liquid was then fractionally distilled: yield 88%; bp 57–59 °C (1.0 mm); d^{20}_4 0.8997; ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 6 H, *N*-Si(CH_3)$_2$), 0.94 (s, 9 H, *N*-Si(CH_3)$_3$), 2.05 (s, 3 H, CH_3C), 2.79 (s, 3 H, NCH_3); mass spectrum, *m/e* (relative intensity) 187 (M^+, 11), 127 (17), 130 (100), 147 (74), 73 (66), 59 (93). Anal. Calcd for $C_9H_{21}NOSi$: C, 57.70; H, 11.30; N, 7.48; Si, 14.99. Found: C, 57.32; H, 11.12; N, 7.59; Si, 14.96.

***N*-Methyl-*N*-(*tert*-butyldimethylsilyl)formamide (MTBSF).** Synthesis of MTBSF is the same as that for MTBSA except that 59.01 g (1.0 mol) of *N*-methylformamide was used in place of *N*-methylacetamide: yield 93%; bp 84–85 °C (1.2 mm); mp 32 °C (moist solid); ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 6 H, *N*-Si(CH_3)$_2$), 0.93 (s, 9 H, SiC(CH_3)$_3$), 2.76 (s, 3 H, NCH_3), 8.27 (s, 1 H, HC); mass spectrum, *m/e* (relative intensity) 173 (M^+, 18), 158 (22), 147 (67), 116 (100), 59 (86). Anal. Calcd for $C_8H_{19}NOSi$: C, 55.44; H, 11.05; N, 8.08; Si, 16.20. Found: C, 55.63; H, 10.88; N, 8.19; Si, 15.99.

***N*, *O*-Bis(*tert*-butyldimethylsilyl)acetamide (BMTBSA).** Synthesis of BMTBSA is the same as for MTBSA except that 29.5 g (0.5 mol) of acetamide was used in place of *N*-methylacetamide: yield 88.7%; bp 91–92 °C (2.0 mm); d^{20}_4 0.859; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 6 H, *O*-Si(CH_3)$_2$), 0.22 (s, 6 H, *N*-Si(CH_3)$_2$), 0.87 (s, 18 H, 2 SiC(CH_3)$_3$), 1.93 (s, 3 H, CH_3C); mass spectrum, *m/e* (relative intensity) 287 (M^+, 15), 272 (13), 230 (100), 189 (33), 155 (78), 147 (74), 116 (22). Anal. Calcd for $C_{14}H_{33}NOSi_2$: C, 58.47; H, 11.57; N, 4.87; Si, 19.53. Found: C, 58.28; H, 11.52; N, 4.81; Si, 19.44.

***tert*-Butyldimethylsilylation.** All derivatizations were performed under dry nitrogen in Teflon-faced septum-capped reaction vials and flasks. Prior to silylation the organic compounds, if solid, were dissolved in a minimal amount of either dry acetonitrile or tetrahydrofuran or, if liquid, were mixed with an equal volume of acetonitrile. In all experiments performed 0.1 μM, 1.0 mM, and 50 mM concentrations of each compound were used. *tert*-Butyldimethylsilylation was accomplished by adding, via a gas-tight syringe, 10.0 equiv (based on the number of silylatable functions), of one of the following reagents: (A) MTBSTFA + 1% TBDMSCl, (B) MTBSA + 1% TBDMSCl, (C) 1.0 m TBDMSCl + 2.0 M imidazole in DMF. *tert*-Butyldimethylsilylation with reagents A and B were allowed to proceed at room temperature for 5 min and for 20 minutes. Reaction mixtures with reagent C were heated at 40 °C, with the progress of the reaction being determined by gas–liquid chromatography every 30 min for 10 h.

Isolation of compounds following *tert*-butyldimethylsilylation with reagent A was accomplished by removal of the acetonitrile or tetrahydrofuran in vacuo followed by the concomitant sublimation at 35 °C (15 torr) of the MTBSTFA, *N*-methyltrifluoroacetamide, and TBDMSCl from the mixture. The remaining clear residues (≥97% purity by GLC) were then sublimed or distilled. Compounds *tert*-butyldimethylsilylated with reagent B were sublimed immediately following the removal of the reaction solvent. Compounds *tert*-butyldimethylsilylated with reagent C were generally isolated by adding the final reaction mixture to one volume of benzene or hexane and washing the mixture several times with water. The organic layer was then reduced in volume in vacuo, and the contaminating *tert*-butyldimethylsilanol was removed by sublimation at 35 °C (15 torr). Due to the presence of DMF in reagent C, sublimation or distillation of the silylated product from the initial reaction was impossible.

Registry No. MTBSTFA, 77377-52-7; MTBSA, 82112-20-7; MTBSF, 68944-33-2; MtBSA, 82112-21-8; RO(CH_2)$_3$OR (R = *tert*-butyldimethylsilyl), 82112-22-9; ROCH$_2$CH(OR)CH$_2$OR (R = *tert*-butyldimethylsilyl), 82112-23-0; C_6HsOR (R = *tert*-butyldimethylsilyl), 18052-27-2; $CH_3CH_2CH_2SR$ (R = *tert*-butyldimethylsilyl), 82112-24-1; $(CH_3)_2CHSR$ (R = *tert*-butyldimethylsilyl), 82112-25-2; RS(CH_2)$_3$SR (R = *tert*-butyldimethylsilyl), 82112-26-3; RSCH$_2$CH(OR)CH$_2$OR (R = *tert*-butyldimethylsilyl), 82112-27-4; RSCH$_2$CH$_2$OR (R = *tert*-butyldimethylsilyl), 82112-28-5; RSCH$_2$COOR (R = *tert*-butyldimethylsilyl), 82112-29-6; ROCH$_2$CH$_2$COOR (R = *tert*-butyldimethylsilyl), 82112-30-9; RO-*m*-C_6H_4COOR (R = *tert*-butyldimethylsilyl), 67226-77-1; RO-*o*-$C_6H_4CH_2OR$ (R = *tert*-butyldimethylsilyl), 82112-31-0; RO-*p*-$C_6H_4CH_2COCOOR$ (R = *tert*-butyldimethylsilyl), 82112-32-1; DL-C_2HsCH(NHR)COOR (R = *tert*-butyldimethylsilyl), 82112-33-2; C_2HsCH(NHR)CH$_2$OR (R = *tert*-butyldimethylsilyl), 82112-34-3; $CH_3CH(NHR)CH_2OR$ (R = *tert*-butyldimethylsilyl), 82134-49-4; 2,4-(OR)-6-(RNH)pyrimidine (R = *tert*-butyldimethylsilyl), 82112-35-4; $C_6HsCH_2NR(CH_3)$ (R = *tert*-butyldimethylsilyl), 82112-36-5; 1,3-propanediol, 504-63-2; glycerol, 56-81-5; phenol, 108-95-2; 1-propanethiol, 107-03-9; 2-propanethiol, 75-33-2; 1,3-propanedithiol, 109-80-8; 2-mercapto-1,2-propanediol, 96-27-5; 2-mercaptoethanol, 60-24-2; mercaptoacetic acid, 68-11-1; 3-hydroxypropionic acid, 503-66-2; *m*-hydroxybenzoic acid, 99-06-9; 2-hydroxybenzyl alcohol, 90-01-7; *p*-hydroxyphenylpyruvic acid, 156-39-8; DL-2-aminobutyric acid, 2835-81-6; 2-amino-1-butanol, 96-20-8; 2-amino-1-propanol, 78-91-1; 4-amino-2,6-dihydroxypyrimidine, 873-83-6; benzylmethylamine, 103-67-3; *tert*-butyldimethylsilyl chloride, 18162-48-6; *N*-methyltrifluoroacetamide, 815-06-5; *N*-methylacetamide, 79-16-3; *N*-methylformamide, 123-39-7; acetamide, 60-35-5.

Reactions of Enamines with Trifluoroacetic Anhydride: Trifluoroacetylation and the Formation of 1,3-Oxazines

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In relation to our work on the synthesis of analogues of the antitumor antibiotic mitomycin C, we are currently interested in the reactions of pyrrolizines, prepared by reaction of 1-(1-pyrrolidinyl)cycloalkenes and dimethyl acetylenedicarboxylate (DMAD), with trifluoroacetic anhydride (TFA). Kametani et al. used this reagent for the conversion of pyrroloindoles into azocines.[1] Recently, we have reported that one of the pyrroloindoles that we have synthesized, viz., methyl 7a,8,9,10-tetrahydro-7-(methoxycarbonyl)-7*H*-benzo[*g*]pyrrolo[1,2-*a*]indole-7-acetate, reacted in a different way with TFA, namely, via trifluoroacetylation of the aromatic ring.[2] This result led us to investigate reactions of other pyrrolizines with TFA.

We found that methyl 1,2,3,5,6,7,7a,8-octahydro-8-(methoxycarbonyl)cyclopenta[*b*]pyrrolizine-8-acetate (**1**, E = $COOCH_3$)[3] reacted smoothly with TFA at room temperature to give one product in 65% yield. According to the mass spectrum and elemental analysis, the elemental composition of the reaction product was $C_{17}H_{20}F_3NO_5$, indicating that trifluoroacetylation had taken place.

In the ^{1}H NMR spectrum, the characteristic NCH absorption at δ 4.74 (dd, *J* = 5 and 12 Hz) was still present. X-ray diffraction showed that the compound had the methyl 1,2,5,6,7,7a,8,8a-octahydro-8-(methoxycarbonyl)-3-(trifluoroacetyl)cyclopenta[*b*]pyrrolizine-8-acetate (**3**) structure (Figure 1). We assume that this reaction of **1** proceeds via its tautomeric form **2** (Scheme I) in which trifluoroacetylation takes place at the β-enamine carbon atom.

The surprising result of the reaction of **1**, which possesses an enamine moiety, with TFA led us to study the reaction of other enamines with this reagent. To our knowledge such reactions have not been reported in the literature, although reactions with acetic anhydride[4,5] and

(1) Kametani, T.; Takahashi, K.; Ihara, M.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1847.
(2) Verboom, W.; Visser, G. W.; Reinhoudt, D. N. *Tetrahedron*, **1982**, *38*, 1831.
(3) Verboom, W.; Visser, G. W.; Trompenaars, W. P.; Reinhoudt, D. N.; Harkema, S.; van Hummel, G. J. *Tetrahedron* **1981**, *37*, 3525.

0022-3263/82/1947-3339$01.25/0

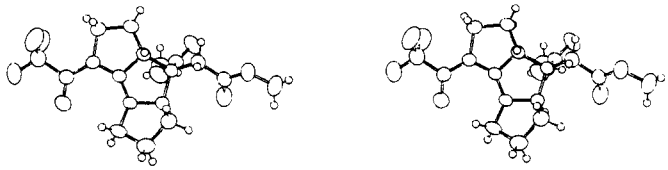
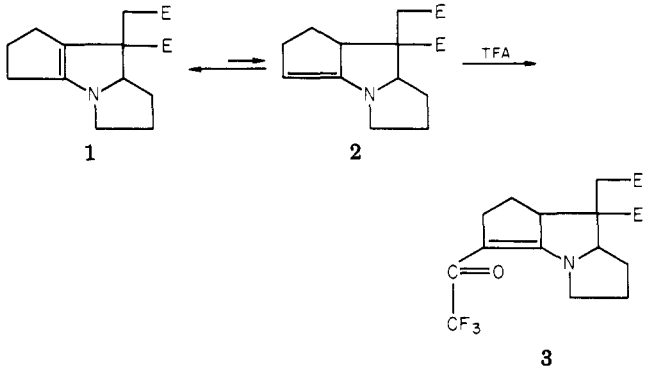
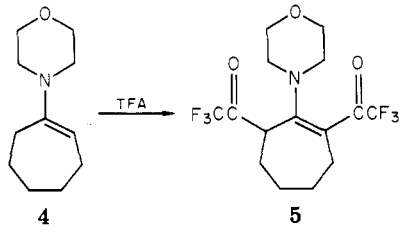


Figure 1. Stereoscopic view of compound **3**.

Scheme I



Scheme II



with trichloroacetic anhydride[6] are known.

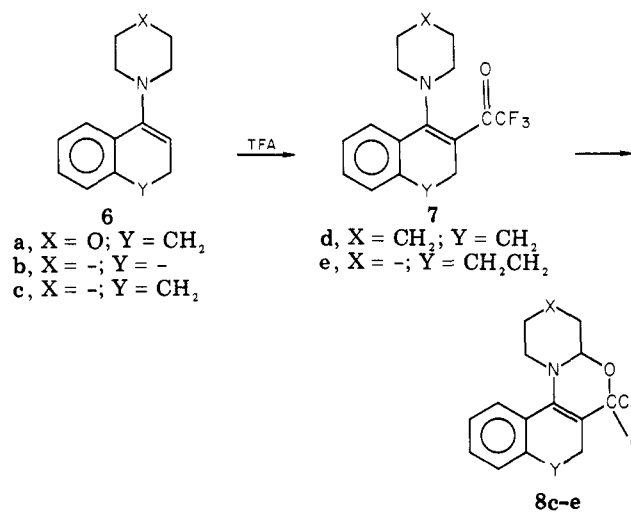
Reaction of 4-(1-cyclohepten-1-yl)morpholine (**4**) with 2.5 equiv of TFA in tetrahydrofuran (THF) at room temperature afforded the 4-[2,7-bis(trifluoroacetyl)-1-cyclohepten-1-yl]morpholine (**5**), which after distillation was isolated in 57% yield (Scheme II). The mass spectrum and elemental analysis showed that two CF_3CO groups had been introduced.

More reactive enamines, such as 4-(1-cyclopenten-1-yl)morpholine and 1-(1-cyclohexen-1-yl)pyrrolidine, reacted even at low temperature, to give very complicated reaction mixtures. It has been reported that these types of enamines react with an excess of acetic anhydride to produce only monoacetylation.[4]

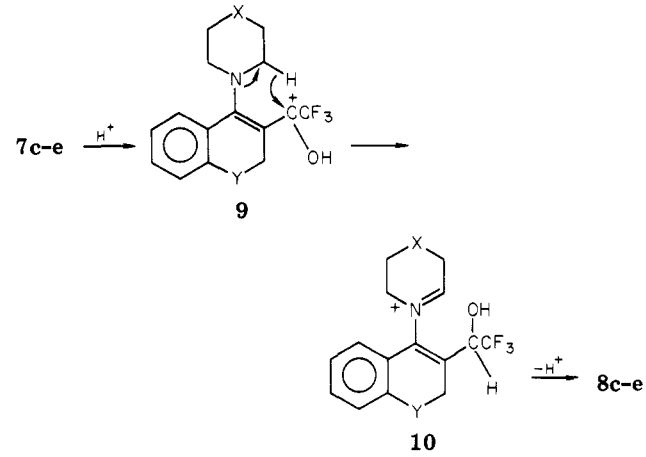
4-(3,4-Dihydro-1-naphthalenyl)morpholine (**6a**) and 1-(1*H*-inden-3-yl)pyrrolidine (**6b**) reacted with TFA in THF to give, after distillation, the trifluoroacetylated compounds **7a,b** in yields of 83 and 82%, respectively (Scheme III). Isolation of **7a,b** by column chromatography of the crude reaction mixture on silica gel or alumina was not possible because of decomposition.

Reaction of 1-(3,4-dihydro-1-naphthalenyl)pyrrolidine (**6c**) with TFA in THF, however, afforded, after distillation, a mixture of products, of which the minor compound was the trifluoroacetylated compound **7c**. After column chromatography (alumina), the major reaction product, a white crystalline compound, was isolated in a yield of 53%. Mass spectrometry and elemental analysis exhibited that a CF_3CO moiety had been introduced, but the absence of a carbonyl group (IR and ^{13}C NMR spectroscopy) ruled

Scheme III



Scheme IV



out a structure like **7c**. The ^1H NMR spectrum showed characteristic absorptions at δ 5.05 (br d, J = 4.2 Hz, 1 H) and 4.54 (q, J = 7.8 Hz, 1 H), and the ^{13}C NMR spectrum showed characteristic absorptions at δ 86.5 (d) and 72.8 (dq, J = 29.6 Hz). On the basis of these and other spectroscopic data, we concluded that the reaction product was 1,2,3,3a,6,7-hexahydro-5-(trifluoromethyl)-5*H*-naphtho[1,2-*d*]pyrrolo[2,1-*b*][1,3]oxazine (**8c**). TLC of the *crude reaction mixture* revealed that **6c** had reacted possibly to **7c**. However, **8c** was not present, so that further reaction must have occurred during the distillation.

1-(3,4-Dihydro-1-naphthalenyl)piperidine (**6d**) reacted similarly to give, after distillation, the 2,3,4,4a,7,8-hexahydro-6-(trifluoromethyl)-1*H*,6*H*-naphtho[1,2-*d*]pyrido[2,1-*b*][1,3]oxazine (**8d**) in 44% yield as a mixture of two isomers.

Reaction of 1-(6,7-dihydro-5*H*-benzocyclohepten-9-yl)pyrrolidine (**6e**) with TFA afforded, after distillation, **7e**, slightly contaminated with the 1,3-oxazine **8e** in a yield of 87%. Compound **7e** could not be isolated in a pure state on account of decomposition on silica gel and alumina. Heating of **7e** in toluene in the presence of trifluoroacetic acid for 3 days yielded, after column chromatography, the 1,2,3,3a,5,6,7,8-octahydro-5-(trifluoromethyl)benzo[6,7]cyclohepta[1,2-*d*]pyrrolo[2,1-*b*][1,3]oxazine (**8e**) in a yield of 30% as a mixture of isomers. This experiment demonstrated that the 1,3-oxazine formation takes place via the trifluoroacetylated compounds **7**. Starting from **7**, the formation of **8** can be rationalized as depicted in Scheme IV. Protonation of **7c–e** will give the stabilized carboca-

(4) Cook, A. G., Ed. "Enamines: Synthesis, Structure and Reactions"; Marcel Dekker: New York, 1969.
(5) Weber, J.; Faller, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *281*, 389.
(6) Morimoto, T.; Sekiya, M. *Chem. Pharm. Bull.* **1978**, *26*, 1586.

tion **9**, in which a hydride transfer takes place to **10**. Subsequently, intramolecular addition of the hydroxy group to the iminium double bond gives rise to compounds **8c–e**. An intermediate such as **10** has also been proposed in order to explain the formation of dihydrobenzimidazoles by reaction of anils of ortho-substituted amines in the presence of acid as described by Meth-Cohn et al.;[7] the conversion of **10** into **8c–e** represents the well-known reaction of alcohols with iminium salts.[8]

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra ($CDCl_3$) were recorded with a WP80-FT spectrometer (Me_4Si as internal standard). Mass spectra were obtained with a Varian Mat 311A spectrometer, and IR spectra were obtained with a Perkin-Elmer 257 spectrophotometer. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under supervision of W. J. Buis. THF was distilled prior to use from sodium benzophenone ketyl. All reactions were carried out under a nitrogen atmosphere.

Methyl 1,2,5,6,7,7a,8,8a-Octahydro-8-(methoxycarbonyl)-3-(trifluoroacetyl)cyclopenta[*b*]pyrrolizine-8-acetate (3). A suspension of **1**[3] (1.0 g, 3.6 mmol) in 10 mL of TFA was stirred at room temperature for 45 min. The TFA was removed under reduced pressure, and the residue was dissolved in 25 mL of $CHCl_3$. This solution was stirred for 30 min with K_2CO_3 (5 g). After filtration, the $CHCl_3$ was evaporated to give an oil, which after crystallization from Et_2O gave 65% of **3**: mp 128–129 °C; IR (KBr) 1730 (C=O, esters), 1665 (O=CCF$_3$) cm^{-1}; ^1H NMR δ 4.74 (dd, J = 5 and 12 Hz, NCH), 4.0–3.6 (m, 2H, NCH_2), 3.72 and 3.67 (s, OCH_3), 3.25 and 2.55 (AB q, J = 18 Hz, CH_2E), 3.3–3.1 (m, 1 H, CH), 3.0–2.7 (m, 2 H, H_2CC=), 2.2–1.1 (m, 6 H, CH_2); ^{13}C NMR δ 172.3 and 171.3 (s, C=O), 117.5 (q, J = 291 Hz, CF_3), 79.7 (d, NCH), 61.7 (d, CH), 52.4 and 51.9 (q, OCH_3), 48.8 (t, NCH_2), 47.4 [s, C(E)CH_2E], 38.4 (t, CH_2E), 33.2, 26.6, 26.2, and 25.5 (t, CH_2); mass spectrum, m/e 375.130 (M$^+$; calcd 375.129).

Anal. Calcd for $C_{17}H_{20}F_3NO_5$: C, 54.40; H, 5.37; N, 3.73. Found: C, 54.44; H, 5.36; N, 3.64.

4-[2,7-Bis(trifluoroacetyl)-1-cyclohepten-1-yl]morpholine (5). To a stirred solution of **4**[10] (3.6 g, 20 mmol) in 15 mL of THF was added TFA (10.5 g, 50 mmol), the temperature being kept between 15 and 25 °C. After 1.5 h of stirring, the solvent was removed under reduced pressure. Distillation of the resulting oil afforded 57% of **5** as an oil, bp 137–139 °C (2 mm), which after crystallization from Et_2O gave yellow crystals: mp 167–169 °C; ^1H NMR (Me_2SO-d_6) δ 3.9–3.5 (m, 4 H, OCH_2), 3.4–3.0 (m, 4 H, NCH_2), 2.9–1.2 (m, 8 H, CH_2); ^{13}C NMR (Me_2SO-d_6) δ 130.7 (q, J = 280 Hz, CF_3), 65.6 (t, OCH_2), 52.1 (t, NCH_2), 28.5, 28.2, and 27.4 (t, br, CH_2); mass spectrum, m/e 373.114 (M$^+$; calcd 373.111).

Anal. Calcd for $C_{15}H_{17}F_6NO_3$: C, 48.26; H, 4.59; N, 3.75. Found: C, 48.10; H, 4.61; N, 3.75.

2,2,2-Trifluoro-3′,4′-dihydro-1′-morpholino-2′-acetonaphthone (7a) and 3-(1-Pyrrolidinyl)inden-2-yl Trifluoromethyl Ketone (7b). TFA (4.2 g, 20 mmol) was added to a solution of **6a**[11] and **6b**[12] (10 mmol) in 15 mL of THF at 15–25 °C, and the solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure. Distillation [bp 139–143 °C (0.5 mm)] afforded **7a** as a solid in 83% yield, and **7b**, after trituration with isopropyl ether, as a solid in 82% yield, respectively.

7a: mp 134–137 °C dec (MeOH); ^1H NMR δ 7.8–7.6 (m, 1 H, Ar H), 7.45–7.1 (m, 3 H, Ar H), 4.0–3.7 (m, 4 H, OCH_2), 3.15–2.8 (m, 4 H, NCH_2), 2.8–2.3 (m, 4 H, CH_2); ^{13}C NMR δ 159.9 (s, NC=), 142.5 (s), 130.7 (s), 130.5 (d), 128.3 (d), 127.2 (d), 126.3 (d) (Ar C), 117.0 (q, J = 290 Hz, CF_3) 109.9 (s, NC=C), 66.9 (t, OCH_2), 52.2 (t, NCH_2), 29.0 and 23.6 (t, CH_2); mass spectrum, m/e 311.116 (M$^+$; calcd 311.113).

Anal. Calcd for $C_{17}H_{18}F_3NO_2$: C, 61.73; H, 5.18; N, 4.50. Found: C, 61.67; H, 5.23; N, 4.36.

7b: mp 149–150 °C (Et_2O); ^1H NMR δ 8.0–7.8 (m, 1 H, Ar H), 7.6–7.2 (m, 3 H, Ar H), 4.0–3.7 (m, 6 H, NCH_2 and CH_2C=), 2.3–1.9 (m, 4 H, CH_2); ^{13}C NMR δ 168.2 (q, J = 30 Hz, C=O), 162.7 (s, NC=), 145.8 (s), 137.6 (s), 129.9 (d), 126.5 (d), 125.3 (d), 124.8 (d) (Ar C), 118.4 (q, J = 291 Hz, CF_3), 102.8 (s, NC=C), 54.6 (t, NCH_2), 34.7 (t, CH_2C=), 25.8 (t, CH_2); mass spectrum, m/e 281.103 (M$^+$; calcd 281.103).

Anal. Calcd for $C_{15}H_{14}F_3NO$: C, 64.05; H, 5.02; N, 4.98. Found: C, 64.28; H, 4.94; N, 4.92.

1,2,3,3a,6,7-Hexahydro-5-(trifluoromethyl)-5*H*-naphtho[1,2-*d*]pyrrolo[2,1-*b*][1,3]oxazine (8c) and 2,3,4,4a,7,8-Hexahydro-6-(trifluoromethyl)-1*H*,6*H*-naphtho[1,2-*d*]pyrido[2,1-*b*][1,3]oxazine (8d). Starting from **6c**,**d**[11] (10 mmol), the reaction was carried out as described above. The solvent was removed under reduced pressure, and the resulting oil was distilled. The fraction with bp 139–143 °C (0.5 mm) was purified by column chromatography [alumina (V), petroleum ether (bp 60–80 °C) with 5% $CHCl_3$], yielding **8c** and **8d** in 53 and 44% yield, respectively.

8c: mp 85–86.5 °C (MeOH); IR (KBr) 1638 (C=C) cm^{-1}; ^1H NMR δ 7.5–7.0 (m, 4 H, Ar H), 5.05 (d, br, J = 4.2 Hz, NCHO), 4.54 (q, J = 7.8 Hz, F_3CCH), 3.7–3.35 [m, 1 H, NC(H)H], 3.0–1.7 (m, 9 H); ^{13}C NMR δ 139.6, 136.6, and 131.0 (s, NC= and Ar C), 127.6, 127.4, 126.3, and 123.7 (d, Ar C), 124.6 (q, J = 288 Hz, CF_3), 109.1 (s, NC=C), 86.5 and 86.4 (d, NCHO), 72.8 (dq, J = 29.6 Hz, F_3CCH), 50.7 (t, NCH_2), 31.9, 28.0, 24.1, and 23.2 (t, CH_2); mass spectrum, m/e 295.119 (M$^+$; calcd 295.118).

Anal. Calcd for $C_{16}H_{16}F_3NO$: C, 65.13; H, 5.45; N, 4.64. Found: C, 65.07; H, 5.46; N, 4.74.

8d: mp 87–90 °C dec (MeOH); IR (KBr) 1646 (C=C) cm^{-1}; ^1H NMR δ 7.6–7.0 (m, 4 H, Ar H), 4.9–4.5 (m, 2 H, NCHO and F_3CCH), 3.2–1.5 (m, 12 H, CH_2); ^{13}C NMR δ 144.25 (s, NC=), 136.7 (s), 136.3 (s), 130.3 (s), 129.6 (s), 127.4 (d), 127.2 (d), 126.1 (d), 122.6 (d) and 122.2 (d) (Ar C), 124.3 (q, J = 288 Hz, CF_3), 113.5 (s, NC=C), 82.9 and 81.7 (d, NCHO), 75.0 and 73.2 (dq, J = 29 Hz, F_3CCH), 46.1 (t, NCH_2); mass spectrum, m/e 309.134 (M$^+$; calcd 309.134).

Anal. Calcd for $C_{17}H_{18}F_3NO$: C, 66.01; H, 5.87; N, 4.53. Found: C, 66.02; H, 5.90; N, 4.41.

1,2,3,3a,5,6,7,8-Octahydro-5-(trifluoromethyl)benzo[6,7]cyclohepta[1,2-*d*][1,3]oxazine (8e). Reaction of **6e**[13] (2.1 g, 10 mmol) with TFA (4.2 g, 20 mmol) gave, after distillation [bp 145–150 °C (0.7 mm)], **7e** in 87% yield in an impure state. This fraction containing compound **7e** (1.0 g, 3.2 mmol) was heated in 15 mL of toluene in the presence of 2 mL of trifluoroacetic acid for 3 days. The reaction mixture was washed with sodium bicarbonate solution and then dried ($MgSO_4$). Column chromatography [alumina (V), petroleum ether (bp 60–80 °C) with 5% $CHCl_3$] gave **8e** (30% yield) as an oil in an impure state because of decomposition. Compound **8e** could not be crystallized from organic solvents.

7e: ^1H NMR δ 7.6–7.1 (m, 4 H, Ar H), 3.6–3.2 (m, 4 H, NCH_2), 2.7–2.4 (m, 2 H, $ArCH_2$), 2.3–1.7 (m, 8 H, CH_2); mass spectrum, m/e 309.135 (M$^+$; calcd for $C_{17}H_{18}F_3NO$ 309.134).

8e: ^1H NMR δ 7.55–7.0 (m, 4 H, Ar H) 5.1–4.4 (m, 2 H, NCHO and F_3CCH), 3.5–1.5 (m, 12 H, CH_2); ^{13}C NMR δ 124.5 (q, J = 283 Hz, CF_3), 87.6 (d, NCHO), 75.2 (dq, J = 30 Hz) and 71.8 (dq, J = 29 Hz, (F_3CCH), 50.2 and 49.3 (t, NCH_2); mass spectrum, m/e 309.133 (M$^+$; calcd for $C_{17}H_{18}F_3NO$ 309.134).

Crystallographic Data and X-ray Structure Analysis of 3. Crystals of **3** have triclinic symmetry, space group $P\bar{1}$; a = 13.889 (2), b = 10.462 (1), c = 6.801 (1) Å; α = 73.77 (1), β = 75.10 (1), and γ = 73.42 (1)°; Z = 2; d_c = 1.34 g cm^{-3}. X-ray diffraction intensities were measured with a Philips PW 1100 single-crystal diffractometer [Cu Kα radiation, λ = 1.5418 Å, graphite monochromator, θ–2θ scan mode, 3° < θ < 65°, scan speed (θ) 0.1°/s,

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scan width (deg) 3.3 + 1.0 tg θ]. The total number of reflections measured was 3315, of which 2648 had an intensity greater than the standard deviation estimated from counting statistics. The solution and refinement of the crystal structure are based on the latter reflections. The structure was solved by direct methods[14] and refined by full-matrix least squares[15] to a final R factor of 5.5%. All hydrogen atoms were found from Fourier difference syntheses. The number of parameters refined in the last cycles was 316 (scale factor, extinction parameter, positional parameters of all atoms, anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms). The figure was produced by ORTEP.[16]

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Registry No. 1, 67395-20-4; 3, 82281-38-7; 4, 7182-08-3; 5, 82281-39-8; 6a, 31401-28-2; 6b, 31554-37-7; 6c, 7007-34-3; 6d, 31401-27-1; 6e, 25579-44-6; 7a, 82281-40-1; 7b, 82281-41-2; 7e, 82281-42-3; 8c, 82281-43-4; 8d (isomer 1), 82281-44-5; 8d (isomer 2), 82281-45-6; 8e (isomer 1), 82281-46-7; 8e (isomer 2), 82281-47-8.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances, and bond angles (6 pages). Ordering information is given on any current masthead page.

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Cope and 1,3-Allylic Rearrangements and Ring Closure of the 1,5-Hexadiene Radical Cation Prior to Decomposition in the Gas Phase

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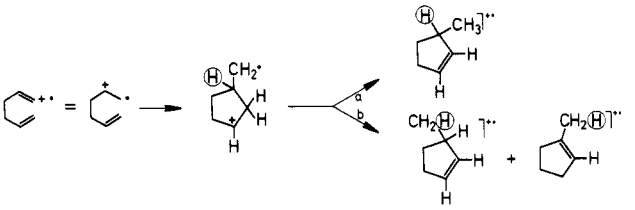
The chemistry of neutral 1,5-hexadiene (1) has been studied extensively. It undergoes the well-known (degenerate) Cope rearrangement under thermal conditions.[1] Facile transformations occur upon irradiation, and depending on the photochemical conditions allylcyclopropane[2] and bicyclo[2.1.1]- and [2.2.0]hexane[3] may be formed. Isotopic separation of deuterated 1 in favor of deuterium situated in the external vinyl sites has been demonstrated with infrared laser;[4] deuterium in the allylic positions, however, is favored under thermal conditions.[5]

In contrast, recent electron impact studies indicate a chemical inertness of the radical cation of 1 ($1^{+\cdot}$). It was shown by photodissociation spectroscopy that $1^{+\cdot}$ remains as an unconjugated diene at low internal energies.[6] Comparison of the heat of formation[7] of $C_5H_7^+$ ions formed by $CH_3\cdot$ loss from isomeric C_6H_{10} radical cations (ions of m/z 67 give rise to base peak in the normal mass spectra of C_6H_{10} isomers[8]) and the kinetic energy release (T)[9] associated therewith showed that $1^{+\cdot}$ among its linear isomers forms the cyclopentenyl cation with the lowest excess energy and smallest T value.[10] This result is in accord with the photodissociation results insofar as $1^{+\cdot}$ cannot isomerize to another linear diene prior to decomposition. The collisional activation mass spectra[11] of C_6H_{10} isomers confirmed that nondecomposing $1^{+\cdot}$ has no or only little resemblance with the radical cations of 1,3-, 1,4-, and 2,4-hexadiene, cyclohexene, and 1-methylcyclopentene.[12]

Scheme I



In light of the apparent retention of structure of $1^{+\cdot}$, this work is concerned with how the cyclopentenyl cation is formed therefrom.

It is necessary to consider which isomeric $C_6H_{10}^{+\cdot}$ ions have heats of formation lying below the energy required for fragmentation of $1^{+\cdot}$ by $CH_3\cdot$ loss and which can display similar kinetic energy release characteristics. From our previous studies,[10,13] these can be reduced to cyclohexene, 2-methyl-1,4-pentadiene, and methylcyclopentene (and methylenecyclopentane); see Table I.

Isomerization of $1^{+\cdot}$ to the cyclohexene radical cation is not likely to occur, because it would involve the formation of bicyclo[2.2.0]hexane$^{+\cdot}$ in the first step, a process having an energy barrier of 16 kcal mol^{-1} (see Table I). Loss of ethylene is an abundant process of the cyclohexene radical cation (RDA elimination),[8] while it is nearly absent in the normal mass spectrum and in the metastable time frame of $1^{+\cdot}$, thus further disfavoring an isomerization.[14]

Ionized 2-methyl-1,4-pentadiene also cannot be involved in the behavior of $1^{+\cdot}$, because the kinetic energy release for the random statistical losses of the deuterium-labeled methyl radicals from 2-methyl-1,4-pentadiene-1,1-$d_2$$^{+\cdot}$ was twice as large as that observed for the unlabeled compound,[13] while this is not the case with labeled 1,5-hexadienes (see also note 23).

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