Diazenium Cations. Part 2.[1] Synthesis and Mechanism of the 'Reduction' of Bicyclic *cis*-Diazenium Derivatives in Alcoholic Media

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Bicyclic *cis*-azo-compounds are protonated by mineral acids to give the corresponding diazenium ions in high yields. When refluxed in an alcohol bearing an α-hydrogen atom, the cations are transformed into mixtures of products difficult to separate, the major component of which is the corresponding hydrazinium species. All products have been characterized by independent synthesis. In an attempt to specify the mechanism of the 'reduction,' unsubstituted, *N*-isopropyl-, and *N*-t-butyl-diazenium salts with various counterions (Cl^-, Br^-, I^-, or ClO_4^-) have been prepared and their thermal properties investigated as a function of solvent and various additives. It is concluded that the unsubstituted diazenium cations react by alkylation, prototopic rearrangement, and subsequent hydrolysis. The mechanistic result has led to a new, high-yield synthesis of the *N*-t-butyldiazenium species.

QUATERNIZED aromatic azo-compounds (aryldiazenium ions) were observed and isolated early in this century.[2] For the protonated species a long-standing controversy as to the site of protonation [3] has finally been resolved by *X*-ray photoelectron spectroscopy.[4] Quaternized azoalkanes have proved more elusive. The search for stable representatives may have been discouraged in part by the knowledge that azobenzene is a slightly weaker base than methanol [pK_a (*trans*-azobenzene) -2.9 [4b,5]]. Furthermore, with the exception of quite recent results,[1,6–8] the only non-aryl diazenium ions (1) known are very labile.

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[1] Part 1, M. L. Heyman and J. P. Snyder, *J. Amer. Chem. Soc.*, 1975, **97**, 4416.

[2] A. Korczynski, *Ber.*, 1908, **41**, 4379; A. Hantzsch, *ibid.*, 1909, **43**, 2129; F. Kehrmann and R. Van der Laar, *ibid.*, 1909, **43**, 2129; 1922, **55**, 511; *cf.* A. N. Ferguson, *Tetrahedron Letters*, 1973, 2889.

[3] (*a*) M. A. Hoefnagel, A. van Veen, and B. M. Wepster, *Rec. Trav. chim.*, 1969, **88**, 562; E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, 1968, **51**, 16; W. Isaks and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1964, **86**, 2209; J. H. Collins and H. H. Jaffé, *ibid.*, 1962, **84**, 4708; G. E. Lewis, *J. Org. Chem.*, 1960, **25**, 2193; (*b*) F. Gerson, E. Heilbronner, A. van Veen, and B. M. Wepster, *Helv. Chim. Acta*, 1960, **43**, 1889.

[4] E. Haselbach, A. Henriksson, A. Schmeizer, and H. Berthou, *Helv. Chim. Acta*, 1973, **56**, 705; n.m.r. evidence indicates that 2,2′-dimethylazopropane is protonated unsymmetrically at the lone electron pair on nitrogen.[5]

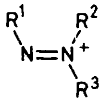
[5] S. Yeh and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1959, **81**, 3274.

[6] E. Haselbach and E. Heilbronner, *Tetrahedron Letters*, 1967, 4531.

[7] S.F. Nelsen and R. T. Landis, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 2719.

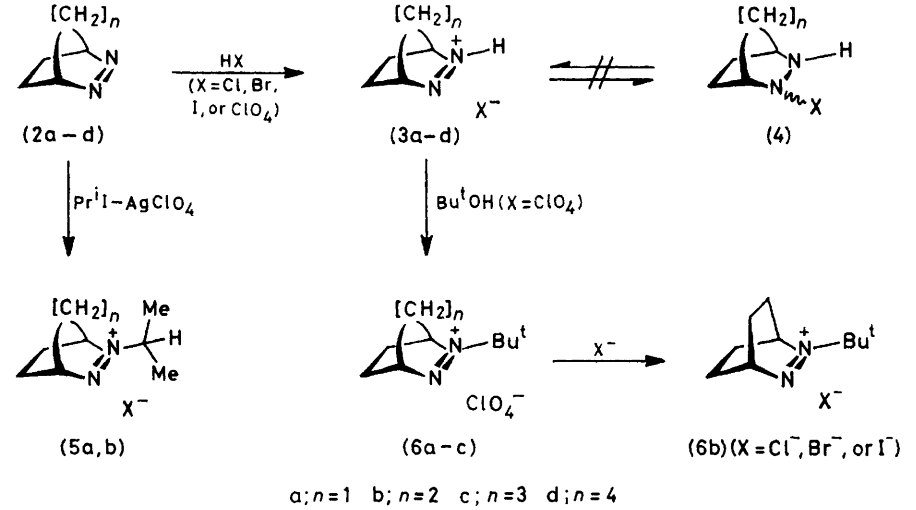
[8] S. F. Nelson and R. T. Landis, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 1788.

For example the 1,2-dialkyl cations[9] (1; R^1 and R^2 both alkyl) as well as protonated azodiformic acid and its esters[10] have been suggested as highly reactive intermediates in a variety of transformations. Certain 1,1-dialkyl species (1; R^2 and R^3 both alkyl, R^1 = H) have been observed spectroscopically and serve as reaction partners in strong acid below 0 °C.[11] However, at room temperature or above the 1,1-dialkyl cations break down to give a complex mixture of products which have been suggested to arise through the intermediacy of diazene.[9a,*]



(1)

The present report describes the preparation of a series of bicyclic diazenium ions and their ready conversion into the corresponding hydrazinium species, an unprecedented overall reduction process.



Preparation of Diazenium Ions; Structural Considerations.—The diazenium salts (3) are generated in a straightforward fashion by protonation of bicyclic *cis*-azoalkanes (2) with mineral acids in ether. The hydrobromide salts (3a—d; X = Br) are thus obtained in 90—100% yields. The salts (3a and b; X = Cl^- or ClO_4^-) have been obtained likewise. The starting azoalkane (2) is regenerated by treatment with base. As in the case of the corresponding azoxyalkanes,[13] the bridgehead protons for all protonated diazenium derivatives described here are not differentiated by ^{1}H n.m.r. (60 MHz). Their signals consistently appear as a broad singlet, τ 4.2—4.8. The spectra are unchanged at −78 °C. This result contrasts with the observations[5] that 2,2′-dimethylazopropane in 96% sulphuric acid at −10 °C yields the corresponding unsymmetrical diazenium ion with t-butyl groups distinguishable by n.m.r.

In principle the covalent hydrazine structure (4) with accidentally coincident bridgehead proton n.m.r. shifts might equally well represent the protonation products of the azo-compounds (2). However, in addition to their sparingly soluble character in non-polar organic solvents, the ionic character of the diazenium systems (3) is supported by two observations. Legitimate hydrazines and their salts [*e.g.* (7) and (8)] exhibit bridgehead proton signals at considerably higher field, τ 5.8—7.2, whereas *N*-alkyldiazenium ion bridgehead protons appear separately [(5) and (6) Δδ 0.15—0.50 p.p.m.] in the range τ 3.5—4.8 (Table 1). Secondly the ^{1}H n.m.r. spectra of the salts with halide counterions are almost identical with those of the salts with the non-nucleophilic perchlorate ion. Thus, although we cannot rule out the presence of the hydrazines (4) at low concentration in solutions of the cations, the ionic species (3) is clearly the major form in both moderately polar organic solvents ($CDCl_3$ or CH_2Cl_2) and water. The magnetic equivalence of the bridgehead protons is consequently attributed to rapid exchange, even at low temperatures. This interpretation is supported by

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[*] Alkoxy-derivatives (1; R^2 and R^3 both alkyl, R^1 = OR^4) are readily isolable.[12]

[9] (*a*) S. Wawzonek and W. Mckillip, *J. Org. Chem.*, 1962, **27**, 3946; (*b*) H. Prinzbach and H. D. Martin, *Chimia* (*Switz.*), 1969, **23**, 37; P. A. S. Smith, 'Chemistry of Open Chain Nitrogen Compounds,' Benjamin, New York, 1966, pp. 304—305; *cf.* K. A. Taiple, *Zhur. obshchei Khim.*, 1924, **54**, 638; 1925, **56**, 81 (*Chem. Abs.*, 1924, **18**, 3049; 1925, **19**, 3478); *Ber.*, 1923, **56**, 954; E. Benzing, *Annalen*, 1960, **631**, 10.

[10] H. Zöllinger, 'Azo and Diazo Chemistry,' Interscience, New York, 1961, pp. 286—290.

[11] W. H. Urry, Z. L. F. Gaibel, J. C. Duggan, and S. S. Tseng, *J. Amer. Chem. Soc.*, 1973, **95**, 4338; W. H. Urry, P. Szecsi, C. Ikoku, and D. W. Moore, *ibid.*, 1964, **86**, 2224; W. R. McBride and E. M. Bens, *ibid.*, 1959, **81**, 5546; W. H. Urry, H. W. Kruse, and W. R. McBride, *ibid.*, 1957, **79**, 6568; W. R. McBride and H. W. Kruse, *ibid.*, 1957, **79**, 572; *cf.* C. M. Lemal, C. D. Underbrink, and T. W. Rave, *Tetrahedron Letters*, 1964, 1955; D. M. Lemal, in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, pp. 388—397; S. Hünig and F. Bruhne, *Annalen*, 1963, **667**, 86.

[12] *Cf.* G. Büttner and S. Hünig, *Chem. Ber.*, 1971, **104**, 1104, and references therein.

[13] J. P. Snyder, V. T. Bandurco, F. Darack, and H. Olsen, *J. Amer. Chem. Soc.*, 1974, **96**, 5158.

Table 6 (see Experimental section) and the solvent-dependent charge-transfer behaviour mentioned below.

The *N*-isopropyldiazenium perchlorates (5a and b; X = ClO_4) are obtained in 90—100% yield by alkylation of the azo precursors (2) with isopropyl iodide and silver perchlorate in methylene chloride. The iodide (5b; X = I) is prepared simply by mixing isopropyl iodide and (2b) (86%). Ion exchange furnishes the bromide (5b; X = Br). Similar attempts to prepare the chloride and sulphonate salts were less successful. Although homogeneous products were observed from time to time, inseparable mixtures of species (5b), (9b), and (7b) were ordinarily obtained.

TABLE 1

Physical data for the diazenium salts

						Reqd. (%) Found (%)			
	X	M.p. (°C) (solvent)[a]	Yield (%)	$\tau(CDCl_3)$	Formula	C	H	N	X
(3a)	Br	114—116 ($CHCl_3$–Et_2O)	97	0.95br (1 H, s), 4.20br (2 H, s), 7.6—8.8 (6 H, m)	$C_5H_9BrN_2$	33.9 33.7	5.1 5.0	15.8 15.9	
	ClO_4	236—237	69	−5.18br[b] (1 H, s), 4.26br (2 H, s), 7.6—9.0br (6 H, m)	$C_5H_9ClN_2O_4$	30.6 30.4	4.6 4.6	14.3 14.3	
(3b)	Cl	145—146	91	−8.20br (1 H, s), 4.33br (2 H, s), 7.5—8.7 (8 H, m)	$C_6H_{11}ClN_2$	49.1 47.9	7.6 7.1	19.1 19.0	24.2 24.3
	Br	198—199	93	−7.83br (1 H, s), 4.22br (2 H, s), 7.4—8.6 (8 H, m)	$C_6H_{11}BrN_2$	37.7 37.8	5.8 5.7	14.6 14.5	41.8 41.5
	ClO_4	241—242	83	4.60br (2 H, s), 7.7—9.0 (8 H, m)	$C_6H_{11}ClN_2O_4$	34.2 34.3	5.3 5.3	13.3 13.6	16.8 16.8
(3c)	Br	198—199	97	−2.31br (1 H, s), 4.40br (2 H, s), 7.3—8.3 (10 H, m)	$C_7H_{13}BrN_2$	41.0 40.4	6.4 6.2	13.7 13.9	
(3d)	Br	209—211	100	0.92br (1 H, s), 4.75br (2 H, s), 6.9—9.1 (12 H, m)	$C_8H_{15}BrN_2$	43.8 43.6	6.9 7.0	12.8 12.6	
(5a)	ClO_4	122—124	99	4.3—4.4[c] (2 H, s), 4.8—5.2 (1 H, m), 7.5—8.7 (6 H, m), 8.35, 8.40 (3 H, 3 H, *d*, *J* 7 Hz)	$C_8H_{15}ClN_2O_4$	40.3 39.4	6.3 6.0	11.7 11.6	
(5b)	Br	151—153	64	3.95br, 4.15br (1 H, 1 H, s), 4.18 (1 H, sept), 7.3—8.5 (8 H, m), 8.30 (6 H, *d*, J 6 Hz)	$C_9H_{17}BrN_2$[e]	46.4 44.9	7.3 7.4	12.0 12.5	
	I	224—225	86	4.12br (2 H, s), 4.34 (1 H, sept, *J* 6.5 Hz), 7.5—8.4 (8 H, m), 8.25 (6 H, d ,*J* 6.5 Hz)	$C_9H_{17}IN_2$	38.6 38.6	6.1 6.2	10.0 10.1	
	ClO_4	227—228 (EtOH)	91	4.18br, 4.44br (1 H, 1 H, s), 4.85 (1 H, sept), 7.5—8.5 (8 H, m), 8.3 (6 H, d, *J* 7 Hz)	$C_9H_{17}ClN_2O_4$	42.8 42.5	6.8 6.5	11.1 11.2	14.0 14.0
(6a)	ClO_4	209—210	86	4.11br (2 H, s), 7.4—8.8 (6 H, m), 8.30 (9 H, s)	$C_9H_{17}ClN_2O_4$	42.8 42.6	6.8 7.0	11.2 11.2	14.0 14.0
(6b)	Cl	191—192 ($CHCl_3$)	78	3.56br, 4.05br (1 H, 1 H, s), 7.4—8.4 (8 H, m), 8.10 (9 H, s)	$C_{10}H_{19}ClN_2$[e]	59.2 58.3	9.4 8.5	13.8 13.7	17.5 17.3
	Br	226—227 ($CHCl_3$)	83	3.58br, 4.01br (1 H, 1 H, s), 7.4—8.4 (8 H, m), 8.10 (9 H, s)	$C_{10}H_{19}BrN_2$	48.6 48.3	7.8 7.9	11.3 11.2	32.4 32.3
	I	223—224 (Pr^iOH)	93	3.74br, 4.05br (1 H, 1 H, s), 7.4—8.6 (8 H, m), 8.11 (9 H, s)	$C_{10}H_{19}IN_2$	40.8 40.7	6.5 6.6	9.5 9.6	43.2 43.3
	ClO_4	254—255	81	4.11br, 4.27br[d] (1 H, 1 H, s), 7.7—8.6 (8 H, m,), 8.29 (9 H, s)	$C_{10}H_{19}ClN_2O_4$	45.0 45.3	7.2 7.1	10.5 10.5	13.3 13.2
(6c)	ClO_4	234—235	85	4.22br, 4.60br (1 H, 1 H, s), 7.4—8.6 (10 H, m), 8.33 (9 H, s)	$C_{11}H_{21}ClN_2O_4$	47.1 46.0	7.5 7.7	10.0 10.2	12.6 12.3

[a] Where no solvent is given, repeated washing with dry ether provided the sample for analysis. [b] $CDCl_3$–CD_3CN. [c] $CDCl_3$–CD_2Cl_2. [d] CD_3CN. [e] Very hygroscopic.

N-Butyldiazenium salts have been prepared earlier in 15—75% yields by direct alkylation of cyclic azoalkanes with t-butyl iodide and silver tetrafluoroborate.[8] Improved access to the t-butyl derivatives utilizes the cations (3) in refluxing t-butyl alcohol. Perchlorates (6a—c) are obtained in 80—90% conversions, and ion exchange introduces Cl^-, Br^-, or I^- in similar yields. Data for the bicyclic diazenium ions are summarized in Table 1.

We have previously reported that the t-butyldiazenium species (6b) exhibits charge-transfer (CT) spectra.[1] In polar solvents the u.v. spectra for all counterion derivatives are characterized by intense absorption below 230 nm and a weak band at 310 nm (ε *ca.* 100). Reduction of solvent polarity leads to the appearance of long wavelength CT absorption dependent on the nature of the counterion and independent of Beer's law.[14] In agreement with the ionization potentials of the gegenions, the magnitude of the effect diminishes as follows: $I^- > Br^- > Cl^-$. The isopropyl series (5b) shows similar behaviour (Table 2). These data provide further evidence for the ionic character of the diazenium salts described here, and emphasize the charge-accepting capacity of the diazenium system.

'Reduction' of Diazenium Salts (3) *in Alcoholic Media.*—Under oxygen-free conditions in alcohols the salts (3a and b; X = Br) are transformed into the corresponding hydrazinium salts simply by heating. Thus a methanolic solution of the hydrobromide (3a; X = Br) upon heating under reflux (24 h) gives a mixture of azoalkane (2a) and hydrazine hydrobromide (7a; X = Br) in variable yields (3—35% and 35—65%, respectively). Proof for the structure of (7a; X = Br) was obtained by its sequential treatment with ethyl chlorocarbonate and phenyl isothiocyanate and heating to give the

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[14] E. Kosower, *J. Amer. Chem. Soc.*, 1955, **77**, 3883; E. M. Kosower and P. E. Klinedinst, *ibid.*, 1956, **78**, 3493.

corresponding thioxotriazolidinone.[15] A similar result was obtained for (3a) when propan-2-ol was used as solvent (N_2; reflux; 24 h). However, in hot chloroform containing 0.75% ethanol as stabilizer, the bishydrobromide (8) was produced in 71% yield within 5 min. Analogously the diazenium homologue (3b; X = Br) in methanol affords the azoalkane (2b) and the hydrazine hydrobromide (7b; X = Br) along with considerable amounts of tarry material. In propan-2-ol (N_2; reflux; 24 h), several runs yielded (2b) and (7b; X = Br) in the ratio *ca.* 1 : 1 with a total conversion of 10—15%. From all runs conducted in propan-2-ol, acetone was a side product.

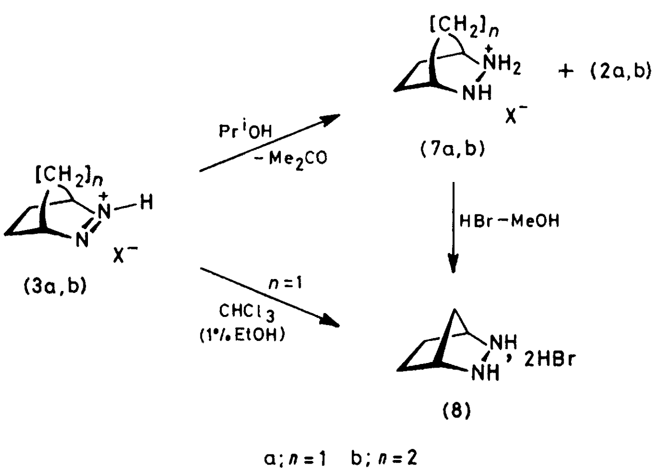
TABLE 2

U.v.–visible absorption maxima at a function of solvent for the isopropyldiazenium salts (5b) ($\lambda_{max.}$/nm) ($\varepsilon_{apparent}$/l mol^{-1} cm^{-1}) [a-c]

	H_2O	MeOH	MeCN	CH_2Cl_2
(5b; X = ClO_4)	309 (110)	309 (90)	308 (105)	309 (110)
(5b; X = I)	308 (115)	308 (110)	308 (120)	309 (250)
		348 (20)	388 (17)	423 (280)

[a] Calculated from the observed optical density and the initial concentration (5.0×10^{-3}M). [b] Both salts show high intensity absorption at <230 nm. [c] If I_3^- is present as a contaminant, the molar ratio of (5b; X = I) to I_3^- is <1 : 150 [$\lambda_{max.}$(I_3^-, MeCN) 368 nm (ε *ca.* 26 000 l-mol^{-1} cm^{-1}) [24]].

The Question of Radical Intermediates.—At the outset of our studies the irreproducibility of yields and the formation of (7) or (8) and acetone suggested a redox reaction, accelerated by a halogenocarbon solvent. This supposition was strengthened by the sporadic appearance of broadened n.m.r. spectra following the transformation of (3b; X = Cl or Br). An e.s.r. spectrum of the chloride in one case exhibited a three-line pattern characteristic of a nitroxide radical[8] (a_N 15.1 G, *g* 2.005 0—2.005 1).



Radical or radical-type intermediates could conceivably arise from a thermally accessible diazenium ion triplet state. Nitrenium ions, of which the function (1) is formally an amino-substituted derivative, behave in this way.[16] In addition intersystem crossing is accelerated by the presence of heavy atoms. To test the possibility of an internal heavy atom effect, diazenium ions with various counterions were thermolysed as described above. The effect of solvent variation in the reaction (3) ⟶ (7) was likewise explored for evidence of an external effect. As indicated by Table 3, neither internal (counterion) nor external (solvent) heavy atoms attenuate product formation. Equally noteworthy was the formation of considerable quantities of alkylated and rearranged products [(5b) and (9b), respectively; *cf.* Scheme 1]. We will return to the latter point later.

Radicals could in principle also arise from thermal charge-transfer excitation[17] as observed for the diazenium ion (10),[1] or by homolytic cleavage of the N–X bond of (4). Again, however, no evidence for a doublet species could be gathered. The formation of hydrazine was not influenced by oxygen purging, light, or the presence of phenylmethanethiol (*cf.* Table 3). In the presence of the thiol (3b; X = Br) was 55% 'reduced,' whereas (3b; X = ClO_4) was unchanged. Control experiments demonstrated the lack of significant dibenzyl disulphide production, and suggested that the thiol functions here as a base (see later).

TABLE 3

Thermolysis of diazenium salts (3b) as a function of counterion, solvent, and additives (88 °C)

		Time	Conversion	Product ratios		
X	Medium	(h)	(%) [a]	(5b)	(9)	(7b)
Cl [e]	Pr^iOH	24	5	0	1	1
		48	11	0	0	1
Br [c]	Pr^iOH	24	10	0	1	3
		48	15	0	0	1
ClO_4 [e]	Pr^iOH	24	20	10	0	1
		48	38	32	1	5
ClO_4	Pr^iOH	118	63	6	1	5
ClO_4	Pr^iOH–CsI (sat.) [c]	118	53	1	1	8
ClO_4	Pr^iOH–NaBr (sat.) [c]	118	36	1	1	3
ClO_4	Pr^iOH–NaF	118	0	0	0	0
ClO_4	Pr^iOH–$Br_2C\!:\!CBr_2$ (1 : 1) [b]	118	63	2	1	3
ClO_4	Pr^iOH–cyclo-C_6H_{12} (1 : 1) [b]	118	18	4	1	2
Br	Pr^iOH–BzSH [d]	24	55	0	0	1
ClO_4	Pr^iOH–BzSH [d]	24	0	0	0	0

[a] (100 − conversion) = unchanged starting material (%); values accurate to ±5%. [b] Volume ratio. [c] A 10 molar excess of MX relative to (3b) was added to the solution at the outset. Although the additive was incompletely dissolved at reflux (88 °C), parallel experiments with 1 mol. equiv. of MX gave clear solutions and results similar to those tabulated. [d] Two mol. equiv. of BzSH; ⩽8% of $(BzS)_2$ was formed. [e] Temperature 82—83 °C.

In order to avoid possible interpretative ambiguities associated with the relative acid strengths of HX and thus the variably displaced equilibria containing HX, (2b), and (3b), the parallel thermal behaviour of the *N*-alkyldiazenium ions was investigated. The t-butyl derivatives (6a; X = ClO_4) and (6b; X = Br or I) are completely inert under conditions forceful enough to convert the species (3). For the isopropyl-substituted cation (5b) a considerable number of experiments was carried out in a wide range of solvents with Cl^-, Br^-, I^-,

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[15] S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, 1961, **83**, 2895.

[16] P. G. Gassman, *Accounts Chem. Res.*, 1970, **3**, 26.

[17] E. M. Kosower, *Progr. Phys. Org. Chem.*, 1965, **3**, 81.

$MeSO_3$, and ClO_4 as counterions. Representative results are in Table 4. Under no circumstances was the isopropylhydrazine (11) or its conjugate acid observed. In every case a mixture of starting material, hydrazine (7b), iminium salt (9b), and acetone resulted. Finally, the reaction of (5b; X = I) was conducted in an n.m.r. cavity at 88 °C, but no signals indicative of the CIDNP effect were produced.

TABLE 4

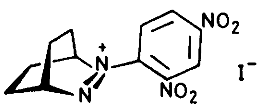
Thermolysis of isopropyldiazenium salts (5b) as a function of solvent and counterion (83 °C)

X	Medium [a]	Time (h)	Conversion (%) [b]	Product ratio (9b)	Product ratio (7b)
Cl	Pr^iOH	0.5	92	3	1
Br	Pr^iOH	2	30	1	0
		6	52	2.7	1
		8	67	1.8	1
I	Pr^iOH	6	16	1	0
		12	29	1	0
		48	61	1	0
		72	76	1	0
ClO_4	Pr^iOH	48	24	1	0
		74	28	1	0
		96	37	1	0
ClO_4	Pr^iOH–cyclo-C_6H_{12} (9 : 1)	48	28	1	0
		74	46	1	0
		96	46	1	0
ClO_4	Pr^iOH–cyclo-C_6H_{12} (3 : 1)	48	25	1	0
		74	29	1	0
		96	43	1	0
ClO_4	Pr^iOH–DCE [c] (3 : 1)	24	64	1	0
		48	94	7	1
$MeSO_3$ [d]	Pr^iOH	5	25	1	2

[a] Volume ratios. [b] (100 − conversion) = unchanged starting material (%); values accurate to ±5%. [c] 1,2-Dichloroethylene. [d] Temperature 75 °C.

In view of these results, radicals or radical-like intermediates seem to be excluded from the major pathway of hydrazine formation.

An Alkylation–Tautomerisation–Hydrolysis Pathway.—The key to the 'reduction' mechanism lies in the transformation of the cations (3b) into a mixture of (5b), (7b), and (9b) (Table 3) and the observation that (5b) is similarly converted into (7b) and (9b) (Table 4). The Scheme portrays an alkylation–tautomerisation–hydrolysis sequence leading to the hydrazine product. In order to verify this sequence, each of the depicted equilibrium components was refluxed in propan-2-ol with 1 equiv. of either acetone or water. The results are shown in Table 5. Although several conclusions may be drawn, two points are of note: (i) salts (5), (9), and (7) all furnish similar mixtures; and (ii) the isopropyl derivatives (5) are thermodynamically unstable with respect to the iminium salt (9) and the hydrazine (7). Since the unsaturated bicyclo[2.2.1]- and [2.2.2]-skeletons are rather strained,[18] it is not extraordinary that isomerisation to the exocyclic imine derivative occurs.



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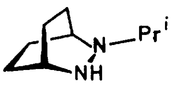
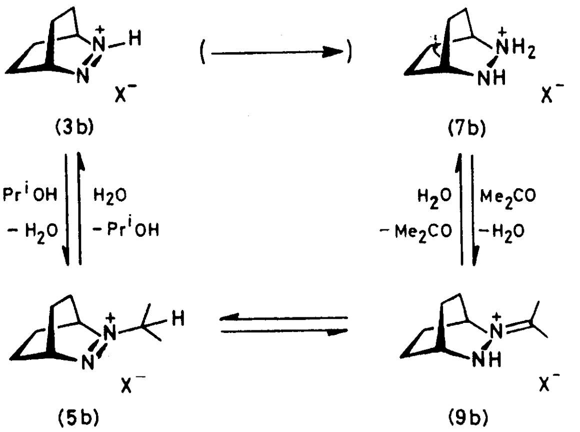


(11)

The ease of rearrangement of the isopropyldiazenium species (5b) is counterion-dependent: $Cl^- \gg Br^- > I^- \gg ClO_4^-$ (Table 4). The order is precisely that of the relative base strengths of the anions [19] and accounts well for the difficulty encountered in preparing (5b; X = Cl) uncontaminated by (9b; X = Cl) and (7b; X = Cl). Similar remarks apply to the sulphonate salt (5b; X = $MeSO_3$). The ions X^- probably exercise a catalytic function in the prototropic rearrangement and the hydrolysis step to hydrazine. However, in spite of the low basicity of ClO_4^-, the bicyclo[2.2.1]perchlorate (5a; X = ClO_4) provides a result comparable to that of the bicyclo[2.2.2]-perchlorate or -bromide (5b) in only 10% of the time (Table 5), undoubtedly the result of strain in the smaller bicycle. The overall trends carry over to the hydrolysis of (9b). Thus in the original 'reduction' experiments with (3a and b; X = Br), the complete absence of alkylated intermediates (5; X = Br) and (9a; X = Br) can be appreciated. Similarly, small quantities of (9b; X = Br) appear early in the reaction, but ultimately give way to the protonated hydrazine (7b; X = Br).



SCHEME

TABLE 5

Equilibration experiments (*cf.* Scheme) in propan-2-ol (88 °C; under N_2)

	Additive [a]	Time (h)	Product ratio (9)	Product ratio (7)
(5b; X = Br) [c]	H_2O	24	3.0	1.0
(9b; X = Br)	H_2O	24	3.3	1.0
(7b; X = Br)	H_2O–Me_2CO	24	2.7	1.0
(5b; X = ClO_4) [c]	H_2O	118	1 [b]	2.5
(9b; X = ClO_4)	H_2O	118	1 [b]	1.9
(7b; X = ClO_4)	Me_2CO	118	1	1.8
(5a; X = ClO_4) [c]	H_2O	2.5	2.0	1.0
(9a; X = ClO_4)	H_2O	2.5	3.7	1.0
		114	1.0	2.3
(7a; X = ClO_4)	Me_2CO	114	1.0	5.3

[a] One mol equiv. [b] Average of two runs differing by <8%. [c] Quantitatively converted into (9) and (7).

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[18] N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, 1972, **94**, 5734; O. Ermer, *Tetrahedron*, 1974, **30**, 3103.

[19] *Cf.* R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827, and 'Hard and Soft Acids and Bases,' ed. R. G. Pearson, Dowden, Hutchinson, and Ross, Pennsylvania, 1973.

Finally the irregular yields of (7; X = Br) and the azo-compounds (2) from refluxing the diazenium species (3) in R_2CHOH are a consequence of the initial alkylation step in the Scheme which requires proton transfer to the alcohol. Over extended periods, hydrogen chloride or bromide is slowly released, at a rate sensitive to the flow-rate of reflux condenser coolant [see Experimental section, Thermolysis (D)].

Synthesis by Means of Reactions in the Scheme.—The transformations of the Scheme can be exploited for synthetic purposes. The improved preparation of t-butyl derivatives (6) was a direct consequence of the realization that diazenium ions (3) are readily alkylated by alcohols. Unfortunately the reaction is limited for practical purposes to alcohols lacking a hydrogen atom α to oxygen. Experience with methanol, ethanol, and propan-2-ol shows that, under alkylation conditions, mixtures typified by those listed in Table 3 are routinely obtained. The low yields of trialkyldiazenium ions unsubstituted by a t-butyl group[8b] are consequently understandable.

The preparation of iminium salts (9) in 80—100% yields from both (5) and (7) has been achieved (see Experimental section). The species (9) is a potentially useful precursor of trialkylhydrazines *via* nucleophilic attack at trivalent carbon.[20] To our knowledge, the only reported bicyclic trialkylhydrazine is prepared by the addition of t-butyl-lithium to the azo-compound (2a) at −80 °C.[8a]

Conclusion.—We conclude that the ' reduction ' of diazenium cations (3) proceeds by the sequence shown in the Scheme. If radicals are generated under the alkylation conditions, they would appear to play only a minor role in the formation of hydrazinium salts. However, electrons are readily transferred to the diazenium system at an electrode[8,21] and by suitable donor systems.[1] Thus it might be expected that radicals or radical-like intermediates will be both thermally and photochemically accessible for this functionality provided that appropriate substituent patterns are exploited.

EXPERIMENTAL

Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and the Microanalytical Laboratory, Department of General and Organic Chemistry, the H. C. Ørsted Institute, University of Copenhagen. M.p.s were measured with a Büchi instrument. I.r. spectra were recorded with a Perkin-Elmer 257 or 337 grating spectrophotometer and u.v.–visible spectra with a Cary 15 or Unicam SP 1800 recording spectrophotometer. N.m.r. spectra were obtained with a Varian A-60A spectrometer. Except where noted, solvents were reagent grade and were used as received.

Protonation of Bicyclic Azo-derivatives.—*General procedure:* 2,3-*diazabicyclo*[2.2.2]*oct-2-ene hydrobromide* (3b; X = Br). Freshly sublimed 2,3-diazabicyclo[2.2.2]oct-2-ene (2b)[22] (DBO) (m.p. 139—140°; 550 mg, 5.0 mmol) in anhydrous ether (100 ml) was treated with a slow stream of commercial hydrogen bromide, with stirring, to give intermediate precipitation. The gas flow was continued until no further precipitate was noticed. The product was allowed to settle and the solution decanted. The solid was washed with anhydrous ether (3 × 35 ml) and dried at 12 Torr and room temperature to give a pale yellow *solid*, m.p. 198—199° (837 mg, 4.7 mmol, 93%).

All the salts (3a—d) were prepared similarly from the corresponding azo precursors: (2a) (m.p. 98—99°), (2c) (m.p. 138—140°), and (2d) (m.p. 93—95°). A slight modification was required for the perchlorate salts: a stirred ethereal solution of the azo-compound was treated dropwise with 1 equiv. of aqueous 70% perchloric acid. The resulting gummy precipitate was triturated several times with anhydrous ether, filtered off, and dried at 12 Torr to furnish a powdery white solid of analytical purity.

Physical data for the diazenium salts (3) are presented in Table 1. Many are hygroscopic, and heating and prolonged subjection to reduced pressure causes dissociation into the azo and HX components ($Cl^- > Br^- > ClO_4^-$). They are best stored in a desiccator.

2-*Isopropyl*-2-*azonia*-3-*azabicyclo*[2.2.1]*hept*-2-*ene Perchlorate* (5a; $X = ClO_4^-$).—Finely powdered and dried (H_2SO_4) silver perchlorate (713 mg, 3.4 mmol) under nitrogen was layered with dry dichloromethane (15 ml) and treated with freshly sublimed 2,3-diazabicyclo[2.2.1]hept-2-ene (BDH)[22,23] (2a) (329 mg, 3.4 mmol), then dropwise with isopropyl iodide (10 ml). The latter and the dichloromethane were each passed through a separate portion of basic alumina (2 cm) before use. The resulting mixture was stirred for 2 h (25 °C; N_2), filtered through Celite to remove silver iodide, evaporated (25 °C), washed with dry ether, and dried in a desiccator to yield white *crystals*, m.p. 122—124° (810 mg, 3.4 mmol, 99%) (Table 1)

2-*Isopropyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Iodide* (5b; X = I).—Freshly distilled, iodine-free (u.v.) 2-iodopropane (100 ml) was degassed with a nitrogen stream (25 °C) for 1 h. Freshly sublimed DBO (2b) (1.10 g, 100 mmol) was added with swirling. After 30 min the solution had turned light pink. The flask was flushed with nitrogen, stoppered, covered with aluminium foil, and stored at room temperature for 4 days. The resulting mass was filtered off under nitrogen, washed with anhydrous ether (3 × 50 ml) and dried under a nitrogen stream to afford yellow *crystals*, m.p. 224—225° (decomp.) (2.40 g, 86 mmol, 86%) (Table 1). Storage for prolonged periods led to extensive darkening and rearrangement to (9b). Light hastens the former and water the latter.

2-*Isopropyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Bromide* (5b; $X = Br^-$).—The iodide (5b; X = I) (980 mg, 350 mmol) dissolved in methanol (100 ml) was passed through a column of 10 mol. equiv. of AG MP-1 (Br^-) Bio-Rad ion-exchange resin prepared in and eluted with the same solvent. The pale yellow semi-solid resulting from evaporation (25 °C) of the eluates was cooled in solid CO_2–acetone, triturated with a little cold ethyl methyl ketone, and filtered off in the cold under nitrogen to give a white crystalline *solid*, m.p. 151—153° (320 mg, 224 mmol, 64%) (Table 1). Use of water as eluant causes extensive depropylation.

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[20] M. L. Heyman and J. P. Snyder, unpublished work.

[21] S. F. Nelsen and R. T. Landis, jun., *J. Amer. Chem. Soc.*, 1975, **95**, 6454, 5422.

[22] P. Gassman and K. T. Mansfield, *Org. Synth.*, 1969, **49**, 1.

[23] M. Heyman, V. T. Bandurco, and J. P. Snyder, *Chem Comm.*, 1971, 297; M. L. Heyman and J. P. Snyder, *Tetrahedron Letters*. 1973, 2859.

Several attempts to prepare the diazenium bromide (5b; X = Br) by dissolving DBO (freshly sublimed) in neat 2-bromopropane (distilled) and leaving the solution at room temperature (72 h; N_2; flask covered with aluminium foil) were unsuccessful. Typically a hygroscopic white solid separated which proved to be contaminated by 10—15% of the hydrazine hydrobromide (7b; X = Br) [see below; τ (CDCl$_3$) 6.45br (3 H, NH), 6.61br (2 H, s), and 7.94 (m)]. Purification by recrystallization was difficult and accompanied by considerable loss of (5b; X = Br).

2-*Isopropyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Perchlorate* (5b; X = ClO_4).—Finely powdered and dried silver perchlorate (2.18 g, 10.5 mmol) was layered with dry dichloromethane (100 ml; passed over basic alumina) and with stirring was treated dropwise with a solution of the iodide (5b; X = I) (0.98 g, 3.5 mmol) in dry dichloromethane (25 ml). A yellow precipitate of silver iodide began to form immediately. The mixture was stirred (25 °C) for an additional 1 h until the solution was water-white; it was then filtered through Celite. The latter was washed with dichloromethane (2 × 25 ml) and the combined filtrates were evaporated *in vacuo* to give a solid, affording white *needles*, m.p. 227—228° (from ethanol) (0.80 g, 3.2 mmol, 91%) (Table 1)

2-*Isopropyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Chloride* (5b$^+$; X = Cl) *and* 2-(*Isopropylidene*)-2-*azonia*-3-*azabicyclo*-[2.2.2]*octane Chloride* (9b; X = Cl).—(A) *Halide exchange with silver chloride*. Silver chloride was prepared by treating silver nitrate in water with an excess of concentrated hydrochloric acid. The resulting slurry was agitated in a Waring blender; the solid was filtered off, washed with water to pH 7, washed successively with methanol and acetone, dried (125 °C; 2 h), and stored in the dark. Analogous to the preparation of (5b; X = ClO_4), treatment of the diazenium iodide (5b; X = I) in methanol with silver chloride in one case gave a very hygroscopic white solid with an n.m.r. spectrum consistent with the expected product: τ (CDCl$_3$) 3.72br (1 H, s), 3.98 (1 H, sept, *J* 6 Hz), 4.05br (1 H, s), 7.5—8.4 (8 H, m), and 8.30 (6 H, d, *J* 6 Hz). No satisfactory elemental analytical data were obtained. The hygroscopic material is extremely prone to tautomerization and subsequent hydrolysis (*cf*. Table 4). Accordingly in all other preparative attempts (AgCl in $CHCl_3$, MeCN, Me_2CO, or MeOH), intimate mixtures of the imine (9b; X = Cl) [n.m.r. (from results of Table 4, entry 4): τ (CDCl$_3$) 1.95br (1 H), 5.20br (1 H, s), 6.35br (1 H, s), 7.39 (6 H, d, $\Delta\delta$ 6.5 Hz), 7.5—8.5 (8 H, m); *cf*. (9b) spectra below] and the hydrazine salt (7b; X = Cl) [n.m.r. (Table 4, entry 4): τ (CDCl$_3$) 6.62br (2 H, s) and 7.89br (s); see (7b) below] were obtained.

(B) *Ion exchange resin*. The iodide (5b; X = I) was passed through a column of resin AG-MP-1 (Cl$^-$) under conditions similar to those for the preparation of (5b; X = Br). With a single exception (in H_2O) a series of experiments (in H_2O, CH_2Cl_2, or MeOH) led to the mixture described in method (A).

The thermolysis experiment with (5b; X = Cl) (Table 4) involved use of the n.m.r.-homogeneous material obtained by method (A).

2-(*Isopropyl*)-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Methanesulphonate* (5b; X = $MeSO_3$).—To a rapidly stirred solution of the diazenium iodide (5b; X = I) (2.80 g, 10.0 mmol) in dry dichloromethane (20 ml) under nitrogen was added silver methanesulphonate [3.03 g, 1.50 mmol; Eastman; washed with small amounts of CH_2Cl_2 to remove a pink impurity and dried over P_2O_5 (0.01 Torr; 25 °C; 12 h) in the dark prior to use]. An immediate deep red solution deposited a solid and gradually turned pale yellow over 10 min. The mixture was filtered through Celite, the solids were washed with dichloromethane (20 ml) and the solvent was finally removed *in vacuo* at or below 25 °C to give an off-white hygroscopic solid. The latter was dried (P_2O_5; 0.01 Torr; 25 °C; 3 h); m.p. 126—127° (1.8 g, 7.2 mmol, 72%). No satisfactory analytical data were obtained, probably owing to the compound's tendency to gather moisture and undergo hydrolysis (see Table 4). The n.m.r. spectrum leaves no doubt as to the molecular constitution: τ (CDCl$_3$) 4.05br (2 H, s), 4.35 (1 H, sept, *J* 6.5 Hz), 7.28 (3 H, s), 7.5—8.5 (8 H, m), and 8.30 (3 H, d, *J* 6.5 Hz). This material was used for the run listed in Table 4. A large number of other attempts to prepare (5b; X = $MeSO_3$) in this way consistently led to mixtures of the latter, its tautomer (9b; X = $MeSO_3$) (as determined by n.m.r.), and small amounts of free silver. Owing to the hygroscopicity of the material, purification by recrystallization could not be achieved.

2-*t*-*Butyl*-2-*azonia*-3-*azabicyclo*[2.2.1]*hept*-2-*ene Perchlorate* (6a; X = ClO_4).—The perchlorate (3a; X = ClO_4) (1.59 g, 8.01 mmol) in t-butyl alcohol (75 ml) was refluxed for 20 min. The mixture was cooled and the white crystals filtered off, washed with dry ether (3 × 10 ml), and air-dried to yield white *needles*, m.p. 220—221° (1.46 g, 5.80 mmol, 73%) (Table 1).

2-*t*-*Butyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Perchlorate* (6b; X = ClO_4).—The perchlorate (3b; X = ClO_4) (1.05 g, 5.00 mmol) suspended in t-butyl alcohol (50 ml; distilled from CaH_2) was refluxed under nitrogen. After 8 h the solution was cooled and filtered. The precipitate was washed with t-butyl alcohol (2 × 10 ml) and air-dried to yield white *needles*, m.p. 254—255° (1.08 g, 4.05 mmol, 81%) (Table 1). The combined filtrates were evaporated to give starting material (165 mg). Repetition on twice the scale gave similar results. No attempt was made to obtain complete conversion.

2-*t*-*Butyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Chloride* (6b; X = Cl).—The perchlorate (6b; X = ClO_4) (1.06 g, 4.00 mmol) in 2 : 1 acetonitrile–water (50 ml) was eluted through a column of 20 mol. equiv. of AG MP-1 (Cl$^-$) Bio-Rad ion-exchange resin prepared in the same solvent. Recrystallization of the product (minimum volume of $CHCl_3$) gave hygroscopic white *needles*, m.p. 191—192° (0.630 g, 3.1 mmol, 78%) (Table 1).

2-*t*-*Butyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Bromide* (6b; X = Br).—This preparation was identical with that of the chloride except for the use of an AG MP-1 (Br$^-$) Bio-Rad resin. Recrystallization ($CHCl_3$) gave a white *solid*, m.p. 226—227° (820 mg, 83%) (Table 1).

2-*t*-*Butyl*-2-*azonia*-3-*azabicyclo*[2.2.2]*oct*-2-*ene Iodide* (6b; X = I).—To a stirred solution of the chloride (6b; X = Cl) (398 mg, 2.00 mmol) in dry acetonitrile (25 ml) was added dropwise a solution of sodium iodide (600 mg, 4.0 mmol) in the same solvent (15 ml). The mixture was stirred under nitrogen for 30 min. Filtration, washing of the insoluble solids with acetonitrile (2 × 15 ml), and evaporation of the combined filtrates led to a yellow solid. The dried *crystals* (81 °C; 0.1 Torr; 24 h) had m.p. 223—224° (553 mg, 1.86 mmol, 93%); (Table 1). Recrystallization may be accomplished from propan-2-ol, but care must be exercised to maintain the product under an inert atmosphere in order to prevent the formation of tri-iodide [$\lambda_{max.}$ (MeCN) 368 nm (ε *ca.* 26 000M^{-1} cm^{-1})].[24]

2,3-*Diazabicyclo*[2.2.2]*octane Hydroperchlorate* (7b; X = ClO_4^-).—DBO (2b) [22] (550 mg, 5.0 mmol) dissolved in methanol (35 ml) was hydrogenated (25 °C; 1 atmosphere) over 5% palladium–charcoal (100 mg). Uptake usually ceased within 1 h. The solution was filtered under nitrogen, treated with aqueous 70% perchloric acid (640 mg, 4.5 mmol), and evaporated *in vacuo* to give a white semi-solid. Trituration with anhydrous ether gave a granular white *solid*, which was dried (42 °C; 0.1 Torr; 24 h); m.p. 215—216° (590 mg, 4.5 mmol, 90%) (Found: C, 33.9; H, 6.1; Cl, 16.7; N, 13.2. $C_6H_{13}ClN_2O_4$ requires C, 33.9; H, 6.2; Cl, 16.7; N, 13.2%); $\nu_{max.}$ (KBr) 3 270s, 3 140—2 500s, 1 615s, 1 450s, 1 150—1 050s, and 630s cm^{-1}; τ (D_2O) 6.63br (2 H, s, $W_{\frac{1}{2}}$ 5 Hz) and 7.6—8.7 (8 H, m, centre of envelope at 8.08, $W_{\frac{1}{2}}$ 5 Hz).

2,3-*Diazabicyclo*[2.2.2]*octane Hydrochloride* (7b; X = Cl).—DBO (2b) (550 mg, 5.00 mmol) in methanol (35 ml) was hydrogenated as above and subsequently treated with dry hydrogen chloride (164 mg, 4.5 mmol) in dry ether (25 ml). Removal of solvent produced a white *solid* which was triturated with dry ether and recrystallized ($CHCl_3$); m.p. 241—242° (590 mg, 4.0 mmol, 88%) (Found: C, 48.5; H, 8.1; Cl, 24.0; N, 19.0. $C_6H_{13}ClN_2$ requires C, 48.5; H, 8.8; Cl, 23.8; N, 18.8%); $\nu_{max.}$ (KBr) 3 150s, 3 000—2 300s, 1 610m, 1 450m, 1 010m, and 858s cm^{-1}; τ (D_2O) 6.65br (2 H, s, $W_{\frac{1}{2}}$ 6 Hz) and 7.6—8.6 (8 H, m, centre of envelope at 8.10, $W_{\frac{1}{2}}$ 8 Hz).

2,3-*Diazabicyclo*[2.2.2]*octane Hydrobromide* (7b; X = Br).—DBO (2b) was treated with anhydrous hydrogen bromide as in the preparation of the hydrochloride (7b; X = Cl). Work-up led to a white granular *solid*, m.p. 204—205° (from chloroform) (790 mg, 91%) (Found: C, 37.4; H, 6.7; Br, 41.4; N, 14.8. $C_6H_{13}BrN_2$ requires C, 37.3; H, 6.8; Br, 41.5; N, 14.5%); $\nu_{max.}$ (KBr) 3 150s, 3 000—2 500s, 1 610m, 1 490m, 1 000s, and 850 cm^{-1}; τ (D_2O) 6.59br (2 H, s, $W_{\frac{1}{2}}$ 6 Hz) and 7.8—8.3 (8 H, m, centre of envelope 8.05, $W_{\frac{1}{2}}$ 5 Hz).

2,3-*Diazabicyclo*[2.2.1]*heptane Hydroperchlorate* (7a; X = ClO_4) *and the Bis*(*hydroperchlorate*).—The Diels–Alder adduct of cyclopentadiene and dibenzyl azodiformate (7.3 g, 20 mmol) dissolved in methanol (200 ml) was hydrogenated over 5% palladium–carbon (550 mg) (Paar apparatus; 25 °C; 2 h; 40 lb in^{-2}). The mixture was filtered through Celite and evaporated *in vacuo* under nitrogen. (An inert atmosphere is essential as 2,3-diazabicyclo[2.2.1]heptane is very readily oxidized in air to the corresponding azo-alkane.[23,25]) The resulting crystals were dissolved in dry ether (40 ml) and treated with aqueous 70% perchloric acid (1.5 g, 20 mmol). The white *precipitate* was isolated by decanting the solvent, trituration of the solid with dry ether (3 × 40 ml), filtration, and drying (H_2SO_4); m.p. 220—221° (decomp.) (2.75 g, 14 mmol, 71%) (Found: C, 30.8; H, 5.0; N, 14.0. $C_5H_{11}ClN_2O_4$ C, 30.2; H, 5.6; N, 14.1%); $\nu_{max.}$ (KBr) 3 280—3 100s, 2 758m, 2 558m, 1 610s, 1 450m, 1 390s, 1 370s, and 1 100s cm^{-1}; τ (D_2O) 5.84b (2 H, s, $W_{\frac{1}{2}}$ 6 Hz) and 7.8—8.4 (6 H, m). Repeated preparations were unsuccessful in producing a product with satisfactory elemental analytical figures, although the spectroscopic data and subsequent reactions showed no deviant character. This result is the consequence of contamination with the bis(hydroperchlorate). When a sample of (7a; X = ClO_4) was boiled in dichloromethane–acetonitrile and the solution then diluted with dichloromethane, an insoluble crystalline *product* was obtained; m.p. 236—238° (Found: C, 20.2; H, 4.4; N, 9.4. $C_5H_{12}Cl_2N_2O_8$ requires C, 20.1; H, 4.0; N, 9.4%); $\nu_{max.}$ (KBr) 3 500—3 100s, 1 600s, 1 500s, and 1 090s cm^{-1}; τ (D_2O) 6.30br (2 H, s, $W_{\frac{1}{2}}$ 7 Hz) and 7.0—8.4 (6 H, m).

2-(*Isopropylidene*)-2-*azonia*-3-*azabicyclo*[2.2.1]*heptane Perchlorate* (9a; X = ClO_4).—Finely powdered and dried (H_2SO_4) silver perchlorate (1.82 g, 8.8 mmol), moist azo-alkane (2a) (0.90 g, 9.4 mmol), and dry dichloromethane (15 ml; passed over basic alumina) were mixed under nitrogen and treated dropwise with stirring with dry (basic alumina) isopropyl iodide (10 ml). The mixture was stirred for 2 h and filtered through Celite. The filtrates were concentrated *in vacuo* and the resulting crystals were washed with dry ether, filtered off, and dried. By n.m.r. it was determined that a 7 : 3 mixture of (5a; X = ClO_4) and (9a; X = ClO_4), had been obtained. The material was returned to a desiccator for 14 days (over conc. H_2SO_4) after which the conversion into the *iminium salt* (9a; X = ClO_4) was complete; m.p. 71—72° (1.86 g, 7.8 mmol, 82%). Conditions for effecting a more rapid isomerization were not sought, but the experiments described below suggest a ready method (Found: C, 40.2; H, 6.2; N, 11.8. $C_8H_{15}ClN_2O_4$ requires C, 40.3; H, 6.3; N, 11.7%); $\nu_{max.}$ (KBr) 3 400—3 280s, 1 680m, and 1 090s cm^{-1}; τ ($CDCl_3$) 4.03br (1 H, s), 5.02br (1 H, s), 5.92br (1 H, s), 7.60 (3 H, s), 7.68 (3 H, s), and 7.8—8.3 (6 H, m).

2-(*Isopropylidene*)-2-*azonia*-3-*azabicyclo*[2.2.2]*octane Bromide* (9b; X = Br).—The diazenium bromide (5b; X = Br) (470 mg, 2.0 mmol) was dissolved in 2 : 1 cyclohexane–propan-2-ol (300 ml) and refluxed for 5 h. Solvent removal *in vacuo* (25 °C) gave a white solid (465 mg, 99%). Recrystallization (min. amount of propan-2-ol) provided a white crystalline *solid*, m.p. 168—169° (Found: C, 46.3; H, 7.4; Br, 34.3; N, 12.1. $C_9H_{17}BrN_2$ requires C, 46.4; H, 7.3; Br, 34.3; N, 12.0%); $\nu_{max.}$ (KBr) 3 070s, 1 480m, 1 450m, 1 285m, 1 210s, and 990m cm^{-1}; τ ($CDCl_3$) 1.97br (1 H, s, $W_{\frac{1}{2}}$ 10 Hz), 5.22br (1 H, s, $W_{\frac{1}{2}}$ 7 Hz), 6.45br (1 H, s, $W_{\frac{1}{2}}$ 8 Hz), 7.40 (3 H, s), 7.48 (3 H, s), and 7.7—8.4 (8 H, m).

Refluxing DBO in 2-bromopropane (18—24 h) consistently led to mixtures of the isopropylidene salt (9b; X = Br) and (7b; X = Br^-) (under N_2, 7 : 1; no N_2, 1.2 : 1, respectively; total yield 40—50%).

2-(*Isopropylidene*)-2-*azonia*-3-*azabicyclo*[2.2.2]*octane Iodide* (9b; X = I).—The diazenium iodide (5b; X = I) (700 mg, 2.5 mmol) in methanol (100 ml) was refluxed for 6 h. Solvent removal *in vacuo* furnished a pale yellow solid, which by n.m.r. was shown to be free of starting material (690 mg, 99%); recrystallization (propan-2-ol) led to a white *solid*, m.p. 179—180° (Found: C, 38.5; H, 6.1; N, 10.1. $C_9H_{17}IN_2$ requires C, 38.6; H, 6.2; N, 10.0%); $\nu_{max.}$ (KBr) 3 080s, 2 940s, 1 370m, 1 210m, 1 090m, and 860m cm^{-1}; τ ($CDCl_3$) 2.68br (1 H, s, $W_{\frac{1}{2}}$ 8 Hz), 5.22br (1 H, s, $W_{\frac{1}{2}}$ 8 Hz), 6.40br (1 H, s, $W_{\frac{1}{2}}$ 8 Hz), 7.40 (3 H, d, *J* 3.6 Hz), 7.45 (3 H, d, *J* 3.6 Hz), and 7.6—8.4 (8 H, m).

2-(*Isopropylidene*)-2-*azonia*-3-*azabicyclo*[2.2.2]*octane Perchlorate* (9b; X = ClO_4).—(A) Finely powdered, dry silver perchlorate (621 mg, 3.0 mmol) layered with dry dichloromethane (50 ml; passed through a column of basic alumina) was treated with stirring under nitrogen with a solution of the iodide (9b; X = I) (280 mg, 1.0 mmol) in dry dichloro-

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methane (15 ml). The mixture was agitated for 1 h (25 °C), filtered through Celite, and washed with dichloromethane (2 × 20 ml). The combined filtrates were concentrated *in vacuo* to give a fluffy white solid. Recrystallization (EtOH) afforded a white *solid*, m.p. 110—111° (200 mg, 0.80 mmol, 80%) (Found: C, 42.7; H, 6.7; Cl, 13.9; N, 11.1. $C_9H_{16}ClN_2O_4$ requires C, 42.9; H, 6.4; Cl, 14.1; N, 11.3%); $\nu_{\max.}$ (KBr) 3 280m, 1 460m, 1 380m, 1 090s, and 630s cm^{-1}; τ ($CDCl_3$) 2.63br (1 H, s, $W_{\frac{1}{2}}$ 8 Hz), 5.20br (1 H, s, $W_{\frac{1}{2}}$ 7 Hz), 6.38br (1 H, s, $W_{\frac{1}{2}}$ 7 Hz), 7.38 (3 H, d, *J* 3.5 Hz), 7.42 (3 H, d, *J* 3.5 Hz), and 7.6—8.4 (8 H, m).

(B) The hydrazine hydroperchlorate (7b; X = ClO_4) (200 mg, 0.94 mmol) was dissolved in acetone (30 ml; dried by passage over a column of neutral alumina) and propan-2-ol (30 ml; dried by distillation over CaH_2); the solution was refluxed for 1 h, cooled, and evaporated *in vacuo* to give a yellow oil. Crystallization was induced by cooling at 0 °C overnight. The *solid* was washed with dry ether, filtered off, and dried; m.p. 110—111° (218 mg, 0.90 mmol, 95%), and was identical with that obtained from method (A).

Thermolysis of Diazenium Salts (3).—(A) *Bromide* (3a; X = Br) *in methanol*. The bromide (600 mg) dissolved in methanol (8 ml; dried over $MgSO_4$) was refluxed for 24 h under nitrogen ($CaSO_4$ drying tube). The resultant solution was evaporated *in vacuo* leading to a pale yellow oil, which crystallized on standing. The latter was dissolved in $(CD_3)_2SO$ and transferred under nitrogen to an n.m.r. tube. Besides methanol the spectrum revealed only the azoalkane (2a) [τ 4.80br (s, $W_{\frac{1}{2}}$ 5 Hz, bridgehead H) and 8.2—9.4 (m)] and the hydrazine hydrobromide (7a; X = Br) (see below for spectrum and proof of structure). A similar result was obtained by using dry propan-2-ol as solvent, but an additional peak for acetone was observed at τ ($CDCl_3$) 7.85.

A number of other experiments in methanol in which care was not taken to exclude moisture rigorously led to a far less clean result. For example the bromide (3a; X = Br) (14.0 g, 79.1 mmol) in reagent grade methanol (75 ml) was refluxed (24 h; N_2) and evaporated *in vacuo* to an oil which was washed several times with ether. Solvent removal led to the azoalkane (2a) (400 mg, 4.2 mmol). Trituration of the ether-insoluble residue with acetonitrile afforded a brown solid (5.1 g). Recrystallization (CH_2Cl_2–petroleum, 1 : 3) gave a white *solid* (7a; X = Br) (3.0 g, 17 mmol, 21%) (Found: C, 33.6; H, 6.0; Br, 44.6. $C_5H_{11}BrN_2$ requires C, 33.5; H, 6.1; Br, 44.7%); $\nu_{\max.}$ (KBr) 2 530—3 175s, 1 600s, 1 381s, 943m, and 813s cm^{-1}; τ [$(CD_3)_2SO$] 2.82br (3 H, s), 6.02br (2 H, s), and 8.2—8.3 (6 H, sharp unsym. d).

The structure of (7a; X = Br) was verified by converting it into the previously reported thioxotriazolidinone derivative.[15] Following a second conversion of (3a; X = Br) in methanol, the brown oil (3.6 g) was dissolved in acetonitrile (50 ml) and treated with neat ethyl chlorocarbonate (2.2 g, 20 mmol). The mixture was heated on a steam-bath for 15 min. Removal of solvent *in vacuo* afforded a semi-solid which was shaken with aqueous 10% potassium carbonate and extracted with chloroform (3 × 75 ml). The extract was dried ($MgSO_4$) and evaporated to leave a brown oil (3.7 g), the mono-*N*-ethoxycarbonyl derivative corresponding to the hydrazine (7a) [τ ($CDCl_3$) 5.64br (1 H, s), 5.87 (2 H, unsym. q), 6.28br (1 H, s), 8.32br (6 H, s), and 8.75 (3 H, t)]. The latter was taken up in acetonitrile and treated with an excess of phenyl isothiocyanate. After the resultant exothermic reaction had subsided, the solvent was removed *in vacuo* to yield an oily residue (2.6 g), which afforded a pale yellow solid upon recrystallization (ether–hexane, 1 : 1); m.p. 114—115° (lit.,[15] 125—127°) (Found: C, 58.5; H, 6.1; N, 13.7. Calc. for $C_{15}H_{19}N_3SO_2$: C, 58.9; H, 6.2; N, 13.5%); τ ($CDCl_3$) 2.4—2.9 (5 H, m), 4.56br (1 H, s), 5.32br (1 H, s), 5.78 (2 H, q), 7.6—8.5 (6 H, m), and 7.78 (3 H, t). When the latter was heated in benzene for 24 h it cyclized to the thioxotriazolidinone of Cohen *et al.*, m.p. 175—176° (lit.,[15] 177—179°) (Found: C, 59.9; H, 5.1; N, 16.1. Calc. for $C_{13}H_{13}N_3SO$: C, 60.2; H, 5.0; N, 16.2%); τ ($CDCl_3$) 2.57 (5 H, s), 4.95 (1 H, s), 5.22 (1 H, s), and 7.5—8.3 (6 H, m).

(B) *Bromide* (3a; X = Br) *in chloroform; preparation of the hydrazine bishydrobromide* (8). The bromide (3a; X = Br) (450 mg, 2.54 mmol) in dry chloroform [25 ml; 0.75% ethanol as stabilizer (4—5 mmol)] was heated under nitrogen on a steam-bath. Within 5 min a white solid had precipitated. Filtration gave the *hydrazine bishydrobromide* (8), m.p. 174—176° (120 mg, 0.46 mol, 71% based on starting material consumed; see below) (Found: C, 22.8; H, 4.4; N, 10.8. $C_5H_{12}Br_2N_2$ requires C, 23.1; H, 4.6; N, 10.7%); $\nu_{\max.}$ (KBr) 3 420s, 2 810—2 300s, 1 530s, 1 345s, and 980m cm^{-1}; τ (D_2O) 5.78br (2 H, s) and 8.0—8.2 (6 H, sharp unsym. d).

The chloroform filtrate was concentrated to a semi-solid, which when triturated with ether afforded the azoalkane (2a) (100 mg, 1.04 mmol) and the ether-insoluble starting material (3a; X = Br) (150 mg, 0.85 mmol).

The bishydrobromide (8) was prepared independently from both 2,3-diazabicyclo[2.2.1]heptane [22,23] and the monohydrobromide (7a; X = Br) by treatment with hydrogen bromide in methanol. For example the former (980 mg, 10 mmol) dissolved in methanol (50 ml) was purged with hydrogen bromide gas. Solvent removal *in vacuo* afforded a pale yellow solid, m.p. 174—176° (1.75 g, 6.7 mmol, 67%). Spectra were identical with those reported above.

(C) *Bromide* (3b; X = Br) *in propan-2-ol*. Freshly prepared bromide (3b; X = Br) (3.80 g, 19.9 mmol) in propan-2-ol (125 ml; distilled from CaH_2) was refluxed under nitrogen. After 24 h the solution was distilled and the distillate treated with 2,4-dinitrophenylhydrazine. Upon cooling the mixture deposited acetone 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 124—125°. The crude solid residue was triturated with ether (2 × 25 ml) to afford the azoalkane (2b) (355 mg, 3.2 mmol) from the ethereal extract. The remaining solid was further triturated with chloroform (3 × 25 ml) to give starting material (3b; X = Br) (2.18 g, 11.4 mmol) from the extracts. The remaining white solid was recrystallized from chloroform affording a granular white solid (7b; X = Br), m.p. 204—205° [423 mg, 2.19 mmol, 41% based on unrecovered (3b; X = Br) and (2b); a second run yielded 56%].

(D) *Derivatives* (3b; X = Cl, Br, *or* ClO_4) *in propan-2-ol* (*Table* 3). For comparison of these three anions the starting salts were prepared by passing commercial hydrogen chloride through concentrated sulphuric acid then a column of solid calcium chloride, and commercial hydrogen bromide through tetrahydronaphthalene then a column of solid calcium bromide prior to combination with the azo-compound (2b). Salts (3b) (0.05M) in propan-2-ol (analytical grade; distilled from CaH_2; checked by g.l.c. for the absence of acetone) were maintained at 82—83 °C. The reactions were monitored by n.m.r. (D_2O or $CDCl_3$). Acetone (τ 7.80) was consistently observed.

Interpretation of the n.m.r. spectra is complicated by the fact that hydrogen chloride and bromide gases are gradually expelled from the heated mixture. Bridgehead proton peaks in the τ 4.4—4.8 region consequently reflect a rapid proton transfer equilibration between the azo-compound (2b) and the remaining salts (3b). Table 6 indicates the loss to occur in the following order of propensities: $HCl \approx HBr \gg HClO_4$. It was subsequently discovered that variations in the water flow rate in the reflux condenser caused corresponding variations in the product distributions of the hydrochloride and hydrobromide salts by *ca.* ±10%. Table 3 lists the findings of one run.

The e.s.r. spectra of the 24 h sample listed in Table 3 [entries 1(Cl^-), 2(Br^-), and 3(ClO_4^-)] gave no indication of radicals. Likewise the corresponding n.m.r. spectra were well-resolved throughout. On other occasions, however, the n.m.r. spectra of the Cl^- and Br^- runs were very broad and ill-resolved. An e.s.r. spectrum of a 24 h Cl^- sample gave a three-line pattern (a_N 15.1 G; g 2.005 0—2.005 1). Although these observations were not reproducible, the % conversions and product distributions relative to the non-radical runs were consistently within the ±10% limits indicated above.

TABLE 6

Azoalkane (2b) and diazenium salt (3b) bridgehead protons in the n.m.r. spectra of the product mixtures arising from thermolysis of (3b) [τ (D_2O)] [a] (*cf.* Table 3)

	Time (h)					
X	0 [b]	6	12	24	48	(2b)
Cl	4.43	4.58	4.60	4.69	4.83	4.79
Br	4.43	4.53	4.64	4.76	4.76	4.79
ClO_4	4.43	4.44	4.47	4.48	4.49	4.79

[a] Similar results were obtained from separate sets of reactions in which $CDCl_3$ was used as solvent. [b] Starting material (3b).

(E) *Diazenium salt* (3b; X = ClO_4) *and additives* (*Table* 3). The salt (3b; X = ClO_4) (60 mg, 0.28 mmol) was dissolved in dry propan-2-ol (10 ml; distilled over CaH_2), purged with nitrogen for 15 min, treated with the appropriate additive, and heated at 88 °C under nitrogen for 120 h. For the sake of consistency, during this period the system was wrapped in aluminium foil as a precaution against stray light. Control experiments demonstrated, however, that neither room light nor oxygen (15 min purging prior to heating; no N_2 during run) affected the results. Alkali halides (NaF, NaBr, or CsI) in separate experiments were added in 1 : 1 and 10 : 1 molar ratio with respect to (3b; X = ClO_4). An excess had no effect (Table 3). The propan-2-ol–cyclohexane and propan-2-ol–tetrabromoethylene mixtures (1 : 1; 20 ml total) were composed of dried components.

At the termination of the 120 h period, the solvent was removed *in vacuo* and the remaining solid dissolved in D_2O and analysed by n.m.r. The only products observed were the azo-compound (2b) (τ 5.0), starting material (τ 4.6), the isopropyldiazenium salt (5b; X = ClO_4) (τ 4.2—4.4), the isopropylidene salt (9b; X = ClO_4) (τ 5.4), and the hydrazine hydroperchlorate (7b; X = ClO_4) (τ 6.6). All were prepared independently as described above, so that n.m.r. spectra were available for comparison. Most useful for the quantitative determination were the indicated bridgehead proton chemical shifts. Owing to band overlap in some cases, we consider the values accurate to within ±5%.

(F) *Thermolysis of isopropyldiazenium salts* (5b) (*Table* 4). Solvents were dried and purified before use: propan-2-ol was distilled over calcium hydride; cyclohexane and 1,2-dichloroethylene (DCE) were distilled. The appropriate salt (100 mg) was dissolved in the solvent (15 ml) and heated at a constant temperature under nitrogen for a specified time. A sample was removed and evaporated and the remaining solid analysed by n.m.r. [$(CD_3)_2SO$–$CDCl_3$]. As in the case of the *N*-unsubstituted salts (3), all products were synthesized independently. For the results (±5%) see Table 4.

A large number of other runs were conducted with (5b; X = Cl, Br, I, or $MeSO_3$) in methanol, propan-2-ol, and mixtures of these with cyclohexane, chloroform, carbon tetrachloride, and DCE. In all cases a partial isomerization to (9b) occurred. Where care was not taken scrupulously to remove traces of water, or where this was very difficult (*e.g.* X = Cl or $MeSO_3$), considerable quantities of hydrazine salt (7b) appeared (n.m.r.).

(G) *Attempted thermolysis of the t-butyldiazenium salts* (6a; X = ClO_4) *and* (6b; X = Br *or* I). The salt (1.0 mmol) was dissolved in degassed (N_2 purging) and dried propan-2-ol (75 ml; distilled over CaH_2) and refluxed for 120 (6a) or 24 h (6b) under nitrogen. Solvent removal *in vacuo* led to a quantitative recovery of the starting material (m.p., n.m.r. spectrum).

Thermolysis of Diazenium Salts (3b; X = Br *or* ClO_4) *and* (6b; X = Br) *with Phenylmethanethiol*.—The salt (1.0 mmol), freshly distilled phenylmethanethiol (2.0 mmol), and dry propan-2-ol (30 ml) were heated at 88 °C under nitrogen for 24 h. The solution was cooled and analysed by g.l.c. for dibenzyl disulphide by comparison with standard curves [for BzSH and $(BzS)_2$ in Pr^iOH]. The disulphide was produced in 7—8, 4—5, and 2.5% yields, respectively. A control run without the salt gave no dibenzyl disulphide. The reaction mixtures were evaporated and analysed by n.m.r. The % conversions into disulphide were consistent with the g.l.c. results. The salt (3b; X = Br) was transformed as indicated in Table 3. The salts (3b; X = ClO_4) and (6b; X = Br) were unchanged.

Equilibration Studies (*Table* 5).—The bromide salt (1.0 mmol) or perchlorate salt (0.28 mmol) was dissolved in dry propan-2-ol (29 or 40 ml, respectively), treated with 1 mol. equiv. of water or acetone (dried over neutral alumina), and refluxed under nitrogen for a specified period. The solutions were evaporated *in vacuo*, and the residual solids taken up in $CDCl_3$, CD_3OD, or CD_3CN; the solutions were analysed by n.m.r. The results are in Table 5. In every instance where the diazenium salt (5a or b) was the starting component, it was quantitatively converted into (9) and (7) in the tabulated ratios.

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