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- (34) In our coordinate system the CH_2 (or SO_2) nucleophile is positioned at the origin, whereas in the previous work¹³ the electrophilic partner was so fixed.
- (35) It has been shown that the neglect of overlap required by the ZDO theoretical framework can favor biradicaloid over synchronous transition states³⁶ and result in serious underestimation of nonbonded lone pair-lone pair repulsions.³⁷ For example, CNDO/2 and INDO produce weakly repulsive or attractive potential energy curves for the direct interaction of lone electron pairs. Application of the "water test"³⁷ (orthogonal approach) to CNDO/B results in a properly repulsive potential at all oxygen separations; nonetheless at 1.5 Å the destabilization energy is 5 eV compared with 11 eV for EH. The corresponding 4-31G value is 8.8 eV.
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Diazenium Cations. 3. Formation and Oxidation of a *cis*-Trialkylhydrazine: *cis*-Azomethinimines¹

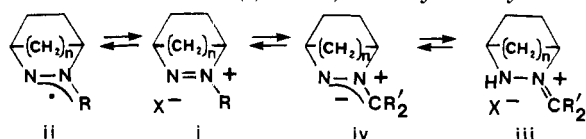
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Isopropyl-substituted bicyclic diazenium cations **i** are readily isomerized via ylides **iv** to the corresponding *exo*-methylene iminium salts **iii**. Thus, in the presence of nucleophiles both are potential precursors to the little studied *cis*-trialkylhydrazine system. Treatment of either **i** or **iii** with CN^- under an inert atmosphere causes attack at carbon and leads to the corresponding oxygen-labile hydrazine. Facile air oxidation presumably generates a trialkylhydrazyl radical which ultimately results in production of azoalkane **6** and the tetrasubstituted cyanohydrazine **7**. Evidence is presented to show that **6** arises via an intermediate azomethinimine (**10c**) followed by protonation and subsequent dealkylation. The bicyclic hydrazine **7** is formed from a second intermediate, diazenium cation **11**, which experiences CN^- attack at nitrogen. The presence of an ylide intermediate is substantiated by demonstrating that azomethinimines **iv** are easily generated from a new series of both salts **i** and **iii**. Although in most instances the 1,3 dipoles were only trapped, isolation succeeded for a diphenyl derivative.

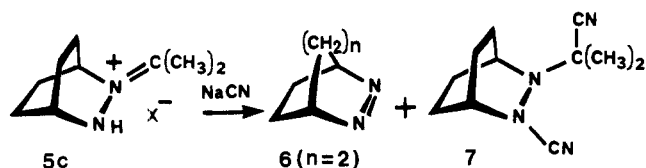
The recent isolation of bicyclic diazenium cations **i** has permitted exploratory studies of the chemistry of this many faceted function. Derivatives with $\text{R} = \text{H}$ and alkyl show charge-transfer behavior¹⁻³ and facile electrochemical reduction to hydrazyl radicals **ii**.⁴ When the substituent is 2,5-dinitrophenyl, chemical electron transfer leads to a complex equilibrium of open- and closed-shell species.² Simple protodiazenium cations (**i**, $\text{R} = \text{H}$) are alkylated by alcohols



of all kinds and serve as particularly efficient precursors to the *tert*-butyl cations.^{1,2} Substituents bearing a proton α to $=\text{N}^+<$ (e.g., $\text{R} = i\text{-Pr}$) undergo rearrangement to the *exo*-iminium salt **iii**.¹ The reaction can be utilized for synthesis of the latter.

In the present discussion further examples of tautomeric pairs **i** and **iii** are reported. Their utility in the generation of azomethinimines **iv** is described. Furthermore, the preparation of a labile *cis*-trialkylhydrazine and its facile air oxidation have been investigated.

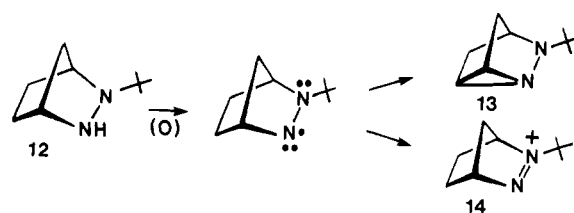
Trialkylhydrazine Formation and Oxidation. In principle, the iminium salts **iii** should be capable of accepting a nucleophile at carbon to produce the corresponding *cis*-tri-



alkylhydrazines, a class of compounds with only a few representatives.^{5,7} Our initial attempts to exploit this reaction employed the weakly basic cyanide ion and derivative **5c** ($X = \text{Br}$). Surprisingly, the combination of the latter and sodium cyanide in chloroform led to diazabicyclooctane (**6**) and dicyanohydrazine **7** in 23 and 38% yields, respectively. The origin of these products is outlined in Scheme I. Evidence for it is developed below.

The key intermediate separating **5c** and **6** and **7** can be intercepted by running the above reaction under an inert atmosphere followed by careful workup in the absence of air. The oxygen-labile trisubstituted hydrazine **8** is thus obtained from both iminium salt **5c** and the diazenium species **9c** as an oil in 92% yield. Proof of structure rests on spectroscopic data, elemental analysis, and further transformation. The substance exhibits CN stretching in the infrared spectrum at 2220 cm^{-1} and a molecular ion at m/e 179 in the mass spectrometer. Its NMR spectrum displays characteristic NH absorption at τ 6.45, bridgehead protons at τ 7.03, and the hydrocarbon backbone and methyl groups between τ 7.7 and 8.6. Treatment of the oil with 1 equiv of phenyl isothiocyanate delivered the *N*-phenylthiosemicarbazide, indicating cyclization with elimination of HCN. Upon standing in air or under the influence of a stream of oxygen, hydrazine **8** is rapidly converted to azobicyclooctane **6**, cyanohydrazine **7**, and acetone. The latter has been demonstrated both by NMR spectroscopy and GLC. The most plausible connectors between hydrazine **8** and the products are ylide **10** and the diazenium cation **11**.⁸

Bicyclo[2.2.1] trialkylhydrazine **12** has recently been shown to be air-oxidized to *N*-*tert*-butyl-2,3-nortricyclene (**13**) and



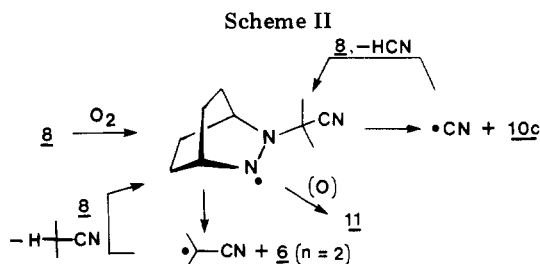
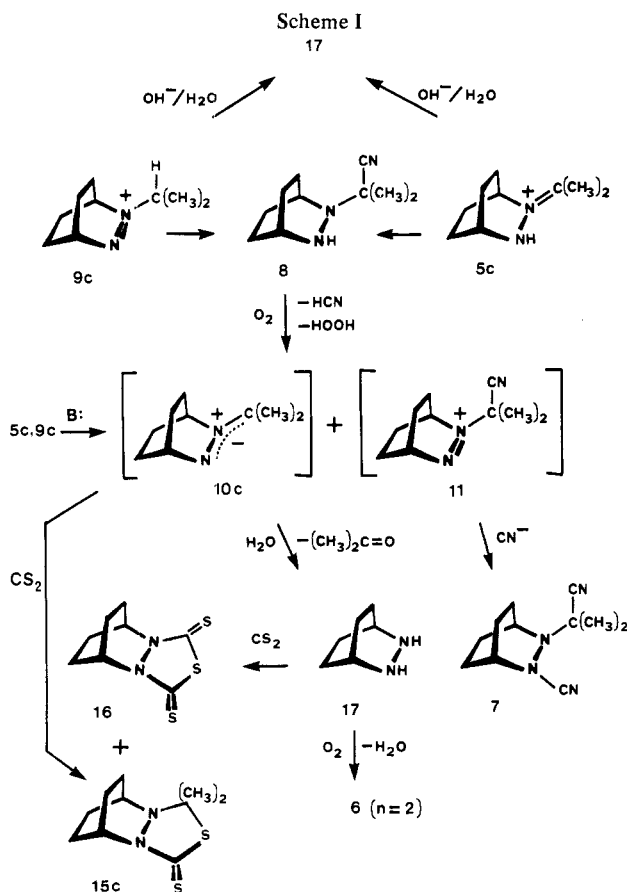
quinone-oxidized to diazenium salt **14** presumably by way of a hydrazyl radical.⁷ A similar transformation for the bridge-expanded hydrazine **8** can be invoked to rationalize the intermediacy of salt **11** (see Scheme II).

Testimony that these reactions are operating under the conditions necessary for oxidation of hydrazine **8** has been gathered as follows. Byproducts of the air oxidation of trialkylhydrazine ought to be the reduced species HO_2^- and H_2O_2 . Indeed, within a few minutes of the introduction of oxygen to a dilute acetonitrile solution of **8**, the pH rises from 7 to 10 and a starch iodide probe develops the characteristic color of iodine.

Furthermore, in the presence of base (CN^- , HO_2^-) unreacted hydrazine **8** might be expected to eliminate hydrogen cyanide with the formation of azomethine **10c**. Accordingly, salts **5c** and **9c** upon treatment with triethylamine at room temperature in the presence of an excess of CS_2 both lead to the thiadiazole adduct **15c** in good yield, 66 and 65%, respectively. Although stable to CS_2 , hydrazine **8** under identical conditions likewise furnishes **15c** (67%).⁹ Verification of the structure is deferred to a subsequent section. A second product, thiadiazolidinedithione **16**, can be isolated in 18–25% yield from all three reactions unless the amine base is rigorously dried (see below). The 1,3 dipole **10c** is thereby suggested as the common intermediate for the reaction trio. The observation that cyanohydrazine **8** arises from both tautomers **5c** and **9c** leads further support to the intermediacy of **10c**. Ylides of this type are well known as 1,3 dipoles,¹⁰ while a bicyclic homologue of **10c** has been generated by a separate route.^{5,6} In agreement, air oxidation of **8** in a 10-mol excess of CS_2 furnishes thiadiazole **15c** as the major product (54%) along with the bicyclic dithione **16** (16%). A control experiment in which adduct **15c** was treated with CS_2 and Et_3N led to the quantitative recovery of starting material, indicating that **16** is not derived from **15c**. Dithione **16** is, however, produced in 83% yield from the simple bicyclic hydrazine **17** and $\text{CS}_2/\text{Et}_3\text{N}$ and is therefore implicated as an intermediate in the oxidation of cyanohydrazine **8**. The formation of thiadiazolidinedithiones from hydrazines and CS_2 has been reported by Thorn.¹¹

Although the formation of azomethine **10c** by the action of bases (CN^- , HO_2^-) generated during the air oxidation of **8** is consistent with the experiments described above, we cannot rule out its direct formation by loss of the cyanide radical from the intermediate hydrazyl radical. Radical chain decomposition could be sustained by subsequent $\text{CN}\cdot$ abstraction of hydrogen from **8** to regenerate hydrazyl (see Scheme II).

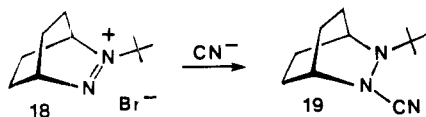
Another possible hydrazyl radical decomposition pathway involves the loss of the 2-cyanopropyl radical to give DBO **6** ($n = 2$). Hydrogen abstraction by the former would generate



additional hydrazyl and 2-cyanopropane. A search for the latter by GLC and combined GLC-MS demonstrated its absence, however, and indicates that DBO 6 arises from another source, i.e., hydrazine 17.

The presence of bicycle 17 is inferred both from the isolation of azo 6 and dithione 16, as well as from the behavior of salts 5c and 9c under basic conditions. The salts are stable in aqueous solution as evidenced by their indefinite stability in D₂O as monitored by NMR spectroscopy. However, the addition of dilute aqueous NaOH to either material causes immediate and complete hydrolysis to hydrazine 17 and acetone. Any ylide generated during the oxidation of cyanohydrazine 8 can scavenge a proton from either water or H₂O₂, resulting in the formation of diazenium cation 9c or the thermodynamically preferred¹ iminium cation 5c. The resulting hydroxide or hydroperoxide in turn rapidly converts the tautomer formed to hydrazine 17 and subsequently to DBO 6 (*n* = 2) and water.

Generation of the azomethinimine 10c from cyanohydrazine 8 releases a mole of HCN. Subsequent attack of cyanide ion from this source or from the reaction with 5c or 9c employing sodium cyanide on the diazenium species 11 accounts for the appearance of the dicyanohydrazine 7. In order to confirm this event, the *tert*-butyl diazenium salt 18 (*X* =

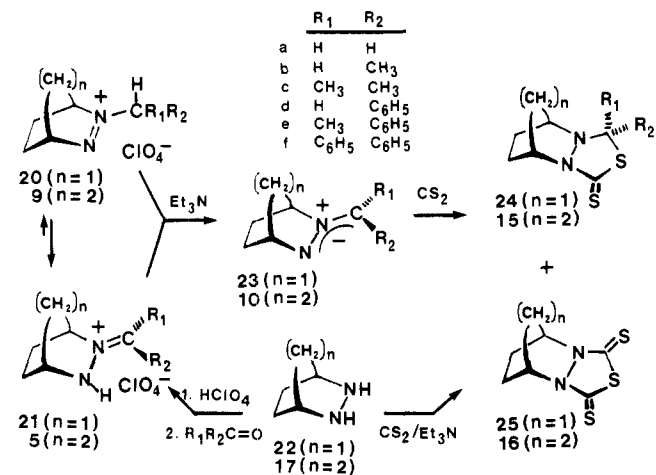


Br) was treated with NaCN at room temperature to give the cyanohydrazine 19 in quantitative yield.

The structures of cyanohydrazines 7 and 19 are confirmed by combustion analysis and spectroscopy, and in the latter case by its synthesis. Both compounds show a weak cyano stretch in the infrared spectra at 2220 cm⁻¹ and exhibit NMR traces resembling that of cyanohydrazine 8. Of significance is the appearance of split bridgehead protons (7, τ 6.48 and 6.70; 19, τ 6.60 and 6.82) which reflect the differing electronic demands of adjacent N-CN and N-CC₃ moieties. These same protons for the monocyano compound 8 appear as a broad unresolved singlet.

The circumstantial evidence surrounding the intervention of azomethinimine 10c and the possibility that cations 5c and 9c might serve as convenient precursors to the ylides in general stimulated efforts to generate the dipoles in a more controlled fashion. Although our goal in this regard was not fully realized, bicyclic ylides iv can be easily generated and trapped, and in one case isolated. Preparation of the appropriate starting materials is described in the following section.

Preparation of Diazenium and Iminium Salts. Diazenium cations 20 and 9 were prepared as reported previously¹



by alkylating DBH and DBO 6 (*n* = 1 and 2, respectively) with alkyl halides and silver perchlorate in methylene chloride. Yields ranged from 63 to 100% (Table I). In a few cases, although the NMR spectra of the salts were uncontaminated with impurities, completely satisfactory combustion analyses could not be obtained. We have noted previously that traces of base, including halide ions, catalyze rearrangement to the iminium tautomer.¹ And unless moisture is very carefully excluded the prototypic shift is accompanied by the further formation of bicyclic hydrazines (e.g., 17 and 22).

The same problem arises of course in attempts to obtain pure samples of the iminium species 21 and 5. These can sometimes be prepared by the controlled rearrangement of 20 and 9.¹ A more satisfactory method consists of treating the corresponding bicyclic hydrazine hydroperchlorates with an excess of the appropriate aldehyde or ketone in dry 2-propanol (49–80%). The derivatives so obtained are listed in Table I.

Ylide Formation and Capture. Passage of the diphenyliminium cation 20 (*R*₁ = *R*₂ = C₆H₅) through a column of basic alumina leads to a bright yellow solution which delivers the stable azomethinimine 23 (*R*₁ = *R*₂ = C₆H₅) in 38% yield. Similar conditions proved to be unsuitable for the isolation of other azomethinylides in this series. Neither low temperatures nor a range of bases were successful. Nevertheless, in situ formation of the bicyclic zwitterions 10 and 23 was demonstrated by their 1,3-dipolar cycloaddition with CS₂. Treatment of either 5, 9, 20, or 21 in an excess of CS₂ with more than 1 equiv of anhydrous triethylamine led to a yellow solution which faded to colorless within 10 min. The corresponding adducts 24 and 15 were obtained in most cases accompanied by dithiones 16 and 25. As for 16, the constitution of 25 was determined by its preparation from 22. The yields of the two products are listed in Table II.

Although every attempt was made to dry the solvents, reagents, and starting materials prior to deprotonation of 5, 9, 20, and 21, the dithione byproducts 16 and 25 were persistent in their appearance. Since we have shown that the latter are not produced by way of 15 and 24, we can only surmise that traces of moisture linger in the reaction system in spite of efforts to remove it. Alternatively, the triethylamine used may have been contaminated by the potent dealkylating agent diethylamine.¹² GLC examination of redistilled and alumina-treated triethylamine showed less than 0.1% of the latter, however.

Carbon disulfide can in principle cycloadd to the azomethinylides 10 and 23 to give either 15 and 24 or 26. Only one isomer was consistently isolated from the reactions. Furthermore, unheated crude product mixtures were routinely monitored by NMR spectroscopy, but no differences from spectra of analytical samples were observed. Thus, it appears as though either the reaction proceeds regiospecifically or the kinetic product rapidly rearranges to the thermodynamically stable species. We assign the 1,3,4-thiadiazole-2-thione structure to 15/24 on the basis of ¹H and ¹³C NMR spectroscopy. Adduct 24c (*R*₁ = *R*₂ = CH₃) exhibits two methyl groups at τ 8.33 and 8.48. Methyl absorption for the corresponding bridge-expanded bicycle 15c (*R*₁ = *R*₂ = CH₃) appears at τ

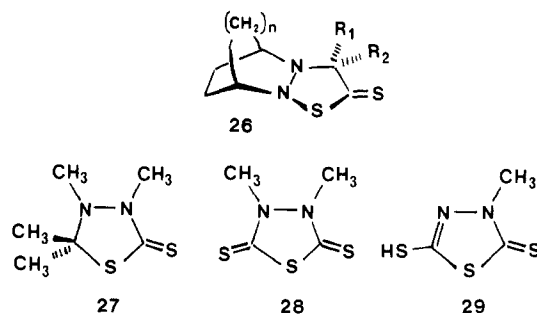


Table I. Physical Data for Diazenium and Iminium Salts (X = ClO₄)

Salt	Registry no.	<i>n</i>	R ₁	R ₂	Mp, °C (solvent) ^a	Yield %	¹ H NMR, τ (CDCl ₃ /Me ₄ Si)	Formula	Analysis, ^j %		
									C	H	N
20a	65621-96-7	1	H	H	150–152 dec	72	4.33 ^b (1 H, broad s) 4.52 (1 H, broad s) 5.63 (3 H, s) 7.7–8.8 (6 H, m)	C ₆ H ₁₁ N ₂ ClO ₄	34.2 34.3	5.3 5.4	13.3 13.2
20b	65621-97-8	1	H	CH ₃	74–76	100	4.31 ^c (1 H, broad s) 4.55 (1 H, broad s) 5.32 (2 H, q, <i>J</i> = 6 Hz) 7.5–8.6 (6 H, m) 8.45 (3 H, t, <i>J</i> = 6 Hz)	C ₇ H ₁₃ N ₂ ClO ₄	37.4 37.4	5.8 6.1	12.5 12.5
20c	64671-88-1	1	CH ₃	CH ₃	122–124	99	4.11 ^c (2 H, broad s) 4.78 (1 H, septet, <i>J</i> = 7 Hz) 7.3–8.6 (6 H, m) 8.30 (3 H, d, <i>J</i> = 7 Hz) 8.34 (3 H, d, <i>J</i> = 7 Hz)	C ₈ H ₁₅ N ₂ ClO ₄	40.3 39.4	6.3 6.3	11.7 11.6
9a	65621-99-0	2	H	H	118–120	99	4.25 ^f (1 H, broad s) 4.62 (1 H, broad s) 5.40 (3 H, s) 7.7–8.5 (8 H, m)	C ₇ H ₁₃ N ₂ ClO ₄	37.4 37.1	5.8 5.8	12.5 12.5
9b	65622-01-7	2	H	CH ₃	72–74	90	4.35 ^d (1 H, broad s) 4.79 (1 H, broad s) 5.22 (2 H, q, <i>J</i> = 7 Hz) 7.7–8.6 (8 H, m) 8.43 (3 H, t, <i>J</i> = 7 Hz)	C ₈ H ₁₅ N ₂ ClO ₄	40.2 39.6	6.3 6.3	11.8 11.6
9c	64672-05-5	2	CH ₃	CH ₃	227–228 (EtOH)	91	4.14 ^c (1 H, broad s) 4.35 (1 H, broad s) 4.71 (1 H, septet, <i>J</i> = 7 Hz) 7.6–8.5 (8 H, m) 8.31 (6 H, d, <i>J</i> = 7 Hz)	C ₉ H ₁₇ N ₂ ClO ₄	42.8 42.5	6.8 6.5	11.1 11.2
9d	65622-03-9	2	H	Ph	100–102	95	2.49 ^d (5 H, broad s) 4.00 (2 H, s) 4.20 (1 H, broad s) 4.58 (1 H, broad s) 7.7–8.7 (8 H, m)	C ₁₃ H ₁₇ N ₂ ClO ₄	51.9 51.7	5.7 5.6	9.3 9.4
9f	65622-05-1	2	Ph	Ph	62–66	69	2.75 ^g (10 H, broad s) 4.36 (1 H, broad s) 4.56 (1 H, broad s) 4.73 (1 H, broad s) 8.21 (8 H, m)	C ₁₉ H ₂₁ N ₂ ClO ₄ ⁱ	60.6 55.0	5.6 6.0	7.4 8.2
21d	65622-07-3	1	H	Ph	164–166	80	1.4–2.7 ^f (6 H m) 5.00 (1 H, broad s) 5.87 (1 H, broad s) 9.08 (6 H, broad s)	C ₁₂ H ₁₅ N ₂ ClO ₄	50.3 49.0	5.3 5.4	9.8 10.1
21e	65622-09-5	1	CH ₃	Ph	82–84	74	2.72 ^e (5 H, broad s) 3.40 (1 H, broad s) 5.32 (1 H, broad s) 5.92 (1 H, broad s) 7.35 (3 H, s) 7.54–8.38 (6 H, m)	C ₁₃ H ₁₇ N ₂ ClO ₄	51.9 50.4	5.7 5.5	9.3 9.3
21f	65622-11-9	1	Ph	Ph	244–246 (CHCl ₃)	64	2.45 ^h (10 H, broad s) 2.80 (1 H, broad s) 4.98 (1 H, broad s) 5.74 (1 H, broad s) 7.3–8.2 (6 H, m)	C ₁₈ H ₁₉ N ₂ ClO ₄	59.6 59.5	5.3 5.4	7.7 7.7
5d	65622-13-1	2	H	Ph	222–223	69	1.1–2.5 ^f (6 H, m) 5.41 (1 H, broad s) 6.34 (1 H, broad s) 6.60 (1 H, broad s) 8.03 (8 H, broad s)	C ₁₃ H ₁₇ N ₂ ClO ₄	51.9 51.7	5.7 5.8	9.3 9.4
5e	65622-15-3	2	CH ₃	Ph	128–130	49	2.2–2.7 ^e (5 H, m) 5.49 (1 H, broad s) 6.24 (1 H, broad s) 7.19 (3 H, s) 7.5–8.3 (8 H, m)	C ₁₄ H ₁₉ N ₂ ClO ₄	53.4 51.8	6.1 6.3	8.9 9.1
5f	65622-17-5	2	Ph	Ph	240–242	85	2.40 ^f (10 H, broad s) 5.54 (1 H, broad s) 6.43 (1 H, broad s) 6.57 (1 H, broad s) 7.5–8.3 (8 H, m)	C ₁₉ H ₂₁ N ₂ ClO ₄	60.6 60.2	5.6 5.1	7.4 7.1

^a Where no solvent is given, the crude crystalline product was washed repeatedly with dry ether to provide the analytical sample. ^b CD₂Cl₂/CD₃OD. ^c CD₂Cl₂/CDCl₃. ^d CD₂Cl₂. ^e CDCl₃. ^f Me₂SO-*d*₆. ^g CD₃CN. ^h Acetone-*d*₆. ⁱ The crude product showed the expected NMR spectrum, but all attempts to purify it led to the iminium tautomer (see Experimental Section). ^j The calculated values are on the first line and the values found appear on the second line.

Table II. Physical Data for CS₂ Adducts and Yields for Dithiones 16 and 25

Ad-duct	Registry no.	<i>n</i>	R ₁	R ₂	Mp °C (solvent)	Yield, % (CS ₂ adduct, 16, or 25)	¹ H NMR, τ (CDCl ₃ /Me ₄ Si)	Formula	Analysis ^h %		
									C	H	N
24a	65651-34-5	1	H	H	85-86 ^b (CCl ₄)	15	5.13 (1 H, broad s)	C ₇ H ₁₀ N ₂ S ₂	45.2	5.4	15.1
						4 (25)	5.39, 5.62 (2 H, AB, <i>J</i> = 7 Hz)		45.0	5.6	15.2
24b		1	H	CH ₃	111-112 ^a (CCl ₄)	57	<i>a</i>	C ₈ H ₁₂ N ₂ S ₂	48.0	6.0	14.0
24c	65622-18-6	1	CH ₃	CH ₃	108-110 (EtOAc/petroleum ether)	60	5.20 (1 H, broad s)	C ₉ H ₁₄ N ₂ S ₂	50.5	6.6	13.1
						0 (25)	6.25 (1 H, broad s)		50.1	6.4	12.9
24d		1	H	Ph	172-174 ^a (CH ₂ Cl ₂)	48	<i>a</i>	C ₁₃ H ₁₄ N ₂ S ₂	59.5	5.4	10.7
						11 (25)			59.4	5.6	10.5
24e		1	CH ₃	Ph	126-127 ^a (CH ₂ Cl ₂ /Et ₂ O)	31	<i>a</i>	C ₁₄ H ₁₆ N ₂ S ₂	60.9	5.8	10.1
24f	65622-19-7	1	Ph	Ph	130 dec (Et ₂ O)	84	2.71 (5 H, s)	C ₁₉ H ₁₈ N ₂ S ₂	67.4	5.4	8.3
						0 (25)	2.75 (5 H, s)		67.2	5.3	8.2
15a ^f	65622-20-0	2	H	H	124-126 ^c (acetone)	20	5.30 ^e (1 H, broad s)	C ₈ H ₁₂ N ₂ S ₂	48.0	6.0	14.0
						25 (16)	5.68 (2 H, s)		48.0	5.8	14.5
15b	65622-21-1	2	H	CH ₃	134-136 ^d (acetone)	24	5.00 (1 H, broad s)	C ₉ H ₁₄ N ₂ S ₂	50.5	6.6	13.1
						19 (16)	5.02 (1 H, q, <i>J</i> = 6 Hz)		50.5	6.4	13.1
15c ^g	65622-22-2	2	CH ₃	CH ₃	163-164 (EtOH)	66	5.00 (1 H, broad s)	C ₁₀ H ₁₆ N ₂ S ₂	52.6	7.1	12.3
						22 (16)	6.63 (1 H, broad s, <i>J</i> = 7 Hz)		52.6	7.0	12.3
15d	65622-23-3	2	H	Ph	184-186 (CCl ₄)	78	2.3-2.8 (5 H, m)	C ₁₄ H ₁₆ N ₂ S ₂	60.9	5.8	10.1
						0 (16)	4.07 (1 H, s)		60.3	6.0	10.2
15e	65622-24-4	2	CH ₃	Ph	72-74 (EtOAc/petroleum ether)	59	4.95 (1 H, broad s)	C ₁₅ H ₁₈ N ₂ S ₂	62.1	6.3	9.7
						0 (16)	7.02 (1 H, broad s)		59.7	6.4	9.0
15f	65651-39-0	2	Ph	Ph	184-186 (benzene/petroleum ether)	40	2.3-3.1 (5 H, m)	C ₂₀ H ₂₀ N ₂ S ₂	68.2	5.7	8.0
						0 (16)	5.02 (1 H, broad s)		68.2	5.6	8.0
							6.89 (1 H, broad s)				
							7.97 (1 H, s)				
							7.8-8.5 (8 H, m)				
							2.83 (10 H, s)				
							5.12 (1 H, broad s)				
							6.74 (1 H, broad s)				
							7.8-9.0 (8 H, m)				

^a See Experimental Section for details. ^b Purification: PLC; silica gel PF (254 + 366), 2.5 mm; benzene/petroleum ether/acetone, 7:5:1. ^c Purification: column chromatography; silica gel 60, 0.063-0.200 mm; benzene/petroleum ether/acetone, 3:3:1. ^d Purification: column chromatography; silica gel 60, 0.063-0.200 mm; benzene/petroleum ether, 1:2. ^e Solvent, CD₂Cl₂. ^f ¹³C NMR: (CDCl₃/Me₄Si) 173.3 (1 C), 55.1 (1 C), 54.7 (1 C), 50.7 (1 C), 23.9 (2 C), 22.0 (2 C) ppm. ^g ¹³C NMR: (CDCl₃/Me₄Si) 171.8 (1 C), 76.4 (1 C), 51.1 (1 C), 49.8 (1 C), 26.5 (4 C), 24.8 (2 C) ppm. ^h The calculated values are on the first line and the values found appear on the second line.

8.35. These values are superimposable with C-CH₃ resonances for the similar heterocycle 27 (τ 8.36).¹³

More instructive, the ¹³C spectrum of compound 15a (Table II) shows six peaks, one at 173.3 ppm and the remainder between 20 and 60 ppm downfield from Me₄Si (CDCl₃). The dimethyl derivative 15c delivers a similar pattern with a single low field carbon at 171.8 ppm. The latter is assignable to N-¹³C=S. Thiacarbonyl ¹³C absorptions for 27, 28, and 29 are at 193, 180, and 187 ppm, respectively.^{13,15} On the contrary,

dithiomethyl acetate, an acyclic model for the alternative adduct 26, displays ¹³C=S absorption at 233 ppm.¹⁶

Conclusion

Bicyclic diazenium and iminium cations are readily interconverted via the azomethinimines iv (10 and 23). The latter ylides can be generated from either cation precursor and prompted to undergo a 1,3 cycloaddition to CS₂. Although we have not explored the efficacy of other dipolarophiles, there

is little doubt that a variety of synthetic goals may be achieved by choosing the appropriate reagent.⁶

Cations i and iii likewise react with weak nucleophiles such as CN⁻. If R in i does not bear a proton α to =N⁺, the nucleophile attacks the divalent nitrogen of the diazenium moiety to give a tetrasubstituted cyanohydrazine such as 7 and 19. Where the mobile α proton is present, the diazenium species i behaves precisely as iminium cation iii and leads to trialkylhydrazine 8. Our work does not allow a decision as to whether CN⁻ first attacks nitrogen as in 11 followed by rearrangement via ylide iv and HCN or whether CN⁻ functions as a base, catalyzing the transformation of i to iii and subsequently attaching itself to carbon. In any case, the resulting trialkylhydrazine mimics the redox lability of the previously reported example 12. The behavior of salts i and iii under the influence of other nucleophiles is under investigation.

Experimental Section

General. Microanalyses were performed by the Microanalytical Laboratory, Department of General and Organic Chemistry, The H.C. Ørsted Institute, University of Copenhagen. Melting points were measured with a Büchi instrument and are uncorrected. IR spectra were recorded with a Perkin-Elmer 257 or 337 grating spectrophotometer and UV-vis spectra with a Cary 15 or Unicam SP 1800 recording spectrophotometer. Mass spectra were obtained on an AEI MS-902 apparatus. The NMR spectra were measured with Varian A-60 and Bruker HX-90E (¹³C) spectrometers. GLC analyses were accomplished with a Perkin-Elmer F 11 gas chromatograph and a Pye Unicam 104 chromatograph. Both were equipped with a flame ionization detector. Reagent grade solvents and liquid reagents (alkyl halides, triethylamine, and CS₂) were all treated by passage through a column of basic alumina (2 × 5 cm) just prior to use. All ketones and aldehydes used were passed through a column of neutral alumina (2 × 5 cm) just before use. 2-Propanol was purified by distillation over CaH₂. Silver perchlorate, finely powdered, was dried and stored over concentrated H₂SO₄.

2-(2-Cyano-2-propyl)-2,3-diazabicyclo[2.2.2]octane (8) and 2-(2-Cyano-2-propyl)-3-cyano-2,3-diazabicyclo[2.2.2]octane (7). To a solution of iminium perchlorate 9c (X = ClO₄)¹ (500 mg, 2.14 mmol) in chloroform (40 mL) cooled to 0 °C under N₂ was added a solution of NaCN (300 mg, 6.12 mmol) in distilled water (10 mL), and the mixture was stirred for 0.5 h. Upon addition the initial light yellow color of the reactants changed immediately to red and remained so throughout the reaction. The organic layer was separated, washed with saturated NaCl (3 × 25 mL), dried (MgSO₄), filtered, and stripped of solvent under reduced pressure to yield a light orange oxygen-sensitive oil (8; 360 mg, 2.01 mmol, 94%). Attempted recrystallization led to decomposition and further conversion: IR ν_{\max} (CHCl₃) 3500–3200 (s), 2225 (s) cm⁻¹; NMR (CDCl₃/Me₄Si) τ 6.45 (1 H, broad s, J = 10 Hz, NH, exchanged with D₂O), 7.03 (2 H, broad s, J = 13 Hz), 6.9–7.2 (8 H, m), 8.66 (6 H, s); MS m/e 179 (M⁺, 0.014), 178 (0.027), 177 (0.18), 152 (0.24, -HCN), 97 (0.45), 41 (0.82), 29 (1.0). Anal. Calcd for C₁₀H₁₇N₃: C, 67.0; H, 9.6; N, 23.5. Found: C, 66.7; H, 9.5; N, 23.7.

Chromatography (PLC; silica gel, 2 × 100 cm; EtOAc, 2 elutions) of a second portion of the oil (950 mg) resulted in two fractions (R_f 0.45 and 0.68, respectively) which were extracted with ether. The first fraction was relieved of solvent in vacuo to produce white solid DBO 6 (126 mg, 1.15 mmol, 20%); mp 138–140 °C; the NMR spectrum was identical with authentic DBO 6 (n = 2).

The second fraction was stripped of solvent and recrystallized (hexane) to give white crystals of the dicyanohydrazine 7 (380 mg, 1.86 mmol, 35%); mp 114–115 °C; IR ν_{\max} (CHCl₃) 2220 (w) cm⁻¹; NMR (CDCl₃/Me₄Si) τ 6.48 (1 H, broad s, J = 6 Hz), 6.70 (1 H, broad s, J = 6 Hz), 7.5–8.2 (8 H, m), 8.42 (6 H, s). Anal. Calcd for C₁₁H₁₆N₄: C, 64.7; H, 7.9; N, 27.4. Found: C, 64.8; H, 8.0; N, 27.3.

Bubbling a stream of O₂ into a solution of hydrazine 8 (60 mg) in CD₃CN (1 mL) in an NMR tube caused the conversion to 6 and 7 within 5 min and acetone (τ 7.90) appeared simultaneously. The presence of acetone was further confirmed by IR spectroscopy (ν_{\max} (neat/KBr) 1720 (C=O) cm⁻¹) and GLC (Carbowax 1500, 45 °C, flow rate 50 mL/min, 3.2 min; the retention time was identical with that of authentic material). The reaction mixture was likewise investigated for 2-cyanopropane by comparison with standard solutions containing the latter, acetone, and acetonitrile (GLC; polypropylene glycol, 38 °C). Its absence was substantiated by examination of the reaction solution and standards with combined GLC-MS [poly(1,4-butane-

diol) succinate, 40 °C; Finnigan MS 1015 S/L (70 eV)]. The pH of the solution was monitored with indicator paper calibrated in 0.5 pH increments and reached a maximum value of 10.5. The presence of an oxidant was established by a strong positive test with starch iodide paper.

The above reactions gave identical results when diazenium bromide 9c (X = Br) was employed instead of the above perchlorate.

Characterization of Cyanohydrazine 7 with PhNCS: 2,4,6-Triaza-3-thio-4-phenyl-5,5-dimethyltricyclo[5.2.2.0^{2,6}]undecane. Cyanohydrazine 7 (113 mg, 0.63 mmol) in CH₂Cl₂ (10 mL) was treated with PhNCS (108 mg, 0.80 mmol) in CH₂Cl₂ (10 mL) for 1 h (25 °C). Removal of the solvent in vacuo gave a white semisolid. Recrystallization (EtOH) yielded a microcrystalline solid (163 mg, 0.57 mmol, 90%); mp 149–150 °C; IR ν_{\max} (KBr) 1510 (s), 1460 (s), 1300 (s), 1215 (s), 1205 (s), 700 (s) cm⁻¹; NMR (CDCl₃/Me₄Si) τ 2.73 (5 H, broad), 5.60 (1 H, broad), 6.80 (1 H, broad), 7.40–8.60 (8 H, m), 8.70 (6 H, m). Anal. Calcd for C₁₆H₂₁N₃S: C, 66.9; H, 7.4; N, 14.6; S 11.2. Found: C, 70.0; H, 7.4; N, 14.7; S, 11.4.

2,6-Diaza-3-thio-4-thia-5,5-dimethyltricyclo[5.2.2.0^{2,6}]undecane (15c) and 2,6-Diaza-3,5-dithio-4-thiatricyclo[5.2.2.0^{2,6}]undecane (16). A solution of diazenium salt 9c (X = I⁻)¹ (2.04 g, 7.29 mmol) and CS₂ (10.6 g, 14.8 mmol) in CH₂Cl₂ (100 mL) under N₂ was treated dropwise with a solution of Et₃N (860 mg, 8.00 mmol; distilled from KOH) in CH₂Cl₂ (10 mL). The reaction was stirred for 1 h at 25 °C, the organic phase was washed with saturated NaCl (4 × 25 mL) and dried (MgSO₄), and the solvent was removed under reduced pressure to yield a solid (1.54 g). Chromatography of the crude solid on two plates (20 × 100 cm silica gel; CH₂Cl₂, 1 elution) furnished two main bands (R_f 0.25 and 0.75), which were extracted with CH₂Cl₂. The substance with R_f 0.75 was recrystallized to give white solid 15c (1.10 g, 4.82 mmol, 66%); mp 163–167 °C. For further physical characteristics, see Table II.

The compound with R_f 0.25 is white solid dithione 16 (370 mg, 1.61 mmol, 22%); mp 222–223 °C (MeOH); IR ν_{\max} (KBr) 1440 (s), 1180 (s) cm⁻¹; NMR (CDCl₃/Me₄Si) τ 4.63 (2 H, broad s, J = 7 Hz), 7.95 (8 H, m); UV λ_{\max} (CH₃OH) 266 nm (log ϵ 4.2), 338 (4.2). Anal. Calcd for C₈H₁₀N₂S₂: C, 41.7; H, 4.4; N, 12.2; S, 41.8. Found: C, 41.8; H, 4.3; N, 12.2; S, 41.6.

B. A solution of iminium salt 5c (X = ClO₄)¹ (700 mg, 2.78 mmol) and CS₂ (2.11 g, 27.8 mmol) in CH₂Cl₂ (30 mL) under N₂ was treated dropwise with a solution of Et₃N (280 mg, 2.78 mmol; distilled from KOH) in CH₂Cl₂ (10 mL). The reaction immediately turned dark orange but gradually faded to light yellow after stirring for 1 h at 25 °C. After workup and chromatography of the crude reaction products as specified above, identical products were isolated, i.e., the CS₂ adduct 15c (410 mg, 1.80 mmol, 65%) and the dithione 16 (164 mg, 0.690 mmol, 25%). No other products were observed.

Reaction of Cyanohydrazine 8 with CS₂/Et₃N. A solution of cyanohydrazine 8 (9.00 mg, 5.00 mmol) and CS₂ (3.80 g, 50.0 mmol) in CH₂Cl₂ (35 mL) under N₂ was treated dropwise with a solution of Et₃N (500 mg, 5.00 mmol; distilled from KOH). The resulting orange solution was stirred for 1 h at 25 °C, worked up as above, and chromatographed (PLC; silica gel; CH₂Cl₂, 2 elutions) to produce two main bands with R_f 0.25 and 0.75, respectively. Extraction with CH₂Cl₂ and solvent removal delivered dithione 16 (213 mg, 0.890 mmol, 18%) and CS₂ adduct 15c (766 mg, 3.36 mmol, 67%).

Reaction of Cyanohydrazine 8 with CS₂/O₂. A solution of freshly prepared cyanohydrazine 8 was dissolved in CD₃CN in an NMR tube and shown to be homogeneous by NMR spectroscopy. Addition of a large excess of CS₂ in CDCl₃ caused no change in the spectrum. Bubbling O₂ into the solution promoted the rapid formation of DBO 6 (n = 2), dicyanohydrazine 7, and the adduct 15c. Continued O₂ introduction led to the complete disappearance of cyanohydrazine 8 and its replacement by the latter compounds (NMR). On a preparative scale a mixture of 8 (1.00 g, 5.55 mmol) and CS₂ (5.30 g, 55.5 mmol; dried over MgSO₄) in CH₃CN (50 mL) was stirred and subjected to a stream of O₂ gas for 1.0 h. Removal of the solvent under reduced pressure gave an orange solid (1.37 g). A portion (300 mg) was chromatographed (PLC; silica gel; CH₂Cl₂, 2 elutions) to give six bands. Those with R_f values of 0.25 and 0.75 were removed, extracted (CH₂Cl₂), and stripped to give off-white solids, the CS₂ adduct 15c (151 mg, 0.66 mmol, 54%) and dithione 16 (46 mg, 0.20 mmol, 16%).

Treatment of CS₂ Adduct 15c with CS₂/Et₃N (Control Experiment). A solution of adduct 15c (250 mg, 1.5 mmol) and CS₂ (300 mg, 4.25 mmol) in CH₂Cl₂ (30 mL) was treated dropwise with a solution of Et₃N (152 mg, 1.5 mmol; distilled from KOH) in CH₂Cl₂ (5 mL). The mixture was stirred for 1 h at 25 °C. TLC (silica gel, CH₂Cl₂) indicated only one spot, corresponding to starting material. Removal of solvent under reduced pressure gave a yellow residue that was triturated with ether (2 × 10 mL) to yield an off-white solid (260 mg).

The material had an NMR spectrum identical with that of starting material. No other product was observed. Adduct **15c** is thus inert to conversion to dithione **16** under these conditions.

Preparation of Dithione 16 from 2,3-Diazabicyclo[2.2.2]octane (17). DBO **6**^{17,18} was catalytically reduced (Pd/C, EtOAc) on a Paar hydrogenation apparatus to 2,3-diazabicyclo[2.2.2]octane (**17**).¹⁸ The consumption of DBO was confirmed by NMR spectroscopy. Hydrazine **17** (1.12 g, 10.0 mmol) in CH₂Cl₂ (25 mL) under N₂ was combined with CS₂ (7.6 g, 100 mmol) in CH₂Cl₂ (25 mL) and then treated dropwise with anhydrous Et₃N (1.01 g, 10 mmol; distilled over KOH) in CH₂Cl₂ (10 mL). The solution rapidly became yellow; stirring was continued for 0.5 h. TLC (silica gel, CH₂Cl₂) evidenced only one product. The solvent was removed under reduced pressure to yield an off-white solid. Trituration with ether gave a white powder of dithione **16** (1.88 g, 8.16 mmol, 82%), mp 223–224 °C (EtOH).

2,6-Diaza-3,5-dithio-4-thiatriicyclo[5.2.1.0^{2,6}]decane (25). 2,3-Diazabicyclo[2.2.1]heptane (**22**) hydrobromide¹ (200 mg, 1.11 mmol), CS₂ (15 mL), Et₃N (10 mL), and CH₂Cl₂ (15 mL) were combined as described above, and the mixture was stirred for 4 h. The solvent was removed in vacuo, and the oily residue was dissolved in CH₂Cl₂ (50 mL), stripped to give a solid, and recrystallized (CCl₄) to give white crystals of the dithione **25** (40 mg, 0.21 mmol, 18%); mp 208–210 °C; NMR (CDCl₃/Me₄Si) τ 4.71 (2 H, broad s), 7.82 (6 H, broad s); IR ν_{\max} (KBr) 1440 (s), 1185 (s) cm⁻¹. Anal. Calcd for C₇H₈N₂S₃: C, 38.9; H, 3.7; N, 12.9. Found: C, 38.8; H, 3.8; N, 12.6.

Reaction of Iminium Iodide 9c (X = I) and Diazenium Iodide 9c (X = I) with Aqueous Base. A sample of iminium iodide **9c** (X = I)¹ (65 mg) was dissolved in CDCl₃ and shaken with 2 drops of D₂O in an NMR tube. The NMR spectrum is nearly superimposable with that taken in dry solvent [(CDCl₃/Me₄Si/D₂O) τ 4.02 (2 H, broad s, J = ca. 10 Hz), 4.15 (1 H, septet, J = 7 Hz), 7.3–8.4 (8 H, m), 8.26 (6 H, d, J = 7 Hz)], demonstrating that the system is stable to water. The D₂O/DSS spectrum is very similar and also stable. Addition of 1 drop of 20% NaOD (Merck) caused an immediate collapse of the observed spectrum and the appearance of the spectrum of hydrazine [(CDCl₃/Me₄Si/D₂O) τ 6.5 (broad s), 7.10 (2 H, broad s, J = 6 Hz), 7.8–8.7 (8 H, m)].¹⁸ Acetone appeared at τ 7.82 (s).

A parallel experiment was carried out with diazenium iodide **9c** (X = I) (65 mg) with identical results.

Preparation of 2-tert-Butyl-3-cyano-2,3-diazabicyclo[2.2.2]octane (19). To a solution of diazenium bromide **18**¹ (600 mg, 2.43 mmol) in CHCl₃ (23 mL) was added a solution of NaCN (300 mg, 6.12 mmol) in distilled water (10 mL). The mixture was stirred for 0.5 h, and the organic phase was separated, washed with saturated NaCl (2 × 15 mL), dried (MgSO₄), filtered, and stripped of solvent to give white solid **19** (400 mg, 2.07 mmol, 85%); mp 76–77 °C (hexane); IR ν_{\max} (CHCl₃) 2220 (w) cm⁻¹; NMR (CDCl₃/Me₄Si) τ 6.60 (1 H, broad s), 6.82 (1 H, broad s), 7.9–8.5 (8 H, m), 8.78 (6 H, s). Anal. Calcd for C₁₁H₁₆N₃: C, 68.4; H, 9.9; N, 21.7. Found: C, 68.5; H, 9.9; N, 21.7.

Preparation of Diazenium Cations 9 and 20: Alkylation of Bicyclic Azoalkanes. The general procedure for the compounds listed in Table I is that given in ref 1 for **9c** (X = ClO₄). Variations from the procedure are noted below in A–C. All diazenium salts exhibit ν_{\max} (KBr) 1150–1060 (broad s, ClO₄⁻) cm⁻¹ in the infrared spectrum.

A. 2-Methyl-2-azonia-3-azabicyclo[2.2.1]hept-2-ene Perchlorate (20a, X = ClO₄). Diazabicyclo[2.2.1]hept-2-ene^{17,18} (226 mg, 2.35 mmol), AgClO₄ (490 mg, 2.35 mmol), CH₂Cl₂ (15 mL), and CH₃I (10 mL) were combined as above. The resulting perchlorate salt is difficultly soluble in CH₂Cl₂ and in most other organic solvents. In order to separate it from AgI, the solids were filtered and washed with dry MeOH (3 × 10 mL). The filtrates were combined and stripped of solvent, and the resulting solid was washed with dry ether and dried in a desiccator to yield white crystals of **20a** (X = ClO₄) (362 mg, 1.65 mmol, 72%), mp 150–152 °C dec (explosion). Care must be taken to exclude moisture from the system. Any trace of water leads to a mixture of isomers **20a** and **21a**, as is readily ascertained by NMR spectroscopy.

B. 2-Benzyl-2-azonia-3-azabicyclo[2.2.2]oct-2-ene Perchlorate (9d, X = ClO₄). DBO **6** (1.33 g, 12.1 mmol), AgClO₄ (2.60 g, 12.5 mmol), CH₂Cl₂ (25 mL), and PhCH₂Br (25 mL) were combined as above. The diazenium perchlorate is difficultly soluble in CH₂Cl₂. Thus, the reaction solids were filtered and washed with CH₂Cl₂ (5 × 10 mL) in order to separate the product from AgBr. The combined filtrates were stripped in vacuo to give a solid. Excess PhCH₂Br was removed by washing with dry ether. After drying under vacuum, colorless crystals of **9d** (X = ClO₄) (3.46 g, 11.5 mmol, 95%) were obtained, mp 100–102 °C.

C. 2-Diphenylmethyl-2-azonia-3-azabicyclo[2.2.2]oct-2-ene Perchlorate (9f, X = ClO₄). DBO **6** (1.00 g, 9.10 mmol), AgClO₄ (2.00

g, 9.60 mmol), CH₂Cl₂ (50 mL), and (Ph)₂CHBr (5.00 g, 20.2 mmol) were combined as above. The product was dissolved by washing the filtered reaction precipitate with CH₂Cl₂ (5 × 10 mL). The combined filtrates were stripped in vacuo and washed with dry ether (5 × 10 mL), yielding white crystals of **9f** (X = ClO₄) (2.36 g, 6.28 mmol, 69%), mp 62–66 °C. Recrystallization (EtOH) causes rearrangement to tautomer **5f** (X = ClO₄), as does utilization of the general procedure below.

Preparation of Iminium Cations 5 and 21: Condensation of Bicyclic Hydrazine Hydroperchlorates with Aldehydes and Ketones. The general procedure for compounds listed in Table I is illustrated by the following.

2-Benzylidene-2-azonia-3-azabicyclo[2.2.2]octane Perchlorate (5d, X = ClO₄). The hydrazine hydroperchlorate of **17**¹ (100 mg, 0.475 mmol) was dissolved in a mixture of *i*-PrOH (15 mL) and benzaldehyde (15 mL). The solution was refluxed for 1 h and allowed to stand (25 °C) under nitrogen overnight. The resulting white crystals were filtered and washed with dry ether (4 × 10 mL), yielding analytically pure product **5d** (X = ClO₄) (100 mg, 0.333 mmol, 69%), mp 222–223 °C.

Variations from this procedure are noted below in A–C. Two iminium cations (B and C) were best obtained by alkylation and in situ tautomerization. All salts showed ν_{\max} (KBr) 1150–1060 (broad s, ClO₄⁻) cm⁻¹ in the infrared spectrum.

A. 2-Methylphenylmethylidene-2-azonia-3-azabicyclo[2.2.2]octane Perchlorate (5e, X = ClO₄). The hydrazine hydroperchlorate of **17** (500 mg, 2.36 mmol) and acetophenone (2.80 g, 23.6 mmol) in *i*-PrOH (25 mL) were refluxed for 0.5 h. The reaction mixture was stored at –25 °C overnight under nitrogen. The solvent was evaporated and the oily residue crystallized by boiling it in a mixture of ether (10 mL) and ethyl acetate (2 mL). The resulting white crystals were filtered, washed with dry ether, and dried under vacuum to give **9e** (X = ClO₄) (362 mg, 1.15 mmol, 49%), mp 128–130 °C.

B. 2-Diphenylmethylidene-2-azonia-3-azabicyclo[2.2.1]heptane Perchlorate (21f, X = ClO₄). DBH **6** ($n = 1$) (1.00 g, 10.4 mmol), AgClO₄ (2.15 g, 10.4 mmol), and (Ph)₂CHCl (2.10 g, 10.4 mmol) in CHCl₃ (50 mL) were stirred (24 h, 25 °C) under nitrogen. The reaction mixture was filtered and stripped of solvent. The partially transformed diazenium product **20f** was completely rearranged by recrystallization (CHCl₃), yielding white crystals of **21f** (X = ClO₄) (2.40 g, 6.61 mmol, 64%), mp 244–246 °C.

C. 2-Diphenylmethylidene-2-azonia-3-azabicyclo[2.2.2]octane Perchlorate (5f, X = ClO₄). A mixture of DBO **6** (600 mg, 5.45 mmol), AgClO₄ (1.13 g, 5.45 mmol), (Ph)₂CHBr (13.5 g, 54.5 mmol), and Al₂O₃ (2.00 g, neutral) was stirred (4 h, 25 °C) under nitrogen in CH₂Cl₂ (25 mL), filtered through Celite, stripped of solvent, and washed with dry ether (5 × 15 mL), yielding colorless crystals of **5f** (X = ClO₄) (1.74 g, 4.62 mmol, 85%), mp 240–242 °C.

2-Diphenylmethylidene-2-azonia-3-azabicyclo[2.2.1]heptane Azomethinimine (23f). Diazenium cation **20f** (X = ClO₄) (900 mg, 2.47 mmol) was dissolved in CHCl₃ (400 mL) and passed through a column packed with basic alumina (activity III, 2 × 5 cm) under N₂. The resulting yellow solution was evaporated to give a yellow solid. Recrystallization (dry ether) yielded yellow crystals of **23f** (250 mg, 0.950 mmol, 38%), mp 111–113 °C. Repeated recrystallization yielded an analytical sample: NMR (CDCl₃/Me₄Si) τ 1.8–3.1 (10 H, m), 5.40 (1 H, broad s), 5.51 (1 H, broad s), 7.9–8.8 (6 H, m); IR ν_{\max} (KBr) 1510 (s), 1490 (s), 1420 (s), 1210 (s), 1150 (s), 1120 (s) cm⁻¹. Anal. Calcd for C₁₈H₁₈N₂: C, 82.4; H, 6.9; N, 10.7. Found: C, 82.4; H, 7.0; N, 10.5.

Generation of Ylides 10 and 23 and Capture by Carbon Disulfide to Give 15, 16, 24, and 25. The general procedure for compounds listed in Table II is the following.

2,6-Diaza-3-thio-4-thiatriicyclo[5.2.1.0^{2,6}]decane (24a). Diazenium perchlorate **20a** (X = ClO₄) (989 mg, 4.71 mmol) was dried (over H₂SO₄) and suspended in a mixture of CH₂Cl₂ (75 mL) and CS₂ (75 mL) under N₂. To the stirred suspension was added Et₃N (20 mL) dropwise. The salt dissolved within a few minutes as the reaction mixture turned yellow. Stirring was continued for 2 h under N₂ followed by solvent removal in vacuo. The oily residue was taken up in CH₂Cl₂ (20 mL), and the major part of the excess amine was removed by washing with water (3 × 20 mL). The organic phase was dried (MgSO₄) and the solvent stripped. The dark brown oily product showed the presence of **24a** and **25** by NMR spectroscopy. The mixture was separated by PLC (silica gel PF (254 + 366), 2.5 mm; benzene/petroleum ether/acetone, 7:5:1). A total of 260 mg was isolated from the plate: (i) 10 mg of unidentified material; (ii) 40 mg of white crystalline **25** (0.19 mmol, 4%), mp 208–210 °C; the NMR spectrum and melting point were identical with an independently prepared sample; (iii) 130 mg of white crystalline **24a** (0.698 mmol, 15%), mp 85–86 °C; recrystallization (CCl₄) provided an analytical sample (85

mg, 0.46 mmol), mp 85–86 °C (cf. Table II); (iv) 80 mg; the NMR spectrum showed a mixture of **24a**, **25**, and an unidentified compound with absorption at (CDCl₃/Me₄Si) τ 4.86 and 6.71.

Different separation procedures were utilized for the various adduct derivatives. All CS₂ adducts showed characteristic strong IR absorptions in two regions: ν_{\max} (KBr) 1180–1140 (s) and 1140–1120 (s) cm⁻¹.

Variations are noted below and in Table II. For further physical characteristics of the CS₂ adducts, Table II should be consulted.

A. 2,6-Diaza-3-thio-4-thia-5-methyltricyclo[5.2.1.0^{2,6}]decane (24b). Diazenium salt **20b** (X = ClO₄) (350 mg, 1.56 mmol), CH₂Cl₂ (20 mL), CS₂ (20 mL), and Et₃N (15 mL) were combined as above. The NMR spectrum of the product mixture (241 mg) showed **24b** and **25** in a ratio of 3:1 (ca. 57 and 17%, respectively). Column chromatography (silica gel 60, 0.063–0.200 mm; benzene/petroleum ether, 1:1) gave a small amount of **24b**, which was recrystallized (CCl₄) to give white crystals (20 mg, 0.10 mmol, 6%), mp 111–112 °C. The NMR spectrum showed a 1:1 mixture of two geometrical isomers: (CDCl₃/Me₄Si) τ 4.90 (1 H, q, J = 6 Hz), 5.18 (1 H, J = 6 Hz), 4.95 (1 H, broad s), 5.20 (1 H, broad s), 6.21 (1 H, broad s), 6.41 (1 H, broad s), 8.42 (3 H, d, J = 6 Hz), 8.49 (3 H, d, J = 6 Hz), 7.8–8.6 (12 H, m).

B. 2,6-Diaza-3-thio-4-thia-5-phenyltricyclo[5.2.1.0^{2,6}]decane (24d). Diazenium cation **20d** (X = ClO₄) (290 mg, 1.01 mmol), CH₂Cl₂ (20 mL), CS₂ (20 mL), and Et₃N (15 mL) were combined as above to yield a mixture of **24d** and **25** (150 mg). The two products were separated by washing the latter with ethyl acetate to extract **24d**. The residue, **25** (24 mg, 0.11 mmol, 11%), was identified by its melting point and NMR spectrum.

Compound **24d** was stripped of solvent and recrystallized (CH₂Cl₂/ethyl acetate) to yield white crystals (130 mg, 0.481 mmol, 48%), mp 172–174 °C. The NMR spectrum of pure **24d** showed a mixture of two isomers (2:3): (CD₂Cl₂/Me₄Si) τ 2.2–2.8 (10 H, m), 3.88 (1 H, s), 4.17 (1 H, s), 4.90 (1 H, broad s), 5.17 (1 H, broad s), 6.38 (1 H, broad s), 6.48 (1 H, broad s), 7.3–8.5 (12 H, m).

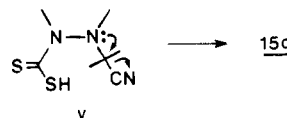
C. 2,6-Diaza-3-thio-4-thia-5-methyl-5-phenyltricyclo[5.2.1.0^{2,6}]decane (24e). Cation **20e** (X = ClO₄) (165 mg, 0.550 mmol), CH₂Cl₂ (15 mL), CS₂ (15 mL), and diisopropylethylamine (10 mL) were combined as above to yield a mixture of the two geometrical isomers of **24e** as evidenced by the NMR spectrum. Recrystallization (CH₂Cl₂/ether) afforded white crystals (47 mg, 0.17 mmol, 31%), mp 126–127 °C. The NMR spectrum showed a 1:1 mixture of the two isomers: (CDCl₃/Me₄Si) τ 2.1–2.7 (10 H, m), 4.85 (1 H, broad s), 5.16 (1 H, broad s), 6.30 (2 H, broad s), 7.84 (3 H, s), 8.00 (3 H, s), 7.7–8.6 (12 H, m).

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Registry No.—**5c** (X = ClO₄), 64801-48-5; **5c** (X = I), 64801-47-4; **6** (n = 1), 2721-32-6; **6** (n = 2), 3310-62-1; **7**, 65621-79-6; **8**, 65621-80-9; **9c** (X = Br), 64672-02-2; **9c** (X = I), 64672-03-3; **16**, 65621-81-0; **17**, 280-49-9; **17** hydroperchlorate, 64671-91-6; **18**, 57163-60-7; **19**, 65621-82-1; **20g** (X = ClO₄), 65621-84-3; **20e** (X = ClO₄), 65621-86-5; **20f** (X = ClO₄), 65621-88-7; **22** HBr, 39158-98-0; **23f**, 65621-89-8; **24b** (isomer I), 65651-38-9; **24b** (isomer II), 65701-03-3; **24d** (isomer I), 65701-04-4; **24d** (isomer II), 65621-90-1; **24e** (isomer I), 65621-91-2; **24e** (isomer II), 65701-05-5; **25**, 65621-93-4; 2,4,6-triaza-3-thio-4-phenyl-5,5-dimethyltricyclo[5.2.2.0^{2,6}]undecane, 65621-92-3; benzaldehyde, 100-52-7; acetophenone, 98-86-2.

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- Hydrogen cyanide addition to a bicyclic azomethinimine has been reported to lead to the corresponding trialkylhydrazine without mention of attendant difficulties.⁷
- It is conceivable that cyanohydrazine **8** is a strong enough base to promote a reversible self-elimination of HCN or nucleophilic enough to add CS₂ to give **v**, which might spontaneously close to **15c**. However, these possibilities are eliminated by the observation that **8** is unchanged in the presence of CS₂ unless treated with either Et₃N or O₂.



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