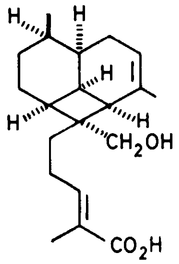
Intramolecular [2 + 2] Photoaddition of a 1,7-Diene

By **Kevin D. Croft, Emilio L. Ghisalberti, Phillip R. Jefferies, Alan D. Stuart, Colin L. Raston,** and **Allan H. White,*** School of Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia

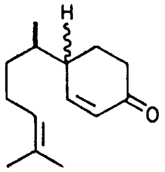
Intramolecular photoaddition of the 1,7-diene system in 4-(1,5-dimethylhex-4-enyl)cyclohex-2-enone (3) yielded, *inter alia*, two ketones containing the tricyclo[5.3.1.$0^{5,11}$]undecan-8-one system. The structure and stereochemistry of these ketones has been determined from *X*-ray crystallographic analyses of suitable derivatives.

THE decipiane diterpenes [*e.g.* (1)], a unique class of diterpenes isolated[1] from *Eremophila decipiens*, contain the tricyclo[5.3.1.$0^{5,11}$]undecane ring skeleton. Of the conceivable synthetic and biosynthetic schemes which can lead to the decipiane skeleton, one that attracted our attention involved a photochemical-like intramolecular cycloaddition of a 1,7-diene system in a monocyclic intermediate [*e.g.* (3)]. Although the formation of cyclobutanes by photochemical addition of an ene to an enone system is well known, at the beginning of this work the photochemistry of the 1,7-diene variant had been neglected.[2] Consequently we chose to study the photochemistry of the easily obtained[3] αβ-unsaturated ketone (2). The two major products obtained have been shown to contain the tricycloundecane ring system. Single crystal *X*-ray analyses of derivatives of these compounds shows them to have the *trans*-AB-ring junction rather than the *cis*-ring junction present in the decipiane diterpenes.

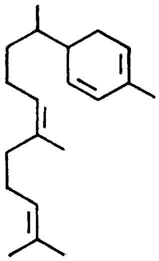
The required enone (2) was prepared, with some



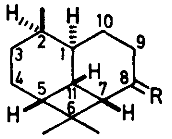
(1)



(2)



(3)

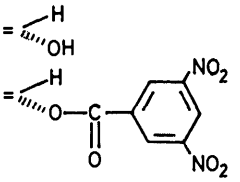


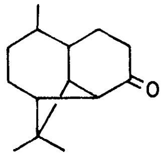
(4) R = O

(6) R = N—NH—C(=O)—NH$_2$

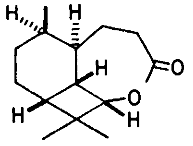
(11) R =

(13) R =

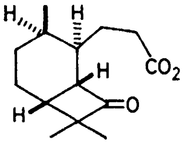




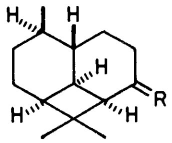
(5)



(7)



(8)

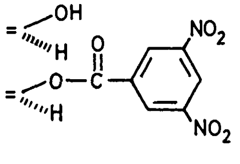


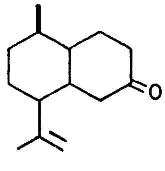
(9) R = O

(10) R = N—NH—C(=O)—NH$_2$

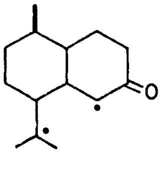
(12) R =

(14) R =

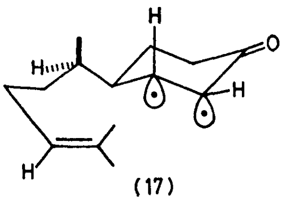




(15)



(16)



(17)

modification, by the method[3] of Joshi and Kulkarni, from (*R*)-(+)-citronellal, $[\alpha]_D^{28}$ +11.8° (74% optical purity) and was a mixture (1 : 1) of the 6*S*,1′*R*- and 6*R*,1′*R*-diastereoisomers, $\lambda_{max.}$ 228 (ε 9 000) and 295 nm (50). Initial irradiations of the enones (2) at 300 nm were monitored by t.l.c. We observed the formation of four major products which appeared simultaneously as the starting material was utilized, with optimum yields being obtained after 7 h. The four compounds were produced in approximately equal amounts. Further irradiation produced a complex mixture. The course of the photolysis was not significantly sensitive to changes of solvent or temperatures (see Experimental section). G.l.c.–m.s. analysis indicated that all four photoproducts were isomeric with the starting material and separation was achieved by a combination of argentation chromatography and preparative g.l.c.

The least polar photoproduct (4), $C_{14}H_{22}O$, showed i.r. absorption at 1 700 cm^{-1}. The n.m.r. spectrum showed signals at δ 1.11 and 1.21, for two tertiary methyl groups, and at δ 1.09 (*J* 7 Hz) for a secondary methyl, as well as a doublet at δ 2.60 (*J* 8 Hz). This suggested that (4) contained a tricyclic structure resulting from [2 + 2] intramolecular cycloaddition. Evidence for direct addition, to give (4), rather than ' crossed ' addition to give (5), comes from the presence of the doublet at δ 2.60, assigned, by analogy,[4] to a cyclobutyl proton α to a carbonyl group and from the m.s. which showed a base peak at *m*/*z* 83 for $O{=}C{-}CH{=}C{-}(CH_3)_2$ and the complementary ion at *m*/*z* 123. Additional evidence for structure (4) was sought by Baeyer–Villiger oxidation to give the ε-lactone (7), $\nu_{max.}$ 1 745 cm^{-1}. Hydrolysis of the lactone followed by oxidation gave a product (8) showing i.r. absorptions at 1 720 cm^{-1} for a carboxylic acid and 1 770 cm^{-1} consistent with the expected carbonyl absorption of a cyclobutanone.[5]

The second photoproduct (9) isolated showed spectroscopic properties essentially similar to those of (4), except that the secondary methyl group gave resonance signals centred at δ 0.79 (*J* 6 Hz), and was clearly a stereoisomer.

Since the spectroscopic data yielded little information regarding the relative configuration of the two photoproducts it was decided to solve this problem by *X*-ray crystallographic analysis of suitable derivatives.

For separation on a larger scale it was found that the two tricyclic ketones could be separated from the other photoproducts by argentation chromatography. Treatment of this mixture with semicarbazide hydrochloride yielded the semicarbazones (6) and (10) which could be separated by fractional recrystallization. The semicarbazone derivative (6) of the less polar compound (4) gave crystals suitable for *X*-ray analysis. Sodium borohydride reduction of the mixture of tricyclic ketones (4) and (9) followed by preparative g.l.c. yielded the two alcohols (11) and (12) which gave crystalline 3,5-dinitrobenzoate derivatives (13) and (14). The derivative of (9) was found to be suitable for *X*-ray analysis.

The most polar photoproduct (15) showed i.r. absorption at 1 710 cm^{-1} and n.m.r. signals at δ 0.93 (d, *J* 7 Hz, secondary methyl group) and 4.90br (s) for two vinylic protons which were shown to be coupled to a vinylic methyl group resonating at δ 1.80. The fourth photoproduct was not obtained pure but its spectroscopic properties indicated it to be a stereoisomer of (15). The most likely structures for these two compounds are those of the bicyclic enones (15) which presumably arise by hydrogen abstraction from an intermediate diradical species (16) in a photochemical ' ene ' reaction.[6]

The results of single crystal *X*-ray diffraction analyses on the semicarbazone (6) and the 3,5-dinitrobenzoate (14) are presented below and reveal that both tricyclic photoproducts contain a *trans*-AB ring junction.

G.l.c.–m.s. examination of the fraction containing the tricyclic photoproducts indicated the presence of two other compounds which are, most probably, the *cis*-AB ring junction stereoisomers but because of the small amounts present were not further investigated. It seems clear that in the intermediate diradical species (16) there is a preference for formation of the *trans*-decalone skeleton. This can be understood by assuming that the triplet state of the cyclohexenone (probably $\pi \longrightarrow \pi^*$)[7] has a distorted geometry in which the singly occupied *p*-orbitals at the α- and β-carbons are essentially axial and equatorial. Attack on the ene portion would occur preferentially from the conformation which is less sterically crowded leading to a *trans*-arrangement of the original C-3 and -4 hydrogens. Analogous results have been obtained recently for the addition of ethylene to 4-t-butylcyclohexene.[8]

From an examination of Dreiding models it is difficult to predict whether attack at C-4′ in (17) would preferentially occur on the *re* or *si* face. Nevertheless only attack on the *si* face can lead to a biradical which can ring close to a cyclobutane with an all-*cis*-hydrogen arrangement (4) and (9). Although hydrogen transfer from this biradical could generate the bicyclic enones (15), it is tempting to postulate that these arise from attack on the *re*-face of C-4′ giving a biradical which undergoes an ene reaction rather than ring closure to a *trans*-substituted cyclobutane.

EXPERIMENTAL

General experimental details have been described.[9] The photolysis experiments were carried out using an Oliphant Photochemical Reactor fitted with lamps emitting at 300 nm (1) or a 125 W high pressure mercury lamp (2).

Solutions for photolyses were deoxygenated by purging with nitrogen for 20 min and were then kept under nitrogen during irradiation. Analytical g.l.c. was carried out with a Perkin-Elmer 880 instrument using 3 m columns packed with (a) 5% FFAP or (b) 3% SE 30 on Chromasorb W (80—100 mesh). Nitrogen (20—25 ml min^{-1}) was used as the carrier gas for preparative g.l.c. An Aerograph Autoprep instrument fitted with a 3 m × $\frac{1}{4}$ in OD 5% Carbowax–2.5% FFAP (Chromasorb W; 80—100 mesh) column with helium as the carrier gas (100 ml min^{-1}) was used.

4-(1,5-*Dimethylhex*-4-*enyl*)*cyclohex*-2-*enone* (2).—The piperidine enamine of (*R*)-(+)-citronellal ($[\alpha]_D$ +11°, 74%

optical purity), prepared following the method of Joshi and Kulkarni,[3] was distilled, b.p. 120° (bath) at 2 mmHg (lit.,[3] 120° at 2 mmHg); δ($\mathrm{CCl_4}$; 60 MHz) 5.67 and 4.08 (ABq, *J* 13 Hz, proton centred at 4.08 showed further coupling, *J* 7 Hz, enamine vinyl protons), 5.07br (t, vinyl proton), 1.66 and 1.55 (s, olefinic methyls), and 0.97 (d, *J* 7 Hz, secondary methyl). Freshly distilled methyl vinyl ketone (10 g) was added dropwise to the enamine (20 g) under nitrogen. The mixture was stirred for 24 h, anhydrous dioxan (20 ml) was added, and the solution refluxed for 4 h. Glacial AcOH (1.5 ml), $\mathrm{H_2O}$ (3 ml), and anhydrous NaOAc (0.7 g) were added and the reflux continued for 4 h. The product (18 g), recovered in the normal way with ether, was distilled (120° and 0.5 mmHg) to give a mixture of (2) and the $\beta\gamma$-unsaturated ketone (8 g). Chromatography of the mixture on $\mathrm{Al_2O_3}$ (activity III, neutral) and elution with 15% $\mathrm{CHCl_3}$ in light petroleum gave (2), $\nu_{\max.}$ (film) 1 690, 1 455, 1 385, 1 145, and 845 $\mathrm{cm^{-1}}$ (lit.,[3] 1 690, 1 613, 1 466, 1 385, 1 143, and 847 $\mathrm{cm^{-1}}$); $\lambda_{\max.}$ 228 (ε 9 000) and 295 nm (ε 50) [lit.,[3] 227.5 nm (ε *ca.* 10 000)]; *m/z* 206 (M^+, 40%), 191 (5), 164, 163, 162 (5), 149 (5), 136, 135 (6), 123 (90), 122 (85), 109 (35), 107 (20), 96 (40), 95 (30), 94 (35), 79 (25), and 69 (100); δ($\mathrm{CCl_4}$; 60 MHz) 6.78br (d, *J* 10 Hz, 2-H), 5.90 (dd, *J* 10 and 2 Hz, 1-H), 5.08br (t, 4′-H), 1.2, 1.1 (s, 5′-Me, 6′-$\mathrm{H_3}$), and 0.94 (d, *J* 7 Hz, 1′-Me).

Photolysis of (2).—A solution of (2) (1.0 g) in acetone–Bu^{t}OH (1 : 1, 360 ml) was irradiated (Method 1) for 7.5 h. Evaporation of the solvent gave an oil which was shown to be a mixture of four major photoproducts by g.l.c. analysis [columns (a) and (b)]. Use of EtOH, ether, or hexane as solvents had no significant effect on product distribution, nor did changes in temperature (40, 0, or −78°) (Method 2).

Isolation of Photoproducts.—Separation of the major photoproducts was achieved using preparative g.l.c. The purity of each fraction was confirmed by analytical g.l.c. The following compounds were isolated in order of increasing retention time: (a) the *tricyclic ketone* (4), oil (Found: M^+, 206.167. $\mathrm{C_{14}H_{22}O}$ requires *M*, 206.167), $\nu_{\max.}$ ($\mathrm{CCl_4}$) 1 700 $\mathrm{cm^{-1}}$; δ($\mathrm{CCl_4}$; 90 MHz) 2.60 (d, *J* 8 Hz, 7-H), 1.21 and 1.11 (s, 6-$\mathrm{Me_2}$), 1.09 (d, *J* 7 Hz, 2-Me), *m/z* 206 (M^+, 30%), 123 (30), 122 (35), 121 (12), 109 (30), 108 (20), 98 (50), 93 (25), 91 (18), 83 (100); (b) the *ketone* (9), oil (Found: M^+, 206.166. $\mathrm{C_{14}H_{22}O}$ requires *M*, 206.167); $\nu_{\max.}$ ($\mathrm{CCl_4}$) 1 700 $\mathrm{cm^{-1}}$; δ($\mathrm{CCl_4}$; 90 MHz) 2.64br (d, *J* 7 Hz, 7-H), 1.21 and 1.11 (s, 6-$\mathrm{Me_2}$), 0.79 (d, *J* 6 Hz, 2-Me); m.s. as for (4); (c) enone (15a), oil, $\nu_{\max.}$ ($\mathrm{CCl_4}$) 1 710 $\mathrm{cm^{-1}}$; δ($\mathrm{CCl_4}$; 60 MHz) 4.90br (s, $W_{\frac{1}{2}}$ 8 Hz, vinylic protons), 1.80 (s, olefinic methyl), 1.04br (s, secondary methyl); m.s. as for (4); (d) the *enone* (15b), oil (Found: M^+, 206.168. $\mathrm{C_{14}H_{22}O}$ requires *M*, 206.167), $\nu_{\max.}$ ($\mathrm{CCl_4}$) 1 710 $\mathrm{cm^{-1}}$; δ($\mathrm{CCl_4}$; 60 MHz) 4.90br (s, vinylic protons), 1.80 (s, olefinic methyl), 0.93 (d, *J* 7 Hz, secondary methyl); *m/z* 206 (M^+, 35%), 123 (38), 121 (20), 109 (12), 107 (15), 95 (14), 93 (18), 91 (12), 82 (100), and 55 (38).

Formation of Keto-acid (8).—The ketone (4) (80 mg) in $\mathrm{CH_2Cl_2}$ (10 ml) was treated with *m*-chloroperbenzoic acid (200 mg) and left for 40 h at room temperature. Isolation of the product (60 mg) gave the crystalline *ε-lactone* (7), m.p. 75—78° (Found: M^+, 222.158. $\mathrm{C_{14}H_{22}O_2}$ requires *M*, 222.162). $\nu_{\max.}$ ($\mathrm{CCl_4}$) 1 745 $\mathrm{cm^{-1}}$; δ($\mathrm{CDCl_3}$; 90 MHz) 4.42 (d, *J* 7 Hz, methine H), 1.67 (s, tertiary $\mathrm{CH_3}$), 0.93br (s, secondary $\mathrm{CH_3}$), *m/z* 222 (M^+, 30%), 207 (15), 194 (30), 123 (70), and 109 (100). The lactone (7) showed a tendency to hydrolyse to the corresponding hydroxy-acid. Treatment of (7) with 5% KOH–EtOH solution for 30 min at room temperature and extraction with ether gave the hydroxy-acid which on treatment with Jones reagent yielded the *keto-acid* (8) as an oil (Found: M^+, 238.155. $\mathrm{C_{14}H_{22}O_3}$ requires *M*, 238.157), $\nu_{\max.}$ (film) 1 770 and 1 720 $\mathrm{cm^{-1}}$; δ($\mathrm{CDCl_3}$; 80 MHz) 2.9 (X part of an ABX, 4 lines, $W_{\frac{1}{2}}$ 20 Hz, O=C–C–*H*), 1.30 and 1.09 (s, tertiary $\mathrm{CH_3}$), and 0.97br (s, secondary $\mathrm{CH_3}$); *m/z* 238 (M^+, 3%), 210 (4), 179 (65), 151 (40), and 135 (100).

Semicarbazones of (4) *and* (9).—Chromatography on 10% $\mathrm{AgNO_3}$-impregnated $\mathrm{Al_2O_3}$ (activity III, neutral) of a photolysis mixture (2 g) on elution with 5% $\mathrm{CHCl_3}$–light petroleum gave a fraction (0.8 g) of (4) and (9). Treatment of a solution of this fraction in MeOH with aqueous semicarbazide hydrochloride and a few drops of pyridine gave a mixture of (6) and (10). Repeated recrystallization from MeOH gave prisms of the *semicarbazone* (6), m.p. 208—210° (Found: C, 68.2; H, 9.5; N, 16.2. $\mathrm{C_{15}H_{25}ON_3}$ requires C, 68.4; H, 9.6; N, 16.1%). Treatment of (6) (20 mg) with pyruvic acid (30 mg) in AcOH (5 ml) and $\mathrm{H_2O}$ (2 ml) under nitrogen for 18 h regenerated pure (4) as shown by g.l.c. Washing of the residue from the mother liquors with EtOAc gave a fraction containing mainly the semicarbazone of (10). Recrystallization of this fraction from EtOH–$\mathrm{H_2O}$ gave the *semicarbazone* (10) as needles, m.p. 192—195° (Found: C, 68.0; H, 9.4; N, 16.4. $\mathrm{C_{15}H_{25}ON_3}$ requires C, 68.4; H, 9.6; N, 16.1%).

3,5-*Dinitrobenzoate Derivatives of* (11) *and* (12).—A mixture of (4) and (9) in MeOH was treated with $\mathrm{NaBH_4}$ and the two alcohols (11) and (12) formed as single stereoisomers, were separated by preparative g.l.c. Oxidation of each alcohol with pyridinium dichlorochromate and comparative g.l.c. showed that the alcohols retained the relative polarity of the starting ketones. The n.m.r. ($\mathrm{CCl_4}$; 60 MHz) spectrum of (11) showed signals at δ 3.80 (m, X part of ABMX, 8-H), 1.35 and 1.15 (s, 6-$\mathrm{Me_2}$), and 0.95br (s, 2-Me). The corresponding 3,5-*dinitrobenzoate* (13), prepared in the usual way, recrystallized from EtOH as needles, m.p. 158—159.5°, $[\alpha]_D$ +29.4° (*c* 0.5, $\mathrm{CHCl_3}$) (Found: C, 62.80; H, 6.3. $\mathrm{C_{21}H_{26}N_2O_6}$ requires C, 62.7; H, 6.5%), δ(80 MHz; $\mathrm{CDCl_3}$) 5.29 (m, 8-H), 2.66 (t, *J ca.* 7.5—8.0 Hz, 7-H), 1.46 and 1.10 (s, 6-$\mathrm{Me_2}$), and 1.0 (apparent d, 2-Me). The n.m.r. spectrum of (12) showed signals at δ 3.70 (m, X part of ABMX, 8-H), 1.37 and 1.12 (s, 6-$\mathrm{Me_2}$), 0.70 (d, *J* 6 Hz, 2-Me). The corresponding 3,5-dinitrobenzoate (14) was recrystallized from EtOH as needles, m.p. 154—155°, $[\alpha]_D$ −66.8° (*c* 1.0, $\mathrm{CHCl_3}$) (Found: C, 62.6; H, 6.4. $\mathrm{C_{21}H_{26}N_2O_6}$ requires C, 62.7; H, 6.5%), δ(80 MHz; $\mathrm{CDCl_3}$) 5.20 (m, 8-H), 2.72 (t, *J* 7.5 Hz, 7-H), 1.50 and 1.09 (s) 6-$\mathrm{Me_2}$), and 0.76 (d, *J* 6 Hz, 2-Me).

Crystal Data.—*Compound* (6). $\mathrm{C_{15}H_{25}N_3O}$, $M = 263.4$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 7.445(2)$, $b = 12.737(3)$, $c = 15.757(4)$ Å, $U = 1\,494.1(6)$ Å^3, $D_m = 1.16(1)$, $D_c = 1.17$ g cm^{-3}, $Z = 4$, $F(000) = 576$. Monochromatic Mo-K_α radiation, $\mu_{\mathrm{Mo}} = 0.81$ cm^{-1}.

Compound (14). $\mathrm{C_{21}H_{26}N_2O_6}$, $M = 402.5$, orthorhombic, space group $P2_12_12_1$, $a = 36.17(1)$, $b = 9.112(3)$, $c = 6.168(2)$ Å, $U = 2033(2)$, $D_m = 1.32$ g cm^{-3}, $D_c = 1.32$, $Z = 4$, $F(000) = 856$, $\mu_{\mathrm{Mo}} = 1.04$ cm^{-1}.

Structure Determination.—Unique data sets were measured using a Syntex $P\bar{1}$ four circle diffractometer in conventional 2θ–θ scan mode within the limits $2\theta_{\max.} = 40$ (6) and 45° (14). 840, (6), and 1 590, (14), independent reflections were obtained, 669, (6), and 1 223, (14), with $I > 2\sigma(I)$ being considered ' observed ' and used in the refinements without

TABLE 1

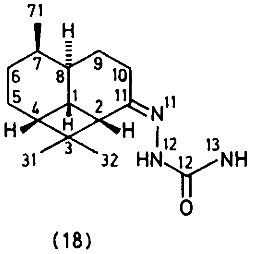
Atomic fractional cell co-ordinates of the hydrocarbon skeleton of (6) and (14). $(x, y, z) \times 10^3$, H; $\times 10^4$, others

	(6)			(14)		
Atom	x	y	z	x	y	z
C(1)	4 918(8)	1 092(4)	2 662(3)	0 952(1)	−4 966(5)	6 600(9)
H(1)	571(6)	167(4)	273(3)	105(1)	−567(5)	786(7)
C(2)	3 394(7)	1 315(4)	2 034(3)	1 186(1)	−3 565(6)	6 313(9)
H(2)	375(7)	189(4)	161(3)	133(1)	−333(5)	773(8)
C(3)	3 615(8)	0 162(5)	1 693(3)	0 814(1)	−2 617(5)	6 337(10)
C(31)	2 121(12)	−0 597(6)	1 957(6)	0 664(2)	−2 087(6)	4 203(12)
H(31a)	081(8)	−039(5)	160(4)	066(1)	−272(6)	278(9)
H(31b)	247(10)	−122(5)	186(4)	044(1)	−156(6)	445(9)
H(31c)	188(9)	−065(5)	259(3)	078(1)	−133(6)	352(9)
C(32)	3 863(11)	0 085(7)	0 721(4)	0 842(2)	−1 370(7)	7 966(14)
H(32a)	435(8)	−071(5)	056(3)	061(2)	−102(7)	799(11)
H(32b)	253(9)	020(5)	040(3)	099(2)	−139(7)	953(10)
H(32c)	477(9)	059(5)	054(4)	099(2)	−059(6)	753(10)
C(4)	5 445(8)	0 115(4)	2 185(4)	0 620(2)	−4 058(6)	7 314(10)
H(4)	636(7)	034(4)	181(3)	063(1)	−387(6)	894(9)
C(5)	6 030(9)	−0 786(5)	2 766(5)	0 255(2)	−4 681(6)	6 517(12)
H(5a)	682(7)	−125(5)	245(3)	006(1)	−421(6)	741(11)
H(5b)	489(8)	−108(5)	296(4)	020(2)	−433(6)	498(10)
C(6)	7 033(10)	−0 300(6)	3 521(5)	0 288(2)	−6 386(7)	6 513(2)
H(6a)	809(8)	013(5)	328(4)	033(1)	−668(7)	833(10)
H(6b)	759(8)	−081(4)	395(4)	004(1)	−679(6)	602(10)
C(7)	5 819(9)	0 414(5)	4 089(4)	0 590(10)	−6 965(5)	4 950(10)
H(7)	513(7)	−001(4)	458(3)	074(1)	−775(5)	567(9)
C(71)	6 855(11)	1 232(7)	4 547(5)	0 432(2)	−7 631(9)	2 887(16)
H(71a)	745(8)	173(5)	393(4)	031(2)	−814(8)	321(15)
H(71b)	617(9)	175(5)	494(4)	026(2)	−687(6)	151(10)
H(17c)	787(9)	086(5)	497(4)	063(2)	−812(7)	201(11)
C(8)	4 236(8)	0 817(4)	3 555(3)	0 858(14)	−5 719(6)	4 450(9)
H(8)	335(6)	020(4)	347(3)	071(1)	−512(5)	367(9)
C(9)	3 127(8)	1 724(5)	3 878(4)	1 212(1)	−6 043(6)	3 167(10)
H(9a)	380(7)	250(4)	380(4)	142(1)	−652(5)	412(8)
H(9b)	276(7)	160(4)	449(3)	117(1)	−663(5)	170(9)
C(10)	1 398(8)	1 745(6)	3 363(3)	1 378(2)	−4 543(6)	2 514(9)
H(10a)	066(7)	242(4)	345(3)	165(1)	−470(5)	179(8)
H(10b)	062(7)	113(4)	353(3)	119(1)	−401(5)	157(8)
C(11)	1 658(7)	1 697(4)	2 409(3)	1 473(1)	−3 636(5)	4 526(9)
H(11)				169(1)	−404(5)	533(7)

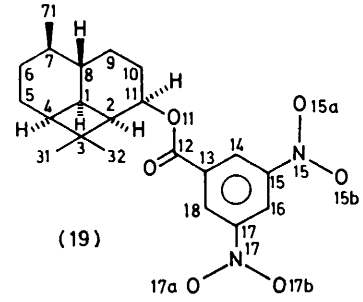
absorption correction after solution by direct methods. Refinement was by 9 × 9 block diagonal least squares; however, hydrogen (x, y, z) were refined jointly in the block of the parent atom. C, N, and O thermal parameters were refined anisotropic; for H, U_H was set at $[\bar{U}_{ii}$ (parent atom) $+ 0.01]$ Å^2. Residuals at convergence were (R,R'): 0.041, 0.042, (6); 0.046, 0.047 (14). Neutral atom scattering factors were used, those for C, N, and O being corrected for anomalous dispersion (f',f'').[10-12] Computation used the X-RAY 76 program system [13] implemented by S. R. Hall on a CYBER 73 computer. Atom numbering for the skeletons is given in (18) and (19); hydrogen atom labelling follows that of the parent atom with suffixes a—c for distinguishing purposes as needed. [Numbering follows that used previously for the related (20) and (21).[1b,14]] Material deposited comprises thermal parameters, hydrogen geometries, and structure factors.*

Structural Commentary.—In both (6) and (14), the unit cell contents comprise discrete molecules, the stereochemistry of which is established as shown; the asymmetric unit of each structure is a single molecule. In (6), a hydrogen bond is found [H(13a) · · · O(12)] $(x - 1/2, 1/2 - y, \bar{z})$, 1.92(6); the associated N–H · · · O angle is 163(5)°. The screw axis parallel to *a* generates an infinite hydrogen-bonded system of the type C–NH–H · · · O=C–NH–H · · · O= along ***a***. In (**14**) no close hydrogen bonds are observed, but close intermolecular contacts of a charge transfer nature are found; these are given in detail in SUP 23131.

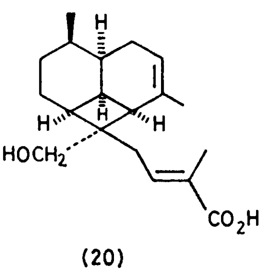
In view of the known chirality of C(7) in each case, it is tempting, *e.g.* as when drawing the above structures, to focus upon this atom as the starting point for describing



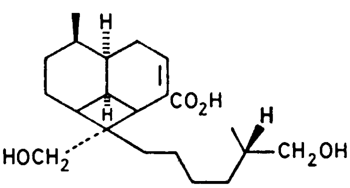
(18)



(19)



(20)



(21)

---

* Supplementary Publication No. SUP 23131 (12 pp.). For details, see Notices to Authors, No. 7 in *J. Chem. Soc., Perkin Trans. 2,* 1980, Index issue.

TABLE 2

Atom co-ordinates for hydrocarbon appendages of (6) and (14). (*x*, *y*, *z*) as for Table 1

Atom	*x*	*y*	*z*
(6)			
N(11)	0 291(6)	2 009(3)	1 974(3)
N(12)	0 451(6)	1 997(4)	1 087(3)
H(12)	145(7)	196(5)	083(3)
C(12)	−1 015(7)	2 294(4)	0 630(3)
O(12)	−0 910(5)	2 355(3)	−0 153(2)
N(13)	−2 525(7)	2 480(5)	1 053(3)
H(13a)	−366(8)	269(4)	074(3)
H(13b)	−253(8)	254(5)	162(3)
(14)			
O(11)	1 567.2(8)	−2 167(3)	3 700(6)
C(12)	1 819(1)	−1 407(5)	4 806(8)
O(12)	1 951.1(9)	−1 763(4)	6 509(6)
C(13)	1 925(1)	−0 014(5)	3 671(9)
C(14)	1 771(1)	0 405(5)	1 702(9)
H(14)	161(1)	−008(5)	108(8)
C(15)	1 882(1)	1 726(5)	0 795(8)
N(15)	1 715(1)	2 190(4)	−1 263(7)
O(15a)	1 822(1)	3 301(4)	−2 115(6)
O(15b)	1 462(1)	1 435(4)	−2 022(7)
C(16)	2 137(1)	2 633(5)	1 725(9)
H(16)	219(1)	361(5)	110(8)
C(17)	2 284(1)	2 177(5)	3 704(9)
N(17)	2 553(11)	3 136(4)	4 773(8)
O(17a)	2 614(1)	4 321(4)	3 974(7)
O(17b)	2 693(1)	2 716(4)	6 447(7)
C(18)	2 187(1)	0 876(5)	4 684(9)
H(18)	229(1)	058(5)	627(8)

TABLE 3

Non-hydrogen molecular geometries of (6) and (14): hydrocarbon skeletons. Entries represent values for (6) then (14)

Atoms	Parameter
Bond lengths (Å)	
C(1)–C(2)	1.532(8), 1.541(7)
C(2)–C(3)	1.573(8), 1.599(7)
C(1)–C(4)	1.506(8), 1.525(7)
C(1)–C(8)	1.537(8), 1.532(8)
C(2)–C(11)	1.501(7), 1.515(7)
C(3)–C(4)	1.569(9), 1.606(8)
C(3)–C(31)	1.546(9), 1.503(9)
C(3)–C(32)	1.531(10), 1.520(9)
C(4)–C(5)	1.531(9), 1.518(8)
C(5)–C(6)	1.535(10), 1.558(9)
C(6)–C(7)	1.563(10), 1.548(9)
C(7)–C(71)	1.483(11), 1.521(11)
C(7)–C(8)	1.536(9), 1.525(7)
C(8)–C(9)	1.509(9), 1.533(8)
C(9)–C(10)	1.521(9), 1.546(8)
C(10)–C(11)	1.517(7), 1.530(8)
C(11)–N,O	1.289(7), 1.473(6)
Bond angles (°)	
C(2)–C(1)–C(4)	91.4(4), 90.9(4)
C(2)–C(1)–C(8)	112.9(5), 113.2(4)
C(4)–C(1)–C(8)	110.7(5), 108.6(4)
C(1)–C(2)–C(3)	88.3(4), 89.2(3)
C(1)–C(2)–C(11)	116.4(4), 115.0(4)
C(3)–C(2)–C(11)	121.8(4), 127.3(5)
C(2)–C(3)–C(4)	87.6(4), 85.9(4)
C(2)–C(3)–C(31)	114.9(5), 117.9(5)
C(2)–C(3)–C(32)	114.3(5), 110.6(4)
C(4)–C(3)–C(31)	118.2(5), 115.8(4)
C(4)–C(3)–C(32)	112.6(5), 113.1(5)
C(31)–C(3)–C(32)	108.4(6), 111.3(5)
C(1)–C(4)–C(3)	89.3(4), 89.5(4)
C(1)–C(4)–C(5)	113.3(5), 112.9(5)
C(3)–C(4)–C(5)	124.9(5), 124.3(5)
C(4)–C(5)–C(6)	107.5(5), 107.9(5)
C(5)–C(6)–C(7)	113.4(6), 113.3(5)
C(6)–C(7)–C(8)	108.9(5), 108.7(4)
C(6)–C(7)–C(71)	112.7(6), 113.1(5)
C(8)–C(7)–C(71)	115.6(6), 111.5(5)
C(1)–C(8)–C(7)	108.9(5), 107.4(4)
C(1)–C(8)–C(9)	108.4(5), 110.4(4)
C(7)–C(8)–C(9)	119.4(5), 119.5(4)
C(8)–C(9)–C(10)	107.3(5), 106.8(4)
C(9)–C(10)–C(11)	114.8(5), 110.7(5)
C(2)–C(11)–C(10)	120.8(5), 117.4(4)
C(2)–C(11)–N,O	124.8(4), 111.8(4)
C(10)–C(11)–N,O	114.4(5), 105.2(4)

TABLE 4

Non-hydrogen molecular geometries of (6) and (14): hydrocarbon appendages

(6)

Atoms	Parameters	Atoms	Parameters
Bond lengths (Å)			
N(11)–N(12)	1.403(6)	C(12)–O(12)	1.238(6)
N(12)–C(12)	1.361(7)	C(12)–N(13)	1.328(7)
Bond angles (°)			
C(11)–N(11)–N(12)	117.3(4)	N(12)–C(12)–N(13)	117.6(5)
N(11)–N(12)–C(12)	117.2(4)	O(12)–C(12)–N(13)	122.8(5)
N(12)–C(12)–O(12)	119.6(5)		

(14)

Atoms	Parameters	Atoms	Parameters
Bond lengths (Å)			
O(11)–C(12)	1.331(6)	N(15)–O(15b)	1.235(5)
C(12)–O(12)	1.199(6)	C(15)–C(16)	1.364(7)
C(12)–C(13)	1.501(7)	C(16)–C(17)	1.395(7)
C(13)–C(14)	1.389(8)	C(17)–N(17)	1.465(6)
C(13)–C(18)	1.394(7)	N(17)–O(17a)	1.208(6)
C(14)–C(15)	1.387(7)	N(17)–O(17b)	1.211(6)
C(15)–N(15)	1.468(6)	C(17)–C(18)	1.376(7)
N(15)–O(15a)	1.204(5)		
Bond angles (°)			
C(11)–O(11)–C(12)	117.0(4)	C(15)–N(15)–O(15a)	119.2(4)
O(11)–C(12)–O(12)	125.6(4)	C(15)–N(15)–O(15b)	118.2(4)
C(13)–C(12)–O(12)	112.1(4)	O(15a)–N(15)–O(15b)	122.6(4)
O(11)–C(12)–C(13)	122.3(4)	C(15)–C(16)–C(17)	116.4(4)
C(12)–C(13)–C(14)	122.5(4)	C(16)–C(17)–C(18)	123.0(5)
C(12)–C(13)–C(18)	117.2(5)	C(16)–C(17)–N(17)	118.0(4)
C(14)–C(13)–C(18)	120.2(5)	C(18)–C(17)–N(17)	119.1(5)
C(13)–C(14)–C(15)	118.4(4)	C(17)–N(17)–O(17a)	118.1(4)
C(14)–C(15)–C(16)	123.5(5)	C(17)–N(17)–O(17b)	118.2(4)
C(14)–C(15)–N(15)	118.6(4)	O(17a)–N(17)–O(17b)	123.7(4)
C(16)–C(15)–N(15)	117.9(4)	C(13)–C(18)–C(17)	118.5(5)

the structures; inspection of Table 5 and Figure 5 shows this viewpoint to be misleading: the ring skeletons in the two systems are similar, albeit of opposite chirality, and it is more appropriate to describe the molecules in terms of the ring system.

In both compounds, the two six-membered rings are fused by a *trans*-junction; the fusion of this bicyclic system to the four-membered ring in both compounds is *cis*, and such that all other carbon atoms in the ring system lie to one side of the four-membered ring ' plane '. In both cases, the four-membered ring is appreciably distorted from planarity by fusion to the remainder of the system, atom deviations being of the order of ±0.1 Å. The angle at C(3), opposite the triple ring junction is less than a right angle in each case and the angle sums for the two rings are 356.5 and 355.5°, respectively. C(1,3) lie out of the ring ' plane ' towards the

TABLE 5

Hydrocarbon skeletal torsion angles of (6) and (14). Carbon atoms are referred to by number only; the two values are for (6), (14), respectively in each entry; the chirality of (14) has been inverted to enable direct comparison with (6)

Atoms	Angle (°)
4–1–2–3	14.5, 16.4
8–1–2–3	−99.4, −94.3
4–1–2–11	139.4, 147.8
8–1–2–11	25.5, 37.2
1–2–3–4	−13.9, −15.6
11–2–3–4	−133.8, −137.0
1–2–3–31	106.4, 101.6
11–2–3–31	−31.5, −19.8
1–2–3–32	−127.4, −128.8
11–2–3–32	112.7, 109.8
2–3–4–1	14.1, 15.7
31–3–4–1	−103.2, −103.4
32–3–4–1	129.4, 126.4
2–3–4–5	131.9, 133.4
31–3–4–5	14.5, 14.3
32–3–4–5	−112.9, −115.9
2–1–4–3	−14.5, −16.3
8–1–4–3	100.9, 98.6
2–1–4–5	−142.0, −143.7
8–1–4–5	−26.6, −28.9
1–4–5–6	−36.3, −34.6
3–4–5–6	−142.1, −140.7
4–5–6–7	64.2, 62.5
5–6–7–71	−154.3, 104.8
5–6–7–8	−23.4, −19.7
6–7–8–1	−40.4, −45.7
71–7–8–1	88.7, −171.0
6–7–8–9	−165.4, −172.3
71–7–8–9	−36.4, 62.4
2–1–8–7	170.3, 173.1
4–1–8–7	69.0, 73.8
2–1–8–9	−58.6, −55.0
4–1–8–9	−159.9, −154.3
1–8–9–10	70.3, 66.6
7–8–9–10	−164.5, −168.2
8–9–10–11	−49.7, −60.8
9–10–11–2	18.4, 45.7
9–10–11–N,O	−161.3, 170.8
1–2–11–10	−5.9, −33.4
3–2–11–10	99.3, 76.2
1–2–11–N,O	173.9, −155.1
3–2–11–N,O	−80.9, −45.5

remainder of the fused skeleton, C(1,4) lie away. The mean bond length in each of the two rings is 1.54_5 and 1.54_6 Å respectively (*cf.* the distance in cyclobutane, 1.56_8 Å); the deviations from the mean within each ring are large, but one bond, notably C(2)–C(3), is considerably elongated relative to the remainder, being 1.573(8) and 1.599(7) Å, indicative, perhaps, of the presence of some tension in this bond, while C(1)–C(2,4) are somewhat compressed. Because of the non-coplanarity of the ring atoms, the substituent positions are not equally disposed on either side: those at C(1,3) lying toward the fused system have an 'axial' character while those on the opposite side are 'equatorial'. The converse is true at C(2,4) (Figure 5).

The angles about the *gem*-dimethyl substituents differ significantly in the two compounds (Table 3), probably as a result of contacts, in (6), from H(31c) to H(8), 2.07(8) Å [next nearest is to H(7b), 2.39(9) Å]; in (14) from H(31a) to H(8), 2.26(7) Å [next nearest is to H(5b), 2.59(8) Å]. The corresponding C • • • C distances are 3.474(9) and 3.387(8) Å, respectively, indicative of a significant change of disposition of the environment of the methyl groups which probably accounts for the angular change referred to, and which may ultimately originate in the change of ring geometry resulting from semicarbazone attachment. There are no other close intramolecular contacts (<2.4 Å) from these methyl hydrogen atoms to other hydrogen atoms in the two molecules. There is however, again a further steric interaction with the substituent at C(11) which may also be relevant (see below).

TABLE 6

Comparison of the geometry of the four-membered ring in (6) and (14) with that of the decipiane system. Entries are for (6), (14), (20), and (21), respectively

Atoms	Parameters
Distance (Å)	
C(1)–C(2)	1.532(8), 1.541(7), 1.553(10), 1.551(10)
C(1)–C(8)	1.537(8), 1.532(8), 1.546(9), 1.518(11)
C(1)–C(4)	1.506(8), 1.525(7), 1.569(9), 1.566(10)
C(2)–C(3)	1.573(8), 1.599(7), 1.600(8), 1.580(9)
C(2)–C(11)	1.501(7), 1.515(7), 1.483(11), 1.474(10)
C(3)–C(4)	1.569(9), 1.606(8), 1.553(9), 1.594(10)
C(4)–C(5)	1.531(9), 1.518(8), 1.499(9), 1.517(12)
Angles (°)	
C(8)–C(1)–C(2)	112.9(5), 113.2(4), 119.4(6), 119.4(6)
C(8)–C(1)–C(4)	110.7(5), 108.6(4), 114.2(6), 115.4(6)
C(2)–C(1)–C(4)	91.4(4), 90.9(4), 90.2(5), 91.0(5)
C(1)–C(2)–C(3)	88.3(4), 89.2(3), 88.4(5), 90.1(5)
C(1)–C(2)–C(11)	116.4(4), 115.0(4), 116.0(5), 115.5(6)
C(3)–C(2)–C(11)	121.8(4), 127.3(5), 118.6(6), 118.2(6)
C(2)–C(3)–C(4)	87.6(4), 85.9(4), 89.1(4), 89.0(5)
C(2)–C(3)–C(31)	114.9(5), 112.9(4), 117.3(5), 116.6(5)
C(2)–C(3)–C(32)	114.3(5), 110.6(4), 108.9(5), 108.3(6)
C(31)–C(3)–C(32)	108.4(6), 111.3(5), 113.3(5), 113.1(6)
C(4)–C(3)–C(31)	118.2(5), 115.8(4), 118.0(5), 117.1(6)
C(4)–C(3)–C(32)	112.6(5), 113.1(5), 107.7(5), 110.4(6)
C(3)–C(4)–C(1)	89.3(4), 89.5(4), 89.5(5), 89.1(5)
C(3)–C(4)–C(5)	124.9(5), 124.3(5), 120.2(6), 118.4(6)
C(1)–C(4)–C(5)	113.3(5), 112.9(5), 112.7(5), 112.6(6)

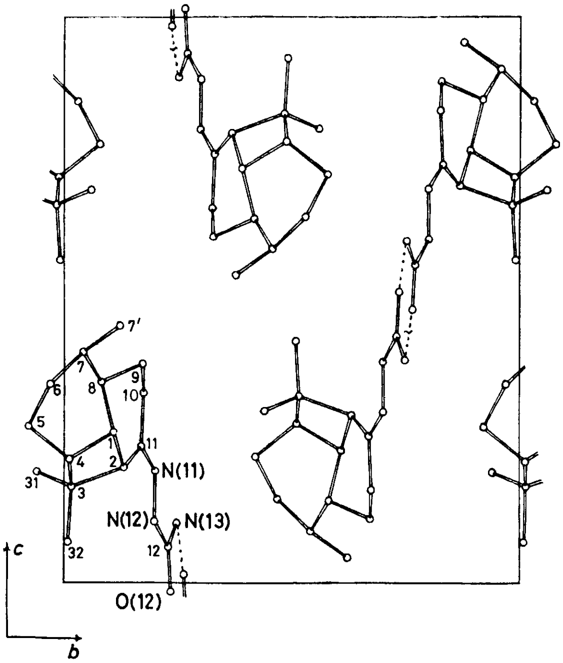


FIGURE 1 Unit cell contents of (6) projected down *a* showing the intermolecular hydrogen bonding and skeletal atom numbering

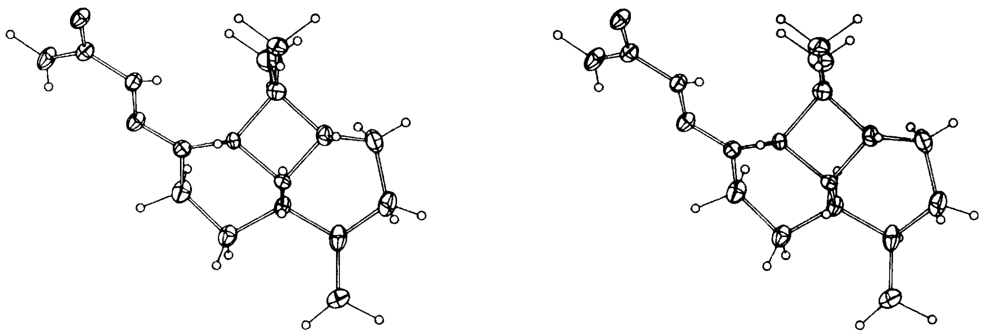


FIGURE 2 Stereoscopic pair of (6); the projection is normal to the 'plane' of the four-membered ring. 20% thermal ellipsoids are shown for the non-hydrogen atoms; the hydrogen atoms are shown with an arbitrary radius of 0.1 Å

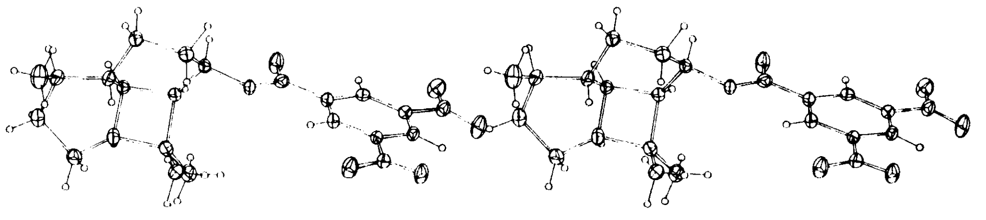


FIGURE 3 Stereoscopic pair of (14), projected as for (6) in Figure 2

In considering the two six-membered rings, we note that in (6), the methyl substituent lies such that the C(7)–C(71) bond is almost normal to the plane of the four-membered ring; in (14) it is almost parallel. Also, in (6), the substituent at C(11) is attached by a double bond. The effect of the latter on the nearby angular ring geometry is small, C(2)–C(11)–C(10) differing from the value in (14) by only 2.6°; in (14) C(2)–C(11) is lengthened rather remarkably. Similar angular differences are found at the adjoining C(10) and C(2); the latter difference may affect the angular geometry of the *gem*-dimethyl system (see above). However, the exocyclic double bond attachment has little effect on the overall molecular stereochemistry as measured by the data of Figure 6 and Table 5.

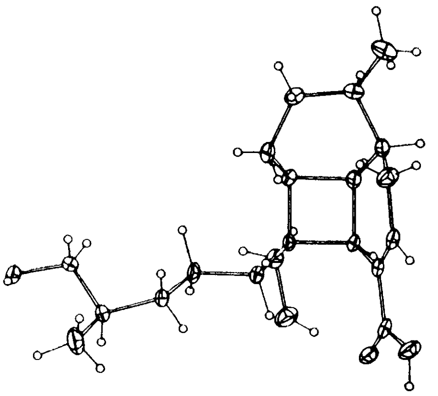


FIGURE 4 A molecular projection of (20), as for (6) in Figure 2, for comparative purposes

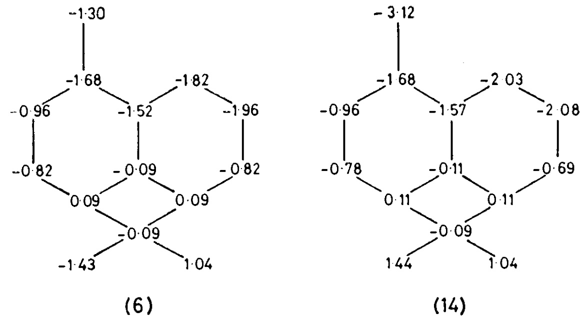


FIGURE 5 Atom deviations (Å) in the ring skeletons of (6) and (14) relative to the least squares plane calculated through C(1—4); signs have been reduced to a common chirality

Further there are no unusually short contacts from the 7-methyl substituent to other atoms in the system; in (6), H(71a) • • • H(1) is 2.29(7) Å, while in (14) H(71c) • • • H(9b) is 2.40(8). It therefore seems that the dominant factor in determining ring stereochemistry is ring strain itself and/or transannular hydrogen • • • hydrogen interactions which are common to both compounds. The latter (<2.4 Å) are to be found in both molecules involving H(8) again, to H(5b), 2.15(8) (6) and 2.11(7) Å (14). Although, despite considerable changes in substituents and their dispositions, the ring disposition is almost identical in both compounds, the two fused six-membered rings are by no means equivalent. C(1,4,5,6,7,8) is most nearly a ' boat ' structure with C(5,8) as the two prows, while C(1,2,8,9,10,11)

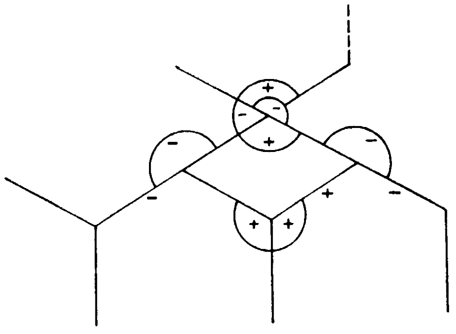


FIGURE 6 Comparison of changes in geometry about the four-membered ring for the present system and the decipiane skeleton. Where a significant consistent change occurs on passing from (6),(14) to (20),(21) this is marked

is a pseudo-chair; these are seen to best advantage in Figure 3.

A feature of both structures is the unsymmetrical nature of the attachment of the substituent at C(11); in both cases the immediate substituent atom is bent away from the *gem*-dimethyl neighbours. In (6), H(12) ··· H(2), 2.10(7) Å, is the only significant intramolecular H ··· H contact which could have any bearing on the matter; the N–N distances [1.403(6) Å] suggests that N(11) ··· N(12) is a normal single bond and it is unlikely that this interaction would have the rigidity to cause a distortion at C(11) of the magnitude observed. The geometry of the terminal $CONH_2$ group of the semicarbazone is indicative of some contribution from the alternative amide resonance form.

In (14), the disposition of the carboxy-group is such (Figure 3) suggests that interaction with the *gem*-dimethyl group is unlikely to cause a serious perturbation to the molecular geometry.

In (14), the aromatic species is substantially planar and coplanar with its substituents, with the geometry of the appendage normal, the aromatic ring showing the expected angular distortions, as does the carboxy-group.

Table 6 compares the geometry about the four-membered ring with that of the decipiane skeleton of (20) and (21); [1a,14] changes in geometry which exhibit a consistent pattern among the four structures are shown in Figure 6.

We gratefully acknowledge a grant from the Australian Research Grants Committee in support of this work.

[1/564 *Received, 9th April,* 1981]

REFERENCES

[1] (*a*) E. L. Ghisalberti, P. R. Jefferies, and P. Sheppard, *Tetrahedron Lett.*, 1975, 1775; (*b*) K. D. Croft, E. L. Ghisalberti, P. R. Jefferies, D. G. Marshall, C. L. Raston, and A. H. White, *Aust. J. Chem.*, 1980, **33**, 1529.

[2] See however M. J. Begley, M. Mellor, and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1979, 235.

[3] G. D. Joshi and S. N. Kulkarni, *Indian J. Chem.*, 1968, **6**, 127.

[4] V. Georgian and M. Saltzman, *Tetrahedron Lett.*, 1972, 4315; P. Singh, *Indian J. Chem.*, 1970, 4089.

[5] 'Atlas of Spectral Data and Physical Constants for Organic Compounds,' ed. J. G. Grasselli, CRC Press, Cleveland, 1973, p. A–42.

[6] E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, 1964, **86**, 5570.

[7] P. De Mayo, *Acc. Chem. Res.*, 1971, **4**, 41.

[8] R. L. Cargill, G. H. Morton, and J. Bordner, *J. Org. Chem.*, 1980, **45**, 3929.

[9] E. L. Ghisalberti, P. R. Jefferies, and A. D. Stuart, *Aust. J. Chem.*, 1979, **32**, 1627.

[10] D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **A24**, 321.

[11] D. T. Cromer and D. L. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1975, **42**, 3175.

[13] 'The X-RAY System—Version of March 1976,' Technical Report, TR-446, Computer Science Centre, University of Maryland, U.S.A.

[14] E. N. Maslen, P. N. Sheppard, A. H. White, and A. C. Willis, *J. Chem. Soc., Perkin Trans. 2*, 1976, 263.