bicyclo[3.2.1]oct-3-en-6-one and numerous other bicyclo[3.2.1]oct-2-ene derivatives. On the other hand, the pattern found in the vinyl region of related bicyclo[2.2.2]octene derivatives was consistently much sharper and more symmetrical.[8]

Experimental Section

3-Cyclohexenylmethyl *p*-Bromobenzenesulfonate (1).—Sodium borohydride reduction of 3-cyclohexenecarboxaldehyde in absolute ethanol gave 3-cyclohexenylcarbinol, bp 64–65° (4.8 mm), n^{25}_{D} 1.4827, in 87% yield. To a solution of 3-cyclohexene-1-carbinol (70 g, 0.625 mol) in 360 ml of anhydrous pyridine at −10° was slowly added 190 g (0.745 mol) of *p*-bromobenzenesulfonyl chloride over a period of 30 min. The reaction mixture was constantly stirred in a methanol–ice bath during addition. The reaction was stirred for 2 hr at −10° after addition was complete, allowed to stand in a refrigerator for 24 hr, and poured directly into a 1-l. ice solution containing 180 ml of concentrated hydrochloric acid. Vigorous stirring produced a white slushy solid. Filtration of the solid, drying over anhydrous magnesium sulfate in methylene chloride, removal of methylene chloride by vacuum distillation, and recrystallization from absolute ethanol at −40 and −78° gave 157 g (0.469 mol, 75%) of 3-cyclohexenylmethyl *p*-bromobenzenesulfonate (1), mp 33–35° (lit.[9] 34.5–35°).

3-Cyclohexenylmethyl Thioacetate (2).—To 400 ml of anhydrous methanol containing 3-cyclohexenylmethyl *p*-bromobenzenesulfonate (80 g, 0.242 mol) was added, with constant stirring at room temperature, 100 ml of anhydrous methanol containing 18.5 ml (0.262 mol) of thioacetic acid and 14.5 g (0.258 mol) of potassium hydroxide. Preparation of the potassium thioacetate solution required a methanolic solution of potassium hydroxide to be added to a cooled methanolic solution of thioacetic acid.

After 24 hr of stirring at room temperature, the reaction was filtered to remove precipitated potassium *p*-bromobenzenesulfonate. Methanol was removed from the filtrate under reduced pressure. To the remaining yellow oil was added 100 ml of water and 200 ml of methylene chloride. The methylene chloride layer was then washed with 100 ml of saturated sodium hydrogen carbonate and finally two 100-ml portions of water. The methylene chloride was then dried over anhydrous magnesium sulfate and evaporated at reduced pressure to give 38.5 g (0.266 mol, 94%) of a clear yellow liquid, bp 62–63° (0.8 mm), n^{25}_{D} 1.5118.

Anal. Calcd for $C_9H_{14}OS$: C, 63.58; H, 8.30. Found: C, 63.57; H, 8.36.

3,4-Dibromocyclohexeneylmethyl Thioacetate (3).—To 40 g (0.235 mol) of 3-cyclohexenylmethyl thioacetate and 200 ml of carbon tetrachloride cooled in an ice bath, in subdued light, was added 38.5 g (0.240 mol) of bromine in small increments, with stirring, over a period of 0.5 hr. After addition, the reaction was kept at 0° for 1 hr. The reaction was then washed with 50 ml of saturated sodium hydrogen sulfite. The carbon tetrachloride solution was dried over anhydrous magnesium sulfate and concentrated at reduced pressure. A 75-g (90%) yield of crude product was obtained, bp 150–155° (0.07 mm), n^{25}_{D} 1.5693. A sample for analysis was obtained by molecular distillation at reduced pressure.

Anal. Calcd for $C_9H_{14}Br_2OS$: C, 32.75; H, 4.28. Found: C, 33.08; H, 4.34.

***endo*-4-Bromo-6-thiabicyclo[3.2.1]octane (5).**—Thirty-five g (0.106 mol) of 3,4-dibromocyclohexylmethyl thioacetate was added to a refluxing solution of 600 ml of methanol containing 15 g (0.268 mol) of potassium hydroxide in a 2-l. flask under nitrogen. After refluxing for 24 hr, an additional 37 g (0.112 mol) of 3,4-dibromocyclohexylmethyl thioacetate in 200 ml of methanol and 100 ml of methylene chloride solution and 17.5 g (0.312 mol) of potassium hydroxide in 100 ml of methanol were added to the refluxing solution. After refluxing for another 24 hr, an additional 15 g (0.265 mol) of potassium hydroxide was added. Twenty hr after the final addition of potassium hydroxide (total reaction time 68 hr), the solvent was removed under reduced pressure. To the crude product was then added 400 ml of methylene chloride. The methylene chloride solution was extracted with two 150-ml portions of water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give a yellow oil. Passing this yellow oil through a column containing 500 g of Woelm's Neutral Alumina with 1% benzene–99% hexane solution gave 2 g of an unknown unsaturated compound. Continued elution with a 10% benzene–90% hexane solution gave 29 g (0.140 mol, 62%) of 5 as a clear liquid, bp 82° (0.09 mm), n^{25}_{D} 1.5762.

Anal. Calcd for $C_7H_{11}BrS$: C, 40.65; H, 5.35. Found: C, 41.02; H, 5.56.

6-Thiabicyclo[3.2.1]octane (6).—*endo*-4-Bromo-6-thiabicyclo[3.2.1]octane (5) (1 mmol, 0.207 g), 0.510 g (1.5 mmol) of triphenyltin hydride, and 5 mg of azobisisobutronitrile were added to a small sublimation apparatus fitted with a drying tube. The reaction mixture was heated at 80° for 24 hr. The cold finger was removed from the sublimator and yielded 20 mg of crystalline compound. The ir[4] of this compound proved to be identical with that of 6-thiabicyclo[3.2.1]octane prepared by Birch and colleagues.[5]

6-Thiabicyclo[3.2.1]oct-3-ene (4).—To 50 ml of ethylene glycol were added 4.14 g (20 mmol) of *endo*-4-bromo-6-thiabicyclo[3.2.1]octane and 8.95 g (160 mmol) of potassium hydroxide. This solution was heated to 180° and kept between 180 and 190° for 18 hr. After 18 hr the reaction was cooled and 400 ml of water was added. The aqueous solution was extracted with three 100-ml portions of pentane. The pentane extracts were combined and solvent was removed at reduced pressure. About 40 ml of water was added to the residual oil and the aqueous mixture was extracted with 40 ml of pentane. The pentane extract was dried over anhydrous magnesium sulfate. Removal of solvent at reduced pressure gave 1.6 g of a clear yellow oil containing 6-thiabicyclo[3.2.1]oct-3-ene. The material was purified by preparative gas phase chromatography on an SE-30 column. Pure 4 had bp 197–200°, n^{20}_{D} 1.5601.

Anal. Calcd for $C_7H_{10}S$: C, 66.62; H, 7.99. Found: C, 66.67; H, 8.05.

Dipole Moment of *endo*-4-Bromo-6-thiacyclo[3.2.1]octane.—The Dipolemeter DM 01 manufactured by Wissenschaftlich-Technische Werkstatten was used for the measurements. The dipole moments were measured in benzene solution at 25 ± 0.01°. The moments were calculated essentially by the method of Halverstadt and Kumler[10] utilizing an IBM 707 computer programmed as described by Allinger.[11] The dipole moment data are $\alpha = 17.491$, $\beta = 0.986$, $e_1 = 2.2724$, $P_2 = 297.7$, $d = 0.87329$, and $M_{\mathrm{D}} = 45.9360$ giving a dipole moment of 3.510 ± 0.019 D.

The model compounds used for calculation of the predicted dipole moments were cyclohexyl bromide (2.24 D),[12] thiane (1.71 D),[13] thiolane (1.90 D),[13] and cyclohexylmethyl sulfide (1.66 D).[14]

Registry No.—**2**, 27345-73-9; **3**, 27345-75-1; **4**, 27345-74-0; **5**, 27345-76-2.

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[8] We thank Professor N. A. LeBel for providing nmr spectra of these model compounds.

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Condensation–Cyclization Reactions of Electron Deficient Aromatics. II. Stable Bicyclic Immonium Zwitterions from Enamines and *sym*-Trinitrobenzene[1]

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It has been known for quite some time that Meisenheimer complexes[2] like **1** are formed from *sym*-trinitro-

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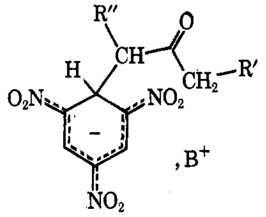
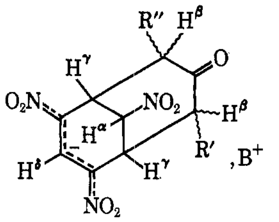
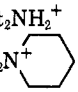
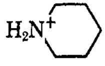
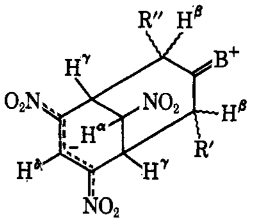
benzene (TNB), tertiary amines, and ketones when R′ and R″ are hydrogen or electron donating (*i.e.*, **1a–d**).[3–6] When R′ and/or R″ are electron withdrawing, only propenide complexes like **2** are formed (*i.e.*, **2d–f**)

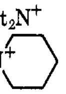


1a, $R' = R'' = H$; $B^+ = Et_3NH^+$
b, $R' = R'' = CH_3$; $B^+ = Et_3NH^+$
c, $R' = CH_3$; $R'' = H$; $B^+ = Et_3NH^+$
d, $R' = H$; $R'' = CH_3$; $B^+ = Et_3NH^+$



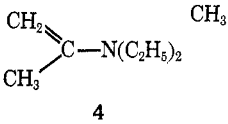
2a, $R' = R'' = CH_3$; $B^+ = Et_2NH_2^+$
b, $R' = R'' = CH_3$; $B^+ = H_2N^+$ 
c, $R' = R'' = H$; $B^+ = Et_2NH_2^+$
d, $R' = H$; $R'' = COCH_3$;
$B^+ = Et_3NH^+$, $Et_2NH_2^+$, or
H_2N^+ 
e, $R' = H$; $R'' = CO_2Et$; $B^+ = Et_3NH^+$
f, $R' = R'' = CO_2CH_3$; $B^+ = Et_3NH^+$



3a, $R' = R'' = CH_3$; $B^+ = Et_2N^+$
b, $R' = R'' = CH_3$; $B^+ = N^+$ 
c, $R' = R'' = H$; $B^+ = Et_2N^+$

when the amine is secondary or tertiary.[1,7,8] With secondary amines, **2** is also formed when R′ and/or R″ are electron donating, **2a**, **2b**,[9] or hydrogen, **2c**.[1,8,10] We have previously proposed carbanion and immonium intermediates to explain these experimental observations.[1] As a confirmation of our proposal, we report here the addition of enamines to TNB under anhydrous conditions and the isolation of the immonium intermediate **3**.

The enamine **4** was too unstable to be isolated and **3c** could not be prepared. Both **5** and **6** were isolable,



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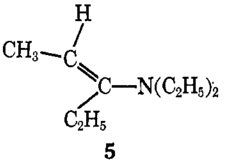

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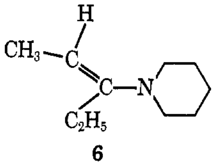

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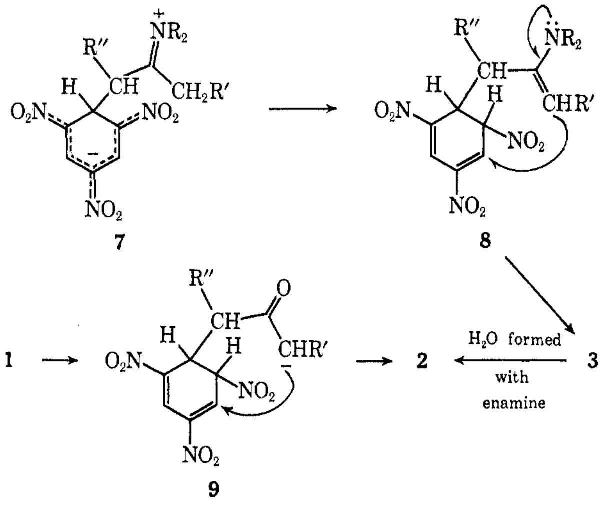
however, and addition of either of these to an anhydrous ether solution of TNB yields a red-brown solution. An oily brown precipitate results after several hours, and after work-up and recrystallization of this crude oil (see Experimental Section) bright red crystals of **3a** and **3b** were obtained. The structurally analogous bicyclic anions **2a** and **2b** were obtained from the reaction of diethylamine and piperidine, respectively, with TNB and diethyl ketone. Pertinent comparative spectral data are summarized in the Experimental Section. Each of the structures, **2a**, **2b**, **3a**, and **3b**, could be mixtures of isomers resulting from asymmetry at the carbon α to the keto or immonium functions and at the $CHNO_2$ bridge. Simplicity of the pmr spectra and sharp melting points lead us to conclude that only a single isomer is formed in each case. The stereochemistry of these adducts will be discussed elsewhere.

The visible spectrum of a solution of enamine and TNB in anhydrous acetonitrile exhibits a double maximum characteristic of the trinitrocyclohexadienate function in **1**.[5,6] This spectrum slowly changes to one with a maximum at ~500 nm, characteristic of the dinitropropenide function in **2** and **3**.[1,8] These spectral changes are consistent with the intermediacy of zwitterionic Meisenheimer complexes like **7**. Solutions of TNB in ethyl acetoacetate or acetylacetone have been studied using pmr and visible spectroscopy. The formation of **2d** and **2e** has been observed to occur through structures analogous to **1** when triethylamine or diethylamine is used as the base.[1,11] There is no question of intermediates like **7** or **8** with triethylamine, and the reaction probably occurs through **1** and **9**. The expected low nucleophilicity of enamines obtained from acidic ketones such as acetylacetone and ethyl acetoacetate make intermediates like **1** and **9** more likely, even with secondary amines. Immonium intermediate precursors to **2** arising from secondary amines, TNB, and relatively *nonacidic* ketones would explain the formation of **2a–c**, however, since with tertiary amines only **1a** and **1b** are isolated. The acidity of the protons α to R′ in **1** or **7** must be great enough so that conversion to the corresponding dienes **9** or **8** is a favorable process. If R′ is electron withdrawing, cyclization may occur through **9** to **2d–f**. If R′ is alkyl or hydrogen and tertiary amines are used, only **1a–d** can be isolated. If secondary amines are used, the formation of **7**, with a formal positive charge on nitrogen, would greatly enhance the acidity of protons α to R′ and facilitate formation of **8**. This latter intermediate could cyclize to **3** which can hydrolyze to **2**. These possibilities are strongly supported by the observation that enamines form rapidly



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and reversibly in ketonic solutions of secondary amines[12] and readily react with nitro olefins.[13] In addition, careful hydrolysis of isolated **3a** yields **2a**.

Experimental Section

Pmr spectra were determined on a Varian A-60 instrument. Chemical shifts are relative to internal TMS. Visible and infrared spectra were measured on Cary-14 and Perkin-Elmer 21 spectrophotometers, respectively. Elemental analyses were performed by G. I. Robertson, Jr., Florham Park, N. J. 07932. All melting points are uncorrected.

Enamine of Diethylamine and Diethyl Ketone (**5**).—This enamine was prepared by the method of White and Weingarten[14] and was purified by distillation on a spinning-band column at reduced pressure: bp 64° (10 mm); ir 1636 cm^{-1} (NC=C); pmr ($CDCl_3$) δ 4.20 (q, 1, J = 7 Hz, NC=CH, cis). The pmr spectrum of the crude oil prior to distillation showed an additional quartet at δ 5.06 (J = 7 Hz) assigned to NC=CH, trans.

Anal. Calcd for $C_9H_{19}N$: C, 76.53; H, 13.56; N, 9.92. Found: C, 76.80; H, 13.50; N, 10.20.

Enamine of Piperidine and Diethyl Ketone (**6**).—The enamine was prepared by the method of Stork and coworkers[12] and was purified as described for **8**: bp 80° (10 mm); ir 1640 cm^{-1} (NC=C); pmr ($CDCl_3$) δ 4.39 (q, 1, J = 7 Hz, NC=CH, cis). The pmr spectrum of the crude oil prior to distillation showed an additional quartet at δ 4.70 (J = 7 Hz) assigned to NC=CH, trans.

Anal. Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 78.51; H, 12.60; N, 9.16.

Diethylammonium and Piperidinium Anions (**2a and 2b**).—TNB (5.45 g), diethylamine (5.56 g), and diethyl ketone (6.55 g) were dissolved in dry DMSO (5 ml). The resulting dark oil was stirred for 24 hr at room temperature. Dry ether (500 ml) was then added and the mixture was stirred for 2 hr. The brown precipitate which formed was filtered and washed with copious amounts of dry ether. Recrystallization of this crude product from an 80:20 mixture of ether–methanol yielded red crystals of pure **2a** (0.5 g): mp 175°; vis max (CH_3OH) 508 nm (ϵ 29,500); ir (KBr) 1715 cm^{-1} (C=O); pmr (DMSO-d_6) δ 8.5 (s, H^δ), 5.7 (t, J = 3 Hz, H^α), 4.6 (broad, 2 H^γ), 3.0 (q, 4, J = 7 Hz, $(CH_3CH_2)_2NH_2^+$), ~2.9 (2 H^β, under $Et_2NH_2^+$), 1.2 (t, 6, J = 7 Hz, $(CH_3CH_2)_2NH_2^+$), 0.9 (d, 6, J = 7 Hz, R′ = R″ = CH_3).

Anal. Calcd for $C_{15}H_{24}N_4O_7$: C, 48.38; H, 6.50; N, 15.05. Found: C, 48.10; H, 6.49; N, 14.88.

Red crystals of **2b** (0.6 g) were prepared with piperidine in a similar manner: mp 161–163°; vis max (CH_3OH) 508 nm (ϵ 26,200); ir (KBr) 1710 cm^{-1} (C=O); pmr (DMSO-d_6) δ 8.4 (s, H^δ), 5.8 (t, J = 3 Hz, H^α), 4.5 (broad, 2 H^γ), 1.6–3.0 (m, 10, $(CH_2)_5NH^+$), ~2.8 (2 H^β, under $(CH_2)_5NH^+$), 0.9 (d, 6, J = 7 Hz, R′ = R″ = CH_3).

Anal. Calcd for $C_{16}H_{24}N_4O_7$: C, 49.99; H, 6.29; N, 14.58. Found: C, 49.37; H, 6.38; N, 13.86.

Diethylimmonium and Piperidinium Zwitterions (**3a and 3b**).—The enamine (**5** or **6**) was added to a solution of TNB (1.0 g) in anhydrous ether (50 ml) under a dry nitrogen atmosphere. An immediate red coloration was observed which intensified with time. After 24 hr at 35°, a dark red oil separated from the solution. This was transferred to 100 ml of an 80:20 ether–methanol solution. The mixture was stirred for 1 hr during which time the oil was transformed into a finely divided red solid. Recrystallization of this material from ether–methanol solution yielded red needles of **3**.

For **3a** (0.3 g): mp 195° dec; vis max (CH_3OH) 505 nm (ϵ 26,700); ir (KBr) 1637 cm^{-1} ($C=N^+$); pmr (DMSO-d_6) δ 8.3 (s, H^δ), 6.1 (t, J = 3 Hz, H^α), 4.2 (broad, 2 H^γ), 3.9 (q, 4, J = 7 Hz, $(CH_3CH_2)\overset{+}{N}_2{=}C$), ~2.6 (2 H^β, under DMSO-d_5), 1.6 (d, 6, R′ = R″ = CH_3), 1.2 (t, 6, J = 7 Hz, $(CH_3CH_2)_2\overset{+}{N}{=}C$).

Anal. Calcd for $C_{15}H_{22}N_4O_6$: C, 50.84; H, 6.26; N, 15.81. Found: C, 50.86; H, 6.27; N, 15.62.

For **3b** (0.5 g): mp 210° dec; vis max (CH_3OH) 505 nm (ϵ 23,800); ir (KBr) 1623 cm^{-1} ($C=N^+$); pmr (DMSO-d_6) δ 8.3 (s, H^δ), 6.0 (t, J = 3 Hz, H^α), 4.1 (broad, 2 H^γ), 1.7–3.2 (m, 10, $(CH_2)_5\overset{+}{N}{=}C$), ~2.6 (2 H^β, under DMSO-d_5), 1.3 (d, 6, R′ = R″ = CH_3).

Anal. Calcd for $C_{16}H_{22}N_4O_6$: C, 52.45; H, 6.05; N, 15.29. Found: C, 52.70; H, 6.26; N, 15.01.

Hydrolysis of 3a.—A solution of **3a** (0.1 g), H_2O (~0.25 ml), and DMSO (5 ml) was stirred at room temperature. Aliquots (1 ml) were taken at intervals of several hours and quenched in 5 ml of ether. Quenching yielded an orange powder which was filtered and dried to remove traces of moisture and diethyl ketone. Infrared spectra of these samples showed them to be a mixture of **2a** and **3a**, the amount of the former increasing as the hydrolysis time increased. After 12 hr at 45°, conversion to **2a** was complete.

Registry No.—**2a,** 27331-99-3; **2b,** 27332-00-9; **3a,** 27332-01-0; **3b,** 27332-02-1; *cis*-**5,** 27332-03-2; *trans*-**5,** 27332-04-3; *cis*-**6,** 27332-05-4; *trans*-**6,** 27384-95-8.

Acknowledgments.—This research was supported by the Army Research Office at Durham, Grant No. DAHCO4 69 C 0064, and the Research Corporation.

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Carbamoyl Chloride Formation from Chloramine and Carbon Monoxide

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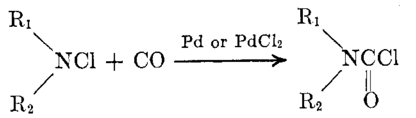
The formation of acid halide from alkyl halide and carbon monoxide in the presence of a group VIII metal compound is well known.[1] The product is described as being derived by the insertion of carbon monoxide into the carbon–halogen bond. As to the insertion of carbon monoxide into the heteroatom–halogen bond, the reaction of sulfenyl chloride with carbon monoxide has been reported recently[2] in which the carbonyl group is inserted into the sulfur–chlorine bond in the absence of any added catalyst. The present report is concerned with the insertion of carbon monoxide into the nitrogen–chlorine bond.

The reaction of chloramine (**1**) with carbon monoxide is effectively catalyzed by palladium metal or palladium chloride to produce carbamoyl chloride (**2**). The reaction proceeds fairly smoothly under milder reaction conditions. Table I summarizes the results of the carbonylation of *N*-chlorodimethylamine. The yield of **2a** ($R_1 = R_2 = CH_3$) depends on the reaction temperature, the nature of solvent, the amount of catalyst, and the carbon monoxide pressure. Here a trace amount of tetramethylurea was detected as the sole by-product. When the reaction temperature was higher than 50°, the yield of dimethylcarbamoyl chloride decreased and



$$R_1R_2NCl + CO \xrightarrow{\text{Pd or PdCl}_2} R_1R_2NC(=O)Cl$$

1 2

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