= $CH_3(CH_2)_2$), 6028-61-1; 1 (R = $CH_3(CH_2)_4$), 13730-36-4; 1 (R = $CH_3OC(O)CH_2$), 75030-38-5; 1 (R = $CH_3(CH_2)_5CHCH_3$), 71243-24-8; 1 (R = $(CH_3)_3C$), 4253-90-1; 1 (R = 4-BrC_6H_4), 20057-86-7; 1 (R = 4-$(CH_3)_3CC_6H_4$), 13846-49-6; **2**, 2283-11-6; **3**, 1608-26-0; **4**, 5815-61-2; **9**, 75030-41-0; (±)-1-phenylethanethiol, 75081-57-1; benzyl isopropyl trisulfide, 75030-39-6; benzyl propyl trisulfide, 75030-40-9; di-4-tolyl disulfide, 103-19-5; bis(4-methoxyphenyl) disulfide, 5335-87-5; diphenyl disulfide, 882-33-7; dibenzyl disulfide, 150-60-7; 2,3-benzodithiin, 253-59-8; di-*n*-propyl disulfide, 629-19-6; di-*n*-pentyl disulfide, 112-51-6; bis[(carbomethoxy)methyl] disulfide, 1665-64-1; benzyl isopropyl disulfide, 57413-29-3; tris(morpholino)phosphine sulfide, 14129-98-7; *meso*-bis(1-phenylethyl) disulfide, 50999-18-3; (±)-bis(1-phenylethyl) disulfide, 50999-19-4; benzyl propyl disulfide, 27657-11-0; bis(isopropyl) disulfide, 4253-89-8; bis(2-octyl) disulfide, 1574-31-8; di-*tert*-butyl disulfide, 110-06-5; bis(4-bromophenyl) disulfide, 5335-84-2; bis(4-*tert*-butylphenyl) disulfide, 7605-48-3.

Proton Nuclear Magnetic Resonance Study of the Addition of Methoxide Ion to 2,4,6-Triphenylpyrylium, 2,4,6-Triphenylthiopyrylium, 1,2,4,6-Tetraphenylpyridinium, and 1-(*p*-Nitrophenyl)-2,4,6-triphenylpyridinium Cations

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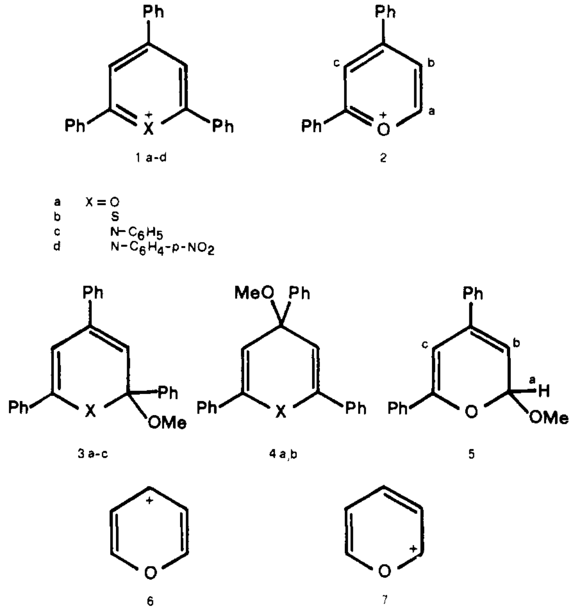
The reactions of 2,4,6-triphenylpyrylium (**1a**) and 2,4,6-triphenylthiopyrylium (**1b**) with methoxide ion are shifted toward the formation of adducts, as shown by ^{1}H NMR. The former yields practically only a 2*H*-pyran adduct in MeCN, Me_2SO, or MeOH. In MeOH, **1b** yields an adduct with a 2*H*-thiopyran structure, whereas in MeCN this adduct is obtained together with the isomeric 4*H*-thiopyran adduct. In Me_2SO or MeCN, the 1,2,4,6-tetraphenylpyridinium cation yields a 1,2-dihydropyridine. In contrast, in MeOH this equilibrium is shifted toward the reagents. The lower degree of delocalization of the positive charge in the pyridinium cation seems to be the main cause of its lower tendency to undergo nucleophilic addition.

Six-membered heteroaromatic cations can react with anionic nucleophilic reagents to give neutral adducts. In the absence of a sufficiently good leaving group at the reaction center, substitution cannot occur, and adducts can be isolated or, at least, detected. Addition occurs preferentially at the α and γ positions, where the electron density is lower. Furthermore, 2-adducts can undergo a thermally allowed, concerted ring-opening reaction, yielding dienic valence tautomers. The synthetic relevance of these reactions has been recently discussed.[1]

In a preceding work[2] we have examined the course of addition of methoxide ion to 2,6-diphenylpyrylium and 4-methoxy-2,6-diphenylpyrylium cations and have shown that the reaction pattern may be strongly affected by the nature of the substrates and the solvent.

Here we describe the results concerning the role of the heteroatom on the pattern of addition of methoxide ion. For this study we have examined the behavior of 2,4,6-triphenylpyrylium (**1a**), 2,4,6-triphenylthiopyrylium (**1b**), and 1,2,4,6-tetraphenylpyridinium (**1c**) cations in different solvents (see Chart I). These substrates share the presence of three phenyl groups at the ring positions conjugated with the heteroatom. A ^{13}C NMR investigation on the reaction of **1b** in Me_2SO-d_6 has been recently carried out.[3]

Chart I



Besides the phenylpyridinium cation **1c**, we have also considered the 1-(*p*-nitrophenyl)-2,4,6-triphenylpyridinium cation (**1d**), where the presence of an electron-withdrawing substituent was expected to increase the electrophilicity of the pyridinium cation and to shift the equilibrium toward a dihydropyridine adduct, as already observed[4] in the reaction of 1-arylpyridinium cations with MeO^-.

The choice of an aryl rather than an alkyl group in position 1 of pyridinium cations is due to the fact that the

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(3) Katritzky, A. R.; Brownlee, R. T. C.; Musumarra, G. *Heterocycles* **1979**, *12*, 775. Cognate work on the interactions between pyrylium cations and nucleophiles has been carried out at the East Anglia University. We thank Professor A. R. Katritzky and his co-workers for comments and discussions. Precedent work on the reaction of **1a** with MeO^- (Balaban, A. T.; Silhan, W. *Tetrahedron* **1970**, *26*, 743) was not able to indicate whether a 2*H*-pyran or a dienone was formed.

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Table I. Chemical Shifts (δ) and Coupling Constants (Hertz) for Compounds 1a-c and Their Adducts with Methoxide Ion

	solvent	H-3	H-5	C_6H_5	OCH_3	$J_{3,5}$
1a	$(CD_3)_2SO$	9.10	9.10	7.7-8.8		
	CD_3CN	8.78	8.78	7.6-7.9, 8.2-8.6		
1b	CD_3CN	9.05	9.05	7.6-8.0		
	CD_3OD	9.20	9.20	7.6-8.4		
1c	CD_3CN	8.33	8.33	7.5-8.2 (m, 5 H), 7.33 (s, 10 H), 7.19 (s, 5 H)		
1d	CD_3OD	8.45	8.45	see text		
3a	$(CD_3)_2SO$	5.83	6.68	7.0-8.1		1.3
	CD_3CN	5.76	6.58	7.3-8.2		1.3
	CD_3OD	5.63	6.50	7.2-8.0		1.4
	CCl_4	5.4	6.30	7.0-8.0	3.25	1.4
3b	CD_3CN	5.80	7.02	7.0-7.7		<1
	CD_3OD	5.66	6.93	7.3-7.8		<1
	CCl_4	5.59	6.82	7.1-7.8	3.22	0.6^a
3c	CD_3CN	5.32	5.65	6.2-7.7	3.57	1.5
	CCl_4	5.3	5.5	6.2-7.6	3.38	
4b	CD_3CN	6.0	6.0	7.0-7.7		
	CCl_4	5.85	5.85	7.1-7.8	3.25	

[a] Measured at 90 MHz.

latter are liable to the breaking of the C–N bond at position 1 under the influence of nucleophilic reagents. The dealkylation reaction, whereby pyridine residues behave as leaving groups, has recently found several interesting applications.[1b]

In order to define some ^1H NMR parameters useful for the definition of the structure of the products of the interaction of the pyrylium derivative, we also took into account the behavior of the 2,4-diphenylpyrylium cation (**2**).

Experimental Section

The perchlorates of **1a**, **1b**, and **2** were prepared according to literature procedures.[5-7] The perchlorate of **1c**[8] was prepared by allowing **1a** to react with an excess of aniline at room temperature for 2 h. Addition of ethyl ether caused the formation of a precipitate of **1c**, which was purified upon solution in CH_3CN and reprecipitation with ether. The perchlorate of **1d** was prepared upon heating 0.1 g of **1a** with 2 equiv of *p*-nitroaniline in acetonitrile at 100 °C for 72 h in a sealed tube. The salt was precipitated with ethyl ether, purified as described above for **1c**, and characterized through its ^1H NMR spectrum in CH_3OD, which shows the expected doublets ($J = 9$ Hz) centered at δ 7.60 and 7.95 and a singlet at δ 8.45, besides the signals of the three phenyl groups.

^1H NMR spectra were recorded on a JEOL C-60 HL instrument (unless otherwise stated) at 25 °C. The chemical shift values are quoted in δ relative to Me_4Si.

In CD_3CN, $(CD_3)_2SO$, and CD_3OD NMR spectra were recorded after the addition of a 4 M solution of sodium methoxide in methanol. Unless otherwise indicated, an equivalent amount of methoxide was added to the 0.1–0.2 M solution of the substrate. The formation of the adducts was immediate and complete, except in the case of the reactions of pyridinium cations in CD_3OD, when no adduct is formed.

Spectra of the adducts in CCl_4 were obtained after removal of the solvent from the CD_3CN or CD_3OD solutions containing equivalent amounts of the reactants and after the organic material was taken up in CCl_4.

Results

The reactions have been studied by ^1H NMR. They were started upon addition of 1 equiv of sodium methoxide to the solution of the substrate in the appropriate solvent. ^1H NMR data are reported in Tables I and II.

Table II. Chemical Shifts (δ) and Coupling Constants (Hertz) for Compound 2 and Its Adduct with Methoxide Ion

	solvent	H-a	H-b	H-c	C_6H_5	OCH_3	coupling const
2	CD_3CN	9.16	*a*	8.82	7.1-7.9, 8.1-8.5		$J_{ab} = 4.5$, $J_{bc} = 2$, $J_{ac} \simeq 0.5$
5	CD_3OD	5.8	5.8	6.45	7.1-8.0		
	CD_3CN	5.8	5.8	6.5	7.1-8.0		
	CCl_4	5.72	5.60	6.22	6.9-7.8	3.45	$J_{ab} = 3.7$, $J_{bc} = 1.5$, $J_{ac} \simeq 0$

[a] Concealed under the C_6H_5 signal at δ 7.1-7.9.

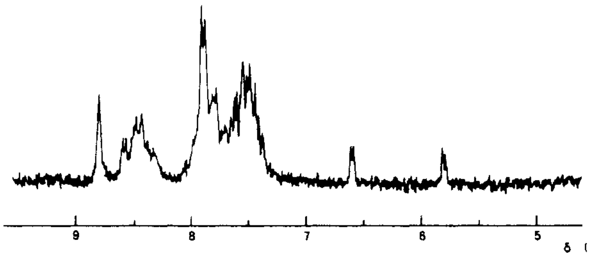

Figure 1. ^1H NMR spectrum in CD_3CN of a 1:1 mixture of **1a** and the corresponding *2H* adduct **3a**, as obtained by addition of 0.5 equiv of MeO^- to **1a**.

(A) Reaction of 2,4,6-Triphenylpyrylium (1a). In $(CD_3)_2SO$ and CD_3CN the addition of methoxide ion leads to the disappearance of the signals of **1a** and the appearance of the signals of *2H*-pyran **3a**. Besides the doublets of **3a**, a weak singlet is detected in Me_2SO at δ 5.71. Also in CD_3CN a singlet can be detected at δ 5.60, but only when the reaction is carried out at low temperature (−40 °C); upon heating, this signal disappears irreversibly. Adduct **3a** was the only species detected by ^{13}C NMR in Me_2SO-d_6 under comparable conditions after longer reaction times.[3] As to the origin of this signal, it should not belong to an open-chain dienone, which should have two scarcely coupled signals: should one of them be concealed under the phenyls, the other could be detected, but at a field somewhat lower than the one actually observed.[2,9] The singlet at δ 5.6–5.7 could be ascribed to a small amount of *4H*-pyran **4a**.[2] Experiments carried out with **1a** and OH^- ion allow one to exclude the possibility

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that the singlet may be ascribed to any product formed from **1a** and OH^-. Pyran **4a** is probably less stable than 2*H*-pyran **3a**, containing a conjugated dienic system. However, both isomers can presumably be formed under kinetic control at the beginning of the reaction.

The addition of 0.5 equiv of MeO^- to the CD_3CN solution of **1a** allows one to observe at the same time the NMR signals of **1a** and **3a** (Figure 1). The absence of coalescence between them shows that the equilibration occurs slowly on the NMR time scale. A temperature change from −20 to +50 °C does not affect the NMR pattern appreciably.

The spectrum of the CCl_4 solution, carried out in the absence of MeOH, shows the presence of **3a** only. The methoxyl group, concealed by MeOH under the above reaction conditions, now becomes detectable. The chemical shift is in agreement with the value expected for a methoxyl group bound to an sp^3 carbon atom.[10]

In CD_3OD at room temperature the reaction of **1a** with methoxide ion yields only **3a**.

(B) Reaction of 2,4,6-Triphenylthiopyrylium Cation (1b). In CD_3CN the addition of MeO^- yields a 1.2:1 mixture of 2*H*-thiopyran **3b** and 4*H*-thiopyran **4b**. In CD_3OD only **3b** is detected as a reaction product. In CCl_4 the spectrum is similar to that observed in CD_3CN, except for the presence of two singlets corresponding to the different thiopyrans, in the methoxyl region.

(C) Reaction of 1,2,4,6-Tetraphenylpyridinium Cation (1c). In $(CD_3)_2SO$ and CD_3CN the addition of MeO^- ion brings about the formation of only 1,2-dihydropyridine **3c**. The NMR spectrum of the organic residue taken up in CCl_4 is very similar to that formed in situ in the above-mentioned solvents, and, moreover, it shows the presence of a methoxyl group. When, after evaporation of the solvent from the CCl_4 solution, the adduct is dissolved in CD_3OD, the NMR spectrum taken immediately after the preparation of this solution shows only the starting substrate **1c**. Accordingly, on addition of MeO^- ion to the MeOH solution of **1c**, the NMR spectrum of the latter stays unchanged even in the presence of an excess of the nucleophile (more than 5 equiv) and after several hours.

(D) Reaction of 1-(*p*-Nitrophenyl)-2,4,6-triphenylpyridinium Cation (1d). This reaction was investigated only in CD_3OD. No adduct was detected under these conditions, although a broadening of the signals of the substrate was observed.

(E) Reaction of 2,4-Diphenylpyrylium Cation (2). The addition of MeO^- leads to the disappearance of the signals of **2** and the appearance of 2*H*-pyran **5**, formed upon addition of MeO^- to the H bearing α position. The structure of adduct **5** cannot be deduced from the NMR spectrum obtained in CD_3CN or $(CD_3)_2SO$ because the signals of the ring protons are by chance overlapping. On the contrary, the structure of adduct **5** is supported by the spectrum taken in CCl_4. The coupling constant $J_{3,5}$ is similar to that previously reported in other 2*H*-pyrans.[2] On the other hand, the coupling constant between the hydrogen at the sp^3 reaction center and the adjacent sp^2 carbon atom is comparable to those observed in neutral[11] and anionic adducts[12] formed from pyridine derivatives. The assignment of the chemical shift values to the ring protons of **5** is supported by the multiplicity pattern; on the other hand, this assignment is of help in determining the chemical shift of positions 3 and 5 of adducts **3**.

Discussion

The interaction of MeO^- ion with all the cations **1** yields adducts having structure **3** and **4**. In the reaction mixture α adducts (**3**) seem thermodynamically favored because of the presence of conjugated double bonds. Ring-opening products have not been observed, probably because bulky groups may have a hindering effect against the attainment of coplanarity of the dienic valence tautomers and the development therein of a full conjugation. In contrast, ring-opening products are formed from **1a** and amines,[13] probably because the conjugation of the carbonyl with amino groups is stronger than with alkoxy groups. Ring-opening products should be characterized by a methoxyl bound to an sp^2 carbon atom and by the two uncoupled signals of the dienic system.[2] From this point of view the spectrum of **3b** is worth some comment. The low coupling observed for the assumed ring positions (3 and 5) could also be in agreement with an open-chain structure. However, the coupling between positions 3 and 5 of 2*H*-thiopyranes is very small.[14] Moreover, judging from the chemical shift value, the methoxyl group seems to be bound to an sp^3 rather than an sp^2 carbon atom.[10]

A different interaction of the nucleophile with the thiopyrylium ring could also have occurred at the heteroatom to yield a thiabenzene derivative. Evidence for the formation of these compounds is usually given by the appearance of a deep purple color and a ^1H NMR signal at δ 7.6.[15] No clean-cut evidence of this kind has been obtained so far for the reaction of MeO^- with **1b**, even if a feeble violet coloration is transiently observed at the initial stages of the reaction. Even if in principle a thiabenzene derivative could be responsible for this coloration, it is likely that it should be rapidly converted into a mixture of the more stable thiopyrans **3b** and **4b**, as observed in the reaction of cation **1b** with alkylmagnesium halides.[15]

Adducts are formed from the pyrylium and thiopyrylium cations **1a** and **1b** in all the solvents employed so far. In contrast, the pyridinium cation **1c** undergoes addition in aprotic solvents only. Moreover, in methanol adduct **3c**, as isolated from CD_3CN, goes rapidly back to the reactants.

This result shows that the pyrylium and thiopyrylium cations have a stronger tendency than the pyridinium cation to undergo nucleophilic addition. Any difference in the tendency of pyrylium and thiopyrylium cations to undergo addition cannot yet be appreciated by the ^1H NMR technique because the equilibria are completely driven toward the adducts.

Under the same reaction conditions unsubstituted 1-arylpyridinium cations undergo nucleophilic addition at position 2, even if the equilibrium constant for the formation of the adduct from 1-phenylpyridinium cation is not high with respect to that of adducts from 2,6-diphenyl-4-X-pyrylium cations.[4,16] Thus the formation of adducts seems to be further negatively affected by the presence of a phenyl group at the reaction center, despite the small electron-withdrawing effect of this substituent. This effect is probably of steric origin.

A structural difference must be also pointed out between the pyridinium cation **1c** and the other cations **1a** and **1b**.

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J. Org. Chem. 1980, 45, 5163–5166

In **1c** the reaction center at position 2 is presumably more crowded because of the presence of three vicinal phenyl groups, which should be forced out of the heteroaromatic cation plane. However, addition is not observed at position 4 of **1c**, where the steric requirements appear to be comparable with those of position 4 of the other cations.

The observed trend in the tendency to undergo nucleophilic addition is consistent with that qualitatively observed for the nucleophilic aromatic substitution of 4-chloro heteroaromatic cations[17] and was subsequently confirmed by kinetic measurements of morpholino demethoxylation of 4-methoxy-2,6-diphenylpyrylium and 4-methoxy-1-methyl-2,6-diphenylpyridinium cations.[18]

It has been suggested that this trend in reactivity corresponds to the increasing contribution of carbonium ion structures in pyridinium, thiopyrylium, and pyrylium cations.[17] Thus the tendency of pyrylium cation to undergo nucleophilic addition is larger than in the other rings just mentioned, because of the presence of the electronegative oxygen atom which causes a strong charge delocalization. ^{13}C NMR data and theoretical calculations of the π-electron charges agree in indicating a lower electron density on the pyrylium ring with respect to the pyridinium ring.[19,20] Resonance formulas such as **6** and **7**, where the positive charge is located on the α or γ carbon atom, visualize satisfactorily the behavior of the pyrylium ring toward nucleophilic reagents.

Acknowledgment. The authors thank Professor G. Illuminati for helpful discussions.

Registry No. 1a, 15959-35-0; **1b**, 18342-83-1; **1c**, 47645-90-9; **1d**, 54231-64-0; **2**, 46897-93-2; **3a**, 71457-44-8; **3b**, 71709-21-2; **3c**, 75102-76-0; **4b**, 71709-22-3; **5**, 75102-77-1; MeO$^-$, 3315-60-4.

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Rearrangement of 1,1'-Spirobiindene and Thermochemical Evidence for Its Spiroconjugative Destabilization

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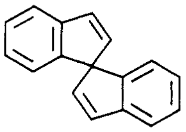
Thermal rearrangement of 1,1'-spirobiindene (1) in a flow system at temperatures above 300 °C leads exclusively to 3,4-benzofluorene, the product of vinyl migration. The same product is formed by direct irradiation at 254 nm or by treatment with potassium in refluxing THF. Determination of the heats of hydrogenation of 1 (−61.0 kcal/mol) and indene (−23.63 kcal/mol) reveals a destabilization in 1 of 13.7 kcal/mol relative to indene, in agreement with literature calculations that spiroconjugated systems like 1 possess high strain energies attributable to unfavorable π-orbital interactions.

Previous papers in this series have provided evidence that 1,1'-spirobiindene (**1**) is a spiroconjugated[1] molecule: the ultraviolet spectrum[2] exhibits a strong bathochromic shift compared to that of indene; the NMR spectrum[2] shows an upfield shift for the C-2 proton compared to simple indenes; the ORD spectrum[2] displays an intense Cotton effect at 233 nm; and, most importantly, the photoelectron spectrum[3] shows a splitting of the indene bands which correlates quantitatively with splittings in other spiroconjugated systems.

The present investigation was undertaken to add some knowledge of chemical stability to these spectroscopic investigations. Spiroconjugation does not automatically confer stabilization on a molecule, particularly when, as in the case of **1** and the parent spiro[4.4]nonatetraene (**2**),[4] the spiroconjugated system is a 4*n* π network. Indeed, molecular orbital calculations on **2** have reached contradictory conclusions on the consequences of spiroconjugation. Using CNDO/2 calculations, Tajiri and Nakajima[5] concluded that spiroconjugation has little, if any, contribution to the stabilization of molecules like **2** in their ground state. On the other hand, Gordon et al.[6] concluded on the basis of CNDO/2, MINDO/3, and SPINDO calculations that spiroconjugation should impart a net stabilization to **2**. The opposite conclusion was reached by Kao and Radom[7] from ab initio (STO-3G) calculations; they argued that the HOMO–HOMO interaction between the two butadiene fragments of **2** involves four electrons and is net destabilizing. Finally, Houk et al.[8] have recently come to the broader conclusion that homoconjugative interactions in general between neutral closed-shell π systems are destabilizing.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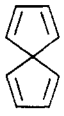
2

We have studied the stability of **1** toward pyrolysis,

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