these rearrangements are even more rapid when the carbonyl oxygen is protonated as in (2).[1] The driving force for the latter process is the formation of the allylic ion (3).



(1)



(2) (3)



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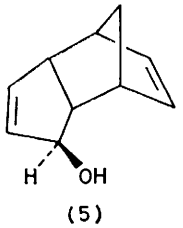

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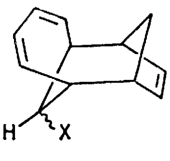


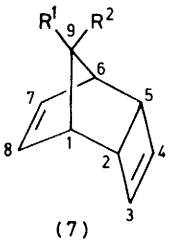
(6)

Consistently, fast Cope rearrangements occur if cationic centres are introduced by solvolysis. Thus, solvolysis of (4) afforded the rearranged structure (5) exclusively.[2] Recently, similar behaviour was observed for compound (6).[3]

In this paper we describe the ionization reactions of 9-chloro-9-methoxy-*endo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (7b,c) and the analogues (8b,c)—(10b,c) of which the former is attended by a facile Cope rearrangement to the tautomeric 7-methoxy-*endo*-tricyclo[4.3.0.$0^{2,5}$]nona-3,9-dienyl cation, which remarkably undergoes the reverse reaction upon quenching.

RESULTS

The parent dimethyl acetal (7a) was prepared from 9,9-dimethoxybicyclo[4.2.1]nona-2,4,7-triene[4] by photolysis. Acetals (8a)—(10a) were prepared according to reported methods.[5-7] They were converted to their corresponding α-chloro-ethers (8b,c)—(10b,c) by PCl_5.[8] The ^1H n.m.r. spectra (Table 1) revealed the existence of epimers, the ratio of which is specific to each compound, by two singlet methyl absorptions. The epimeric α-chloro-ethers are in equilibrium, similar to the behaviour of 7-chloro-7-methoxynorbornene, which we reported earlier.[8a]



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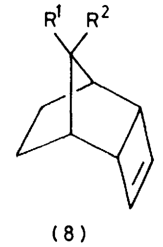
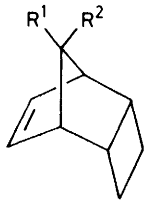


(8)



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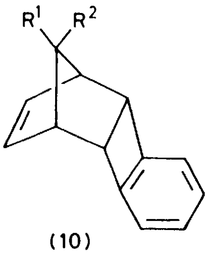

(10)

a; $R^1 = R^2 = OCH_3$
b; $R^1 = Cl, R^2 = OCH_3$
c; $R^1 = OCH_3, R^1 = Cl$

TABLE 1

^{1}H N.m.r. spectral data [a] for bi- and tri-cyclic compounds in CD$_2$Cl$_2$ (δ values relative to internal Me$_4$Si)

Compound	1-, 6-H	2-, 5-H	3-, 4-H	7-, 8-H	OCH$_3$	Other
(7a)	2.66 (m)	2.98 (d, *J* 4)	5.60 (s)	5.67 (t, *J* 2.3)	2.98 (s) 3.10 (s)	
(7b)	3.10 (m)	3.16 (d, *J* 4)	5.86 (s)	5.93 (*t*, *J* 2.3)	3.43 (s)	
(7c)	3.10 (m)	3.16 (d, *J* 4)	5.82 (s)	5.95 (t, *J* 2.3)	3.33 (s)	
(7d)	4.13 (m)	3.46 (d, *J* 4)	5.93 (s)	6.00 (t, *J* 2.3)	3.23 (s)	8.30 (m, 3 H) 9.83 (d, *J* 7, 2 H)
(7e)	4.37 (m)	2.83 (d, *J* 4)	5.80 (s)	6.17 (t, *J* 2.3)	3.27 (s)	8.30 (m, 3 H) 10.23 (d, *J* 7, 2 H)
(8a)	2.08 (m)	3.00 (m)	6.16 (s)	1.60 (m, *ex*) 1.22 (m, *en*)	3.20 (s)	
(8b) (8c)	2.41 (m)	3.00 (m)	6.08 (s)	1.60 (m, *ex*) 1.38 (m, *en*)	3.33 (s)	
(9a)	2.73 (m)	2.73 (m)	1.83 (m,*ex*) 1.23 (m,*en*)	6.30 (t, *J* 2.3)	3.03 (s)	
(9b)	3.00 (m)	2.83 (m)	2.00 (m,*ex*) 1.33 (m,*en*)	6.42 (t, *J* 2.3)	3.23(s)	
(9c)	3.00 (m)	2.83 (m)	2.00 (m,*ex*) 1.33 (m,*en*)	6.42 (*J* 2.3)	3.30 (s)	
(9d)	4.06 (m)	3.17 (m)	2.17 (m,*ex*) 1.43 (m,*en*)	6.43 (t, *J* 2.3)	3.08 (s)	8.26 (m, 3 H) 9.73 (d, *J* 7, 2 H)
(9e)	4.30 (m)	2.83 (m)	2.46 (m,*ex*) 2.43 (m,*en*)	6.63 (t, *J* 2.3)	3.27 (s)	8.26 (m, 3 H) 10.00 (d, *J* 7, 2 H)
(10a)	3.15 (m)	3.73 (d, *J* 4)		5.56 (t, *J* 2.3)	3.03 (s) 3.15 (s)	7.02 (m, 4 H)
(10b)	3.33 (m)	3.81 (d, *J* 4)		5.64 (t, *J* 2.3)	3.43 (s)	7.12 (m, 4 H)
(10c)	3.33 (m)	4.02 (d, *J* 4)		5.64 (t, *J* 2.3)	3.30 (s)	7.12 (m, 4 H)
(10d)	4.20 (m)	4.10 (d, *J* 4)		5.68 (t, *J* 2.3)	3.25 (s)	7.05 (m, 4 H), 8.45 (m, 3 H), 9.55 (d, *J* 7, 2 H)
(10e)	4.45 (m)	3.51 (d, *J*, 4)		5.85 (t, *J* 2.3)	3.45 (s)	6.96 (m, 4 H), 8.45(m, 3 H), 10.00 (d, *J* 7, 2 H)

	[2-, 3-H]	[1-, 4-H]	[5-, 6-H]	OCH$_3$	Other
(18a)	5.96 (t, *J* 2.5)	2.74 (m)	1.90 (m,*ex*) 1.05 (m,*en*)	3.15 (s) 3.11 (s)	
(18b)	5.95 (t, *J* 2.5)	2.93 (m)	1.85 (m,*ex*) 1.05 (m,*en*)	3.32 (s)	
(18c)	5.92 (t, *J* 2.5)	2.93 (m)	1.85 (m,*ex*) 1.05 (m,*en*)	3.25 (s)	
(18d)	6.14 (t, *J* 2.5)	4.07 (m)	2.20 (m,*ex*) 1.15 (m,*en*)	3.20 (s)	9.14—8.30 (m, 3 H) 10.00 (d, *J* 7, 2 H)
(18e)	6.34 (t, *J* 2.5)	4.34 (m)	1.2—1.5 (m,*ex–en*)	3.26 (s)	9.14—8.30 (m, 3 H) 10.37 (d, *J* 7, 2 H)

[a] *J* Values are expressed in Hz.

Generation of Stable Ions.—Compounds (7b,c) exhibit unusual reactivities with respect to the more saturated analogues (8b,c) and (9b,c) and the benzo-derivative (10b,c). Dissolution of (7b,c) in liquid SO$_2$ at −80 °C resulted in the ionization of the C–Cl bond, as revealed by ^{1}H and ^{13}C n.m.r. spectra, whereas the cations derived from (8b,c)—(10b,c) could be obtained in strong proton acids, such as FSO$_3$H, only. Although addition of methanol to (7b,c) in liquid SO$_2$ gives exclusively the starting acetal (7a), the structure of the intervening cation appeared to be rearranged to (11). Moreover, cation (11) is in equilibrium with its covalent precursors (7b,c), as indicated by the temperature dependent ^{1}H n.m.r. spectrum (Figure), which shows an increasing amount of (7b,c) at higher temperatures. The decrease in dipole moment of liquid SO$_2$ at higher temperatures may account for this phenomenon.[9] When FSO$_3$H was added to the solution of (7b,c) in liquid SO$_2$, (11) only was observed, even at temperatures up to −10 °C. However, in this medium two isomers of (11) were present [(11a,b)], which apparently interchange in pure liquid SO$_2$ in which only one structure could be observed.* The assignment of rearranged structure (11) is based on its ^{1}H and ^{13}C n.m.r. data, compared to those of the structurally related ion (12). The latter compound was prepared by dissolution of its α-chloro-ether in FSO$_3$H–SO$_2$. The n.m.r. data are collected in Table 2.

The ^{1}H n.m.r. spectrum of (11) in FSO$_3$H–SO$_2$ shows two singlet methyl resonances in a 1 : 4 ratio, whose mean location (δ 4.76) is 1.4 p.p.m. downfield relative to the mean methoxy-position (δ 3.38) in the covalent precursors (7b,c). Such shifts are typical for methoxy-groups attached to cationic centres. The small separation (0.04 p.p.m.) between the two methoxy-peaks indicates the existence of *syn-* (11a) and *anti-* (11b) forms, due to restricted rotation around the C–O bond. This interpretation is confirmed by

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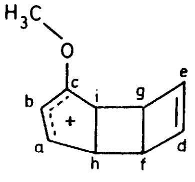
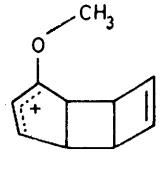
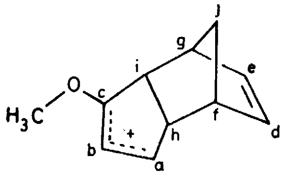
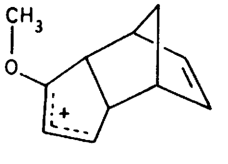
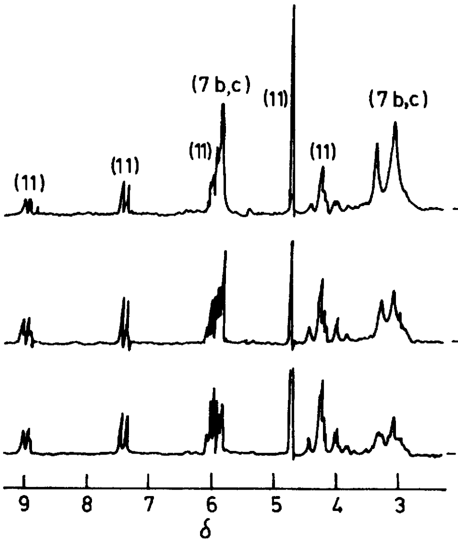
* The exchange process (11a)↔(11b) and (11a.b)↔(7b,c) gave rise to line broadening and obscuring of the allylic resonances for the ethyl derivative described in ref. 8*b*. This phenomenon together with the exclusive recovery of starting material after quenching led us to the assignment of an ionic structure in which the skeletal integrity has been maintained.

TABLE 2

^{1}H and ^{13}C n.m.r. spectral data [a] for ions (11) and (12) in FSO_3H-SO_2 (δ values relative to internal Me_4Si)

		a	b	c	d	e	f	g	h	i	j	OCH_3
 (11a)	^{1}H	8.87 (dd, *J* 5, 2)	7.30 (d, *J* 5)		6.00 (br,m)		3.9—4.2 (br,m)		4.2—4.5 (br,m)			4.78 (s)
	^{13}C	191.93	138.26	226.22	134.31	138.26	39.80 39.61		46.9 45.4			67.34
 (11b)	^{1}H	9.10 (dd, *J* 5, 2)	7.57 (d, *J* 5)		6.00 (br,m)		3.9—4.2 (br,m)		4.2—4.5 (br,m)			4.74 (s)
	^{13}C	196.33	134.28	225.44	135.29	136.86	40.61 42.4		46.4 47.2			67.34
 (12a)	^{1}H	9.13 (dd, *J* 5, 2)	7.25 (d, *J* 5)		6.19 (m)		3.51 (br,m)		4.25 (br,m)		2.25 (br, s)	4.78 (s)
	^{13}C	201.83	130.73	227.37	131.22	133.28	45.0	53.14	54.11	54.96	47.62	67.88
 (12b)	^{1}H	8.89 (dd, *J* 5, 2)	6.93 (d, *J* 5)		6.12 (m)		3.61 (br,m)		4.05 (br,m)		2.35 (br.s)	4.97 (s)
	^{13}C	196.37	133.95	228.83	129.83	134.86	45.62	52.72	55.26	55.81	47.32	67.88

[a] *J* Values are expressed in Hz.



^{1}H N.m.r. spectra of 9-chloro-9-methoxytricyclo[4.2.1.0^{2,5}]nona-3,7-diene[(7b,c)] in liquid SO_2 at various temperatures

the ^{13}C n.m.r. spectrum, which shows two signals for each carbon in the ratio of 1 : 4. Furthermore, the ^{1}H n.m.r. spectrum of both isomers of (11) shows comparable resonances at δ 9.10, 7.57, and 8.87, 7.30 which are consistent with methoxy-stabilized allylic systems. The mutual coupling of 5 Hz indicates that the allylic system forms part of a five-membered ring.[10] Ion (12), which occurs similarly in two isomeric forms (12a and b) (1 : 2), shows analogous spectral data (Table 2).

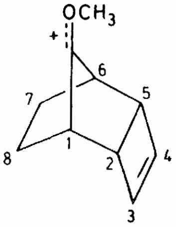
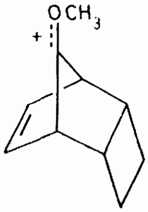
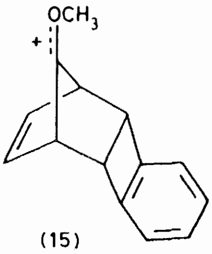
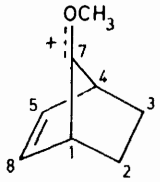
In contrast to (7b,c) the ions derived from (8b,c)—(10b,c) are consistent with the unrearranged structures (13)—(15). The ^{1}H n.m.r. data are collected in Table 3, together with those of the 7-methoxy-7-norbornenyl cation (16) for comparison.[8a]

All spectra reveal the non-equivalence of the bridgehead positions due to the restricted rotation around the C–O bond.[11] The chemical shifts of the olefinic or cyclobutenyl protons of ions (13)—(15) do not indicate any charge delocalization onto these positions. Apparently, the charge-stabilizing ability of the methoxy-group overwhelms the potentially available π participation of the double bond or the σ participation of the four-membered carbocyclic ring.

Products from 9-*Chloro*-9-*methoxy*-endo-*tricyclo*[4.2.1.0^{2,5}]-

TABLE 3

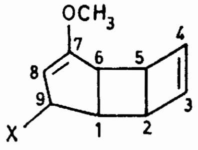
^1H N.m.r. spectral data [a] for 9-methoxytricyclo[4.2.1.0^{2,5}]nonan-9-carbenium ions in FSO_3H–SO_2 (δ values relative to internal Me_4Si)

	1-, 6-H	2-, 5-H	3-, 4-H	7-, 8-H	OCH_3	Other
 (13)	3.30 (m) 3.67 (m)	3.30 (m)	6.50 (s)	2.11—1.56 (m)	4.95 (s)	
 (14)	3.50 (m) 3.73 (m)	3.10 (m)	2.17 (m,*ex*) 1.50 (m,*en*)	6.83 (t, *J* 2.5)	4.80 (s)	
 (15)	4.27 (m)	4.20 (d, *J* 4.5)		6.45 (t, *J* 2.5)	4.90 (s)	7.33 (m, arom)
	1-, 4-H	2-, 3-H		5-, 6-H	OCH_3	
 (16)	3.83 (m) 3.53 (m)	2.23 (m,*ex*) 1.78 (m,*en*)		6.82 (t, *J* 2.5) (t, *J* 2.5)	4.67 (s)	

[a] *J* Values are expressed in Hz.

TABLE 4

^1H and ^{13}C n.m.r. spectral data [a] for tricyclo[4.3.0.0^{2,5}]nona-3,7-dienes (δ values relative to internal Me_4Si)



(17)

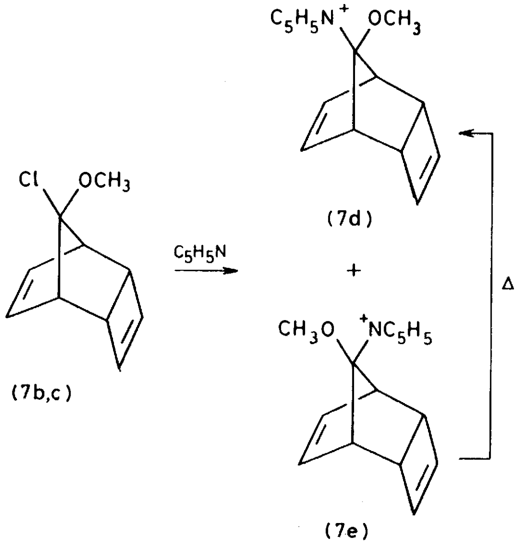
Compound	X		3,4	7	8	9	1,6	2,5	OCH_3	Other
(17a)	$C_6H_5N^+$	^1H	6.16 (m) 6.50 (m)		5.10 (d, *J* 2.5)	5.53 (t, *J* 2.5)	3.6—3.9 (br,m)	3.3—3.6 (br,m)	3.77	7.98—9.03 (arom)
(17b)	$(CH_3)_2S^+$	^1H	6.10 (m) 6.35 (m)		4.95 (d, *J* 2.5)	4.60 (t, *J* 2.5)	3.3—3.7 (br,m)		3.82	2.66 (s, CH_3)
		^{13}C	140.31 137.70	153.14	90.92	63.30	34.47 44.09	46.00 44.09	58.30	28.35 (CH_3)

[a] *J* Values are expressed in Hz.

nonanes.—Compounds (7b,c) yield products from nucleophilic substitution reactions with an unrearranged structure. The reaction with methanol afforded the starting acetal (7a), whereas the reaction with pyridine in CH_2Cl_2 at 0 °C gave rise to a mixture of epimeric pyridinium salts (7d and e). At room temperature the isomer with the pyridinium group *syn* to the cyclobutene moiety (7e) isomerizes to the *anti*-epimer (7d) (Scheme 1). A similar reaction pattern was found for compounds (8b,c)—(10b,c).

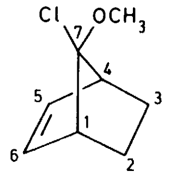
In contrast, the pyridinium salt (17a) of the rearranged structure (11) was observed when the reaction of (7b,c) with pyridine was performed under acidic conditions, such as liquid SO_2 or CH_2Cl_2–$AlCl_3$. Dimethyl sulphide as a nucleophile produced a similar structure (17b). The n.m.r. data are summarized in Table 4.

However, reaction of (7b,c) with methanol using the same conditions produced the starting acetal (7a). This compound was also recovered after dissolution of (17a) in methanol (Scheme 2). The structure of the products of the reference compounds (8b,c)—(10b,c) turned out to be independent of the conditions used. In these cases the starting structures were formed invariably.



SCHEME 1

Kinetic Measurements.—In order to study the impact of the cyclobutene moiety on the reactivity of (7b,c) under conditions of short life, in which no skeletal rearrangement occurs, the reaction of the α-chloro-ethers of (7), (9), (10), and of norbornene (18) has been studied quantitatively. The reactions were monitored by ^1H n.m.r. spectroscopy. Under the reaction conditions used, an epimeric mixture of pyridinium salts was produced for each compound. The ratio of epimers of the starting α-chloro-ethers (7b,c), (9b,c), (10b,c), and (18b,c) and those of the products (7d,e), (9d,e), (10d,e), and (18d,e) were independent of time. They are collected in Table 5. The data reveal both inversion and retention of configuration for compounds (7b,c). Predominantly inversion occurs for (9b,c) and (18b,c) whereas (10b,c) shows especially retention of configuration. The ^1H n.m.r. spectroscopic data are given in Table 1.



(18 b,c)

Probably, the product distribution is controlled by steric factors. In all cases the reaction rates turned out to be proportional to the pyridine concentration, which indicates second-order kinetics. The second-order rate constants, together with some activation parameters, are summarized in Table 6. The large negative values for the entropies of activation are in agreement with a second-order process and similar to the values for analogous ' Menschutkin reactions ', which we have reported earlier.[8]

TABLE 5

Composition of epimeric mixtures of starting α-chloro-ethers (b,c) and their reaction products (d,e) with pyridine (%)

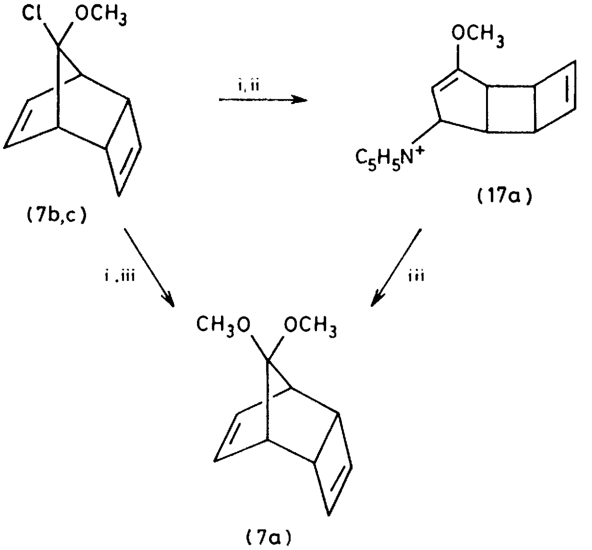
Compound	b	c	d	e
(7)	92	8	63	37
(9)	72	28	35	65
(10)	69	31	69	31
(18)	76	24	33	67

TABLE 6

Rate data for the reaction of pyridine with various 9-chloro-9-methoxytricyclo[4.2.1]nonanes

Compound	t/°C	$10^4\,k_2$/ l mol^{-1} s^{-1}	rel k	$\Delta H^{\ddagger\,a}$/ kcal mol^{-1}	$\Delta S^{\ddagger\,a}$/ cal mol^{-1} K^{-}
(7b,c)	−11.0	9.23			
	20.0	108	45	11.4	−26.6
(9b,c)	20.0	19.3	8		
(10b c)	20.0	14.2	5.9		
(18b,c)	20.0	2.4			
	35.6	7.3	1	12.0	−24.0

[a] $\Delta H^{\ddagger} \pm 0.4$ kcal mol^{-1}; $\Delta S^{\ddagger} \pm 1.3$ cal mol^{-1} K^{-1}.



SCHEME 2 Reagents: i, $AlCl_3$; ii, C_5H_5N; iii, CH_3OH

DISCUSSION

The high degree of ionization of compounds (7b,c) in liquid SO_2 is attended by their skeletal rearrangement, resulting in the formation of the stable ion (11).*

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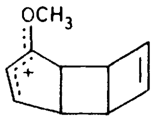
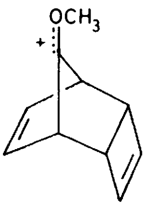
* Skeletal rearrangement prior to ionization of (7b,c) in liquid SO_2 can be ruled out on the basis of the observation that the parent acetal (7a) does not ionize and retains its skeletal arrangement under this condition.

Factors which should be considered with regard to the stability of (11) relative to (7^+) are the resonance energy of its allylic system and the increased ring strain of its ring-contracted structure.

The difference in strain energy is of the order of 14 kcal mol^{-1}.[12] This figure is the difference in standard free energy of bicyclo[2.2.1]heptane and bicyclo[3.2.0]-heptane systems. However, the estimated resonance energy of an allylic cation is 20 kcal mol^{-1}.[13] Therefore, ion (11) will be stabilized substantially with respect to (7^+). In contrast, the covalent derivative (17) of (11) will be 14 kcal mol^{-1} higher in energy than (7b,c). Thus, the formation of retro-rearranged structure (7) after quenching of ion (11) with Cl^- or methanol in liquid SO_2 is the result of thermodynamic product control. If stronger nucleophiles were used, such as pyridine, the stabilized ion (11) was trapped prior to rearrangement in a kinetically controlled reaction to yield (17a), which could be isolated. This indicates that the reverse rearrangement process of (11) to (7) can only occur at some ionic stage.



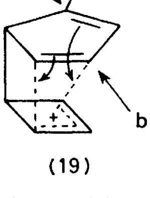
(11)



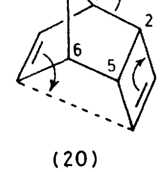
(7^+)

The reaction of (7b,c) with nucleophiles under non-acidic conditions (CH_2Cl_2) invariably afforded products without skeletal rearrangements. The quantitative study of the ionization reactions of (7b,c) with pyridine in CH_2Cl_2 revealed second-order kinetics with epimerization. This kinetic behaviour can be rationalized by assuming the reaction with an intermediate cation to be the rate-determining step. However, at this cationic stage the rearrangement process does not occur. Therefore, a bimolecular displacement mechanism, which involves chloride by pyridine and subsequently pyridine by pyridine, is more likely.

The unique, facile rearrangement of (7) involves its two isolated double bonds. If one of these bonds is saturated [(8) or (9)] or is part of an aromatic system [(10)] rearrangement reactions were not observed. These observations are in accordance with a Cope rearrangement, which is known to be facilitated by conjugation with an external carbenium ion. The Cope intermediate (19) can be described as a 6π-homoaromatic system in which a synchronous flow of electron density between the cyclobutane and cyclopentane rings can give rise to either structure (7) or (11) (routes a and b, respectively). The electron displacement which leads to (19) starting from (7^+) is shown in (20).



(19)



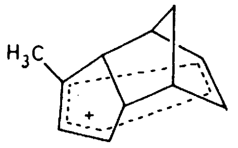
(20)

These processes require very low barriers to bond breaking and bond making, which indicates extensive σ- and π-orbital mixing. This observation is consistent with photoelectron spectral analysis, which revealed considerable through-bond coupling of the two double bonds within the structural framework of (7).[14] The high-lying σ MOs comprising C(1) and C(2) and C(5) and C(6) may interact with cationic centres to produce enhanced chemical reactivity and cationic stability.[15] Indeed, inspection of Table 6 shows the enhanced reactivity of the α-chloro-ethers of structure (7) compared with those of norbornene (18) (k_7/k_{18} 45), in spite of the inductive retardation of the additional double bond. The reactivity of the more saturated analogues (9b,c) and the benzo-derivatives (10b,c) with respect to (18b,c) is enhanced to a much lesser extent (k_9/k_{18} 8.0; k_{10}/k_{18} 5.9). The rate enhancement of (7b,c) is most adequately explained on the basis of participation of the C(1)–C(2) and C(5)–C(6) σ bonds in the rate-determining step.

The smaller rate enhancements observed for (9) and (10) indicate less effective σ participation. This is consistent with the absence of through-bond coupling in the more saturated analogue (9), whereas in (10) this effect is reduced because the cyclobutenyl double bond is delocalized in the aromatic system.

The stabilization of cationic centres by σ-bond participation is also apparent in cation (11). The existence of this ion under relatively mild conditions (liquid SO_2) suggests enhanced stabilization with respect to other allylic systems. The related ion (12), in which through-bond effects are less important due to the absence of high-lying cyclobutane σ bonds, shows indeed quite different properties.

Its preparation could only be achieved under strongly acidic conditions such as FSO_3H–SO_2. Comparison of the n.m.r. data (Table 2) also indicates additional charge stabilization in (11). The differences in the allylic resonances (Δδ) in the ^1H n.m.r. spectra of both isomers of (11) (1.53 p.p.m. for both) are significantly smaller than the corresponding values for both isomers of (12) (1.88 and 1.96 p.p.m., respectively). The ^{13}C n.m.r. values for these positions show a similar trend (Table 2). The consequent delocalization of positive charge may also be conceivable on the basis of through-space interaction of the allylic cation with the cyclobutene double



(21)

bond. This type of interaction has been reported recently to occur in (21).[16]

However, the ^{1}H and ^{13}C n.m.r. parameters for both (11) and (12) do not give any indication for this. Furthermore, it is to be expected that this type of interaction would result in a destabilization of the system, since it is forbidden by MO symmetry arguments.[8c] Therefore, the observed electron release to the allylic cation of (11) most probably takes place by mixing of the allylic π levels with the high-lying cyclobutane σ levels. This may be the origin of the downfield shift of the cyclobutane protons in (11) (δ 3.9—4.5) with respect to the comparable positions in (12) (δ 3.5—4.25).

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on Varian model T-60A and HA-100 spectrometers, equipped with variable-temperature probes. Chemical shifts are reported relative to Me_4Si as internal standard.

^{13}C N.m.r. spectra were obtained using a Varian model HA-100 NMR spectrometer, equipped with Fourier-transform accessory.

9,9-*Dimethoxy*-endo-*tricyclo*$[4.2.1.0^{2,5}]$*nona*-3,7-*diene* (7a).—A solution of 9,9-dimethoxybicyclo[4.2.1]nona-2,4,7-triene[4] (1.0 g, 5.6 mmol) in diethyl ether (100 ml) was purged with nitrogen and irradiated through quartz at room temperature for 4 h with an SP 500-W Philips high-pressure mercury lamp. A positive nitrogen pressure was maintained above the solution during the photolysis. Subsequently, the solution was filtered and concentrated. Vacuum distillation gave (7a) (0.80 g, 80%), b.p. 36—38° at 0.1 mmHg. The spectroscopic data are similar to those reported in the literature.[5]

9-*Chloro*-9-*methoxy*-endo-*tricyclo*$[4.2.1.0^{2,5}]$*nona*-3,7-*diene* (7b,c).—To a stirred solution of (7a) (5.2 g, 29 mmol) in diethyl ether (5 ml) was added phosphorus pentachloride (6.0 g, 30 mmol) in small portions at such a rate that the ether boiled gently. Sometimes heating and addition of some phosphoryl chloride was required to initiate the reaction. Vacuum distillation provided (7b,c) (2.8 g), b.p. 57—59° at 0.01 mmHg.

9-*Chloro*-9-*methoxy*-endo-*tricyclo*$[4.2.1.0^{2,5}]$*non*-3-*ene* (8b,c).—This compound was prepared from (8a)[5,6] according to the above procedure, b.p. 63—65° at 0.01 mmHg.

9-*Chloro*-9-*methoxy*-endo-*tricyclo*$[4.2.1.0^{2,5}]$*non*-7-*ene* (9b,c).—The α-chloro-ethers were prepared from (9a)[5] as described above, b.p. 66—68° at 0.01 mmHg.

1,4,4a,8b-*Tetrahydro*-9-*methoxy*-9-*chloro*-1,4-*methanobiphenylene* (10b,c).—The α-chloro-ethers were prepared from (10a)[7] as described above, b.p. *ca.* 95—99° at 0.002 mmHg.

The ^{1}H n.m.r. spectrum of cation (12) was similar to (3) which was obtained from (2). The precursor for (12) was prepared from 1-oxodicyclopentadiene[1] which was converted into the corresponding dimethyl acetal according to the method as outlined for (7a). The ^{1}H n.m.r. spectra of the isomeric cations (12) are given in Table 2.

For compounds (7)—(10) and their corresponding α-chloro-ethers the ^{1}H n.m.r. spectra are given in Table 1.

Kinetic Measurements.—Equimolar amounts of pyridine and α-chloro-ether dissolved in CD_2Cl_2 were mixed at −80° in an n.m.r. sample tube (0.4—1.2M solution). The runs were performed at temperatures as indicated in Table 6. The progress of the reaction was followed by integrating the ^{1}H n.m.r. methoxy-signals of the α-chloro-ethers and the *ortho*-protons of the pyridinium substituent of the products at appropriate intervals (see also Table 1). The rate constants were determined graphically.

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