Nuclear Magnetic Resonance Spectra of Cations of 4,4-Dialkylcyclohexa-2,5-dienones

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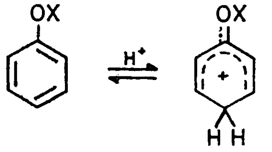
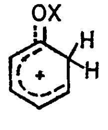
The n.m.r. spectra are reported of the cations of a range of 4,4-dialkylcyclohexa-2,5-dienones. They confirm the hydroxyarenium ion structures previously assigned to various 4-protonated phenol derivatives. Estimates are made of the excess of charge at the ring positions of the cations, but these do not correlate with the rates of dienone–phenol rearrangements of the cations.

CATIONS of type (1) and occasionally (2) have been observed when phenols and their derivatives are protonated at ring carbon atoms. Examples of (1) are obtained from phenol,[1] anisole,[1,2] 3-methylphenol,[1] 3,5-dimethylphenol,[3] 5-isopropyl-2-methylphenol,[4] 3,5-dimethylanisole,[2] 2,5-dimethylanisole,[2] and 3,4,5-trimethylphenol and its methyl ether and acetate.[3] Acids which have been shown to favour carbon (rather than oxygen) protonation are fluorosulphuric acid,[1,3,4,5] sometimes with the addition of antimony pentafluoride,[1,5] hydrogen fluoride, with or without boron trifluoride,[2a] and perchloric acid,[1] with the nature of the cations being established by n.m.r. spectroscopy, usually at −40 to −90 °C to retard hydrogen exchange. Similar hydroxyarenium ions (3b), *etc.*, should be produced by *O*-protonation of cyclohexadienones (3a) *etc.*, and ions of these types are invoked as the first reactive intermediates in dienone–phenol rearrangements.[6] Spectroscopic observation of the cations of some dichloromethylalkylcyclohexadienones [7,8] and the two hexamethylcyclohexadienones [9] have been reported, but very few data [10] are available on the cations of alkylcyclohexadienones which actually undergo the dienone–phenol rearrangement. During our studies of the kinetics and mechanism of this rearrangement [11,12] we have measured the n.m.r. spectra of a number of cyclohexadienones and their cations, and now report on some of these.



(1)



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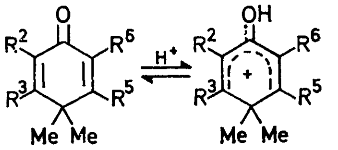
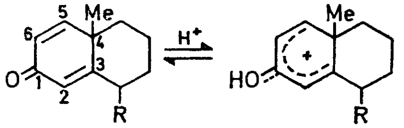
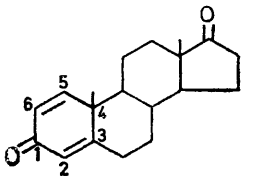


(3a)–(8a) (3b)–(8b)

	R²	R³	R⁵	R⁶
(3)	H	H	H	H
(4)	H	Me	H	H
(5)	H	Et	H	H
(6)	H	Me	Me	H
(7)	H	Et	Et	H
(8)	Me	H	H	H



(9a) R = H (9b) R = H
(10a) R = Me (10b) R = Me



(11a)

EXPERIMENTAL

Our studies of the p*K* and rearrangement kinetics of the various dienones included measurements of their u.v. spectra in a series of acids of known concentrations. From this work we knew the concentration of acid required to effect clean and complete monoprotonation of each dienone.[11,12] As far as possible, to ensure comparability, the n.m.r. spectra of the cations were measured in sulphuric acid of one concentration which was the least acidic completely (>99%) to convert each dienone into its cation; a few more weakly basic dienones were studied in a suitable stronger acid. All spectra are of clean monocations. The acid and internal reference (Me_4N^+) were thermostatted in the spectrometer, which was tuned if necessary on the Me_4N^+ peak. The dienone was added, and spectra run within a minute or two and again at appropriate intervals to check that the rate of loss of cation peaks corresponded

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[1] T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Canad. J. Chem.*, 1964, **42**, 1433.

[2] (*a*) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Rec. Trav. chim.*, 1966, **85**, 109; (*b*) D. M. Brouwer, E. L. Mackor, and C. MacLean, in ' Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley, New York, 1970, vol. 2, ch. 20.

[3] M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc.* (*B*), 1971, 1624.

[4] K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, 1971, **93**, 2323.

[5] T. Birchall and R. J. Gillespie, *Canad. J. Chem.*, 1964, **42**, 502.

[6] Reviewed by (*a*) A. J. Waring, *Adv. Alicyclic Chem.*, 1966, **1**, 129; (*b*) B. Miller, in ' Mechanisms of Molecular Migration,' ed. B. S. Thyagarajan, Interscience, New York, 1968, p. 247.

[7] E. C. Friedrich, *J. Org. Chem.*, 1968, **33**, 413.

[8] V. P. Vitullo, *J. Org. Chem.*, 1969, **34**, 224.

[9] V. G. Shubin, V. P. Chzhu, A. I. Rezvuchin, A. A. Tabatskaya, and V. A. Koptyug, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1967, 2365; V. G. Shubin, V. P. Chzhu, I. K. Korobeynicheva, A. I. Rezvuchin, and V. A. Koptyug, *ibid.*, 1970, 1742.

[10] C. MacLean and E. L. Mackor, *Mol. Phys.*, 1961, **4**, 241.

[11] K. L. Cook and A. J. Waring, *Tetrahedron Letters*, 1971, 1675, 3359.

[12] K. L. Cook, M. J. Hughes, and A. J. Waring, to be published.

with the kinetics obtained by the u.v. method. Spectra were recorded on Varian A60-A or Perkin-Elmer R12B instruments at 60 MHz and/or a Perkin-Elmer R14 at 100 MHz and 36—37 °C, with checks on the accuracy of the chemical shift calibration. All dienones were of analytical purity: (3a), (9a), and (10a) were prepared by literature methods; the preparations of the other new compounds will be published shortly. Compound (11a) is commercially available.

RESULTS AND DISCUSSION

The n.m.r. spectra of the dienones and their cations are in Table 1. The former are fully consistent [6a] with the assigned structures; the latter clearly prove that protonation occurs at the carbonyl group to give the hydroxyarenium ions (3b)—(11b). The cation spectra agree satisfactorily with those reported for the hydroxyarenium ions produced by protonation of phenols and their derivatives, as in (1), when it is noted that the earlier studies used different acids and temperatures, some used external references for the spectral measurements, and none took care to ensure clean but complete monoprotonation: in general our results confirm the previously assigned structures. The cation spectra also parallel those reported for the cations of the analogous hexamethylcyclohexa-2,5-dienone [9] and three 4-dichloromethyldienones [7,8] although the latter have significantly but not consistently lower τ values for all their protons. The differences will reflect the different substitution and conditions of measurement.

TABLE 1

N.m.r. data for dienones and their cations [a]

	2-Substnt.		3-Substnt.		4-Me	5-Substnt.		6-Substnt.		Coupling constants [b]	
Compound		τ		τ	τ		τ		τ	H(2)–H(6)	H(5)–H(6)
(3a)	H	3·93	H	3·24	8·73	H	3·24	H	3·93		*ca.* 10·4
(3b)		3·06		1·93	8·59		1·93		3·06		9—10
(4a) [c]	H	4·04	Me	8·02	8·75	H	3·37	H	3·97	1·8—1·9	*ca.* 9·9
(4b)		3·01		7·57	8·59		1·84		2·99	*ca.* 2·2	*ca.* 10·2
(5a) [d]	H	4·01	Et	7·66	8·76	H	3·38	H	3·96	*ca.* 1·6	10
(5b) [e]		3·02		7·22	8·52		2·00		3·09	*ca.* 2	10
(6a)	H	4·08	Me	7·98	8·73	Me	7·98	H	4·08		
(6b)		3·04		7·53	8·55		7·53		3·04		
(7a) [d]	H	4·05	Et	7·70	8·75	Et	7·70	H	4·05		
(7b) [e]		3·04		7·23	8·56		7·23		3·04		
(8a) [f]	Me	8·19	H	3·53	8·77	H	3·31	H	3·94		*ca.* 9·8
(8b) [f]		7·87		2·12	8·57		1·91		2·99		9
(9a)	H	4·05			8·74	H	3·37	H	3·94	*ca.* 1·7	10
(9b) *		3·01			8·57		1·88		2·96	*ca.* 1·7	*ca.* 9·7
(10a) [g]	H	4·05			8·74	H	3·37	H	3·93	*ca.* 1·6	10
(10b) [h,*]		3·00			8·57		1·90		2·96		*ca.* 9·5
(11a)	H	4·06			8·76	H	3·06	H	3·91	*ca.* 1·7	*ca.* 10·2
(11b) *		3·01			8·56		1·69		2·96		*ca.* 9

[a] τ Values; dienones in CCl_4 with Me_4Si as internal standard: cations in 70% aq. H_2SO_4 unless otherwise stated, with Me_4N^+ as internal standard, τ 6·84 in 70% H_2SO_4, 6·86 in 75% H_2SO_4 (G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, 1970, **92**, 6238). [b] Coupling constants in Hz. [c] H(2)–Me(3) *ca.* 1·1 Hz. [d] CH_2 of ethyl tabulated; CH_3 at τ 8·81—8·82, *J* 7—8 Hz. [e] CH_2 of ethyl tabulated; CH_3 at τ 8·71—8·73, *J* 7—8 Hz. [f] Me(2)–H(3) *ca.* 1·4 Hz in (8a); H(3)–H(5) *ca.* 3 Hz in (8a), *ca.* 2 Hz in (8b). [g] CH(*Me*) τ 8·84, *J ca.* 6·4 Hz; H(2) couples to C*H*(Me), *J ca.* 1·6 Hz. [h] CH(*Me*) τ 8·72, *J ca.* 6 Hz.

* In 72% H_2SO_4.

Formulae (9)—(11) are numbered as derivatives of cyclohexadienone.

All the n.m.r. signals of the dienones move downfield on protonation, those due to the 3- and 5-groups moving most, which is consistent with these positions bearing the greatest positive charge. Attempts have been made in the past to estimate the excess of charge density at the various positions in arenium ions from the n.m.r. chemical shifts of protons or methyl groups attached to those positions.[2b,10] We have made estimates using equations (1) and (2) which are based closely on 'standard' chemical shifts and proportionality constant values quoted by Brouwer and his coworkers,[2b,†] These lead to the estimates of charge given in Table 2.

$$\text{Charge} = 0{\cdot}192(8{\cdot}46 - \tau_{\text{Me}}) \qquad (1)$$

$$\text{Charge} = 0{\cdot}087(3{\cdot}68 - \tau_{\text{H}}) \qquad (2)$$

Although little reliance should be attached to the exact numbers in Table 2 some trends are clear. The

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[†] Some of these values are not explicitly stated in ref. 2*b*, which modifies those used in ref. 10. The methyl standard, τ 8·46, uses Tiers' value of 7·663 for the toluene methyl group [13] corrected by 0·80 for the ring-current effect. The factor 0·192, together with published chemical shifts,[2b] leads to one unit of excess of charge on the pentamethyl- and hexamethyl-benzenium ions. The proton standard, τ 3·68, represents the benzene chemical shift (τ 2·734) [13] corrected by 0·946 for the ring-current.[14] The factor 0·087 leads to the most consistent estimates of total charge on the many methyl-substituted arenium ions discussed by Brouwer and his co-workers,[2b] and is close to the value used by Musher:[15] the results are, however, not completely internally consistent. We have also used equations based on Brouwer's group's earlier values,[10] charge = $0{\cdot}21(8{\cdot}28 - \tau_{\text{Me}}) = 0{\cdot}074(4{\cdot}46 - \tau_{\text{H}})$; the estimates of charge differ somewhat from those in Table 2, but all the conclusions remain unchanged.

[13] G. V. D. Tiers, 'Characteristic N.M.R. Shielding Values for Hydrogen in Organic Structures,' Minnesota Mining and Manufacturing Company, 1958.

[14] B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, 1962, **34**, 18.

[15] J. I. Musher, *J. Chem. Phys.*, 1962, **37**, 34.

charges at C(2), C(3), C(5), and C(6) are significantly smaller (by *ca.* 0·1 unit at each position) than those found in normal arenium ions,[2b,10] the remaining charge being located at the protonated carbonyl group. There is also little variation in the charge at C(3) or C(5) (to which migration occurs in the dienone–phenol rearrangement) when methyl groups are placed at C(2) [C(6)] or even at C(3) or C(5). In particular, there does not appear to be a sufficiently large variation in charge distribution from one cation to another to explain the considerable variations [11,12] in the rates of rearrangement of the dienones discussed here. This conclusion is consistent with the kinetic studies which also show the transition state for the rearrangement to have activity-coefficient behaviour, and therefore detailed structure, quite different from that of the hydroxyarenium ion. That is, the cation of the dienone is not an acceptable model for the transition state through which it rearranges.

TABLE 2

Excess of positive charge (electron units) at ring carbon atoms

	Carbon atoms			
Ion	2	3	5	6
(3b)	0·05	0·15	0·15	0·05
(4b)	0·06	0·17	0·16	0·06
(5b)	0·06		0·15	0·05
(6b)	0·06	0·18	0·18	0·06
(7b)	0·06			0·06
(8b)	0·11	0·14	0·15	0·06
(9b)	0·06		0·16	0·06
(10b)	0·06		0·16	0·06
(11b)	0·06		0·17	0·06

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