Tetrahedron. Vol. 25, pp. 3161 to 3177. Pergamon Press 1969. Printed in Great Britain

TERPENES—VI[1]

ELECTROPHILIC ADDITIONS TO BICYCLO[3.1.0]HEX-3-EN-2-ONES[2, 3]

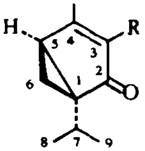
R. T. GRAY* and H. E. SMITH†

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203

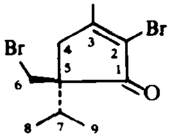
(*Received in the USA* 6 *November* 1968; *Received in the UK for publication* 26 *February* 1969)

Abstract—The initial reaction of (−)-umbellulone (**1**) with N-bromosuccinimide in water and in methanol, N-chlorosuccinimide in water, and hydrogen chloride, hydrogen bromide and bromine in carbon tetrachloride is an electrophilic addition to the C═C double bond followed by attack of a nucleophile at C-4 leading in general to a mixture of two compounds, epimeric at C-4. These compounds are thermally unstable and could not be separated. Structural and configurational assignments were made on the basis of the IR and NMR spectra and the decomposition products of the mixtures. Chlorine also reacts with (—)-umbellulone (**1**) in carbon tetrachloride, but the configuration of the single product, a 3,4-dichlorodihydroumbellulone, could not be deduced from its spectral properties. The compounds with an OH or a MeO group or a Cl atom at C-4 easily lose the elements of water, methanol or hydrogen chloride to form the respective bicyclo[3.1.0]hex-3-en-2-one, (—)-umbellulone (**1**), (—)-α-bromoumbellulone (**2**) or (—)-α-chloroumbellulone (**12**). When a Br atom is situated at C-4, deep-seated rearrangements occur at room temperature which on heating finally lead to 2-cyclopenten-1-ones, separated by distillation of the respective reaction mixtures. Mechanisms for these rearrangements were suggested by examination of the NMR spectra of the respective hydrobromination and bromination reaction mixtures as the reactions proceeded.

IN PREVIOUS papers[1, 4] we have reported the ORD curves and preferred conformations of a number of bicyclo[3.1.0]hexan-2-ones, bicyclo[3.1.0]hex-3-en-2-ones and 2-cyclopenten-1-ones. Among these compounds were (−)-umbellulone[5, 6, ‡] (**1**), (−)-α-bromoumbellulone[7, 8] (**2**) and (−)-umbellulone dibromide[6, 7] (**3**). The latter two ketones were prepared from **1**.



1, R = H
2, R = Br



3

(−)-α-Bromoumbellulone (**2**) is formed by the addition of bromine to (−)-umbellulone (**1**) in carbon tetrachloride followed by treatment of the cold reaction product with piperidine.[8] If instead of the piperidine treatment, the solvent is removed at room temperature, and the almost colorless residue is slowly heated there is a

---

[*] Monsanto Fund Fellow, 1966–1968.

[†] To whom inquiries should be sent.

[‡] Signs in parentheses always refer to rotatory powers observed with sodium D-light and methanol as the solvent.

copious evolution of hydrogen bromide followed by the distillation of two distinct compounds, an unsaturated bromo ketone, $C_{10}H_{13}BrO$, isomeric with but different from 2,[6,8] and (−)-umbellulone dibromide (3).[6,7]

Although the identity of the unsaturated bromo ketone and the mechanism by which (−)-umbellulone (1) is converted to (−)-umbellulone dibromide (3) has remained unknown, some possibilities for the latter have been discussed.[9,10] It seems likely that the initial reaction is an electrophilic addition of bromine to the C=C double bond of 1. The addition would be mechanistically similar to the acid-catalyzed hydrolysis of (−)-(3*S*)-epoxyumbellulone[4,8] (4), which leads to (−)-(3*S*,4*S*)-3,4-dihydroxydihydroumbellulone[4] (5) and (−)-(3*S*,4*R*)-3,4-dihydroxydihydroumbellulone[4,8] (6), isolated in 9% and 38%, respectively. This suggested that there are, in the hydrolysis of 4, additional products analogous to the unsaturated bromo ketone and (−)-umbellulone dibromide (3).

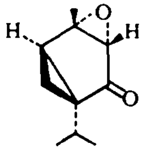
We now wish to report a re-examination of the acid-catalyzed hydrolysis of (−)-(3*S*)-epoxyumbellulone (4), a detailed investigation of the reaction of a number of electrophiles, including bromine, with (−)-umbellulone (1), and the identification of the unsaturated bromo ketone discussed above.

RESULTS

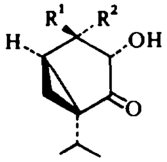
Hydrolysis and methanolysis of (−)-(3S)-*epoxyumbellulone* (4)

As outlined earlier,[4] 4 was subjected to hydrolysis in water using a catalytic amount of sulfuric acid. The crude reaction mixture was isolated and examined by NMR. Only signals assigned to the keto diols 5 and 6 in the ratio 1:19, respectively, were detected. These spectra are summarized in Table 1.[*] These two keto diols then comprise at least 95% of the total hydrolysis product.

In a similar experiment, the NMR spectrum of the crude reaction product from the acid-catalyzed methanolysis of 4 revealed the presence of only one compound,



4



5: $R^1 = CH_3$; $R^2 = OH$
6: $R^1 = OH$; $R^2 = CH_3$
7: $R^1 = OCH_3$; $R^2 = CH_3$

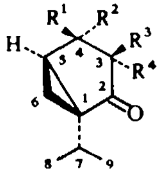
(−)-(3*S*,4*R*)-3-hydroxy-4-methoxydihydroumbellulone (7), (Table 1). No other product could be detected by TLC or column chromatography using silica gel.

The structure and configuration of 7 are assigned on the basis of its spectral properties and of the reaction leading to its formation. The electron-withdrawing effect of the

---

[*] Although there can be no doubt concerning the chemical shift assignments for the respective protons in 5 and 6, the chemical shifts and coupling patterns for the C-5 and C-6 protons could not be assigned due to the complexity of their signal patterns. Hence, the conclusion that in 5 and 6 the proton at C-3 is coupled to that at C-5 rather than to a C-6 proton is not completely certain. The same lack of certainty pertains to the assigned coupling of the C-3 protons in all of the other spectra summarized in Table 1.

TABLE 1. SUMMARY OF NMR[a] DATA FOR SOME BICYCLO[3.1.0]HEXAN-2-ONES



(R^1 or R^2 is C-10.)

Substituents	5	6	7	8	9	10	11	13	14	15	22[b]	23[b]	24[b]	25[b]	30[b]	31[b]	35[b]
R^1	CH_3	OH	OCH_3	CH_3	OH	CH_3	OH	{CH_3,	CH_3	OCH_3	{CH_3,	{CH_3,	CH_3	Br	CH_3	Br	{CH_3,
R^2	OH	CH_3	CH_3	OH	CH_3	OH	CH_3	{OCH_3[c]	OCH_3	CH_3	{Cl[c]	{Cl[c]	Br	CH_3	Br	CH_3	{Cl[c]
R^3	H	H	H	H	H	H	H	{Br,	H	H	H	H	H	H	H	H	{Cl,
R^4	OH	OH	OH	Br	Br	Cl	Cl	{H[c]	Br	Br	H	H	H	H	Br	Br	{H[c]
Protons	Assigned chemical shifts,[d] ppm downfield from TMS = 0																
3	3·72(d)	4·12(d)	4·07(d)	4·36(d)	4·57(d)	4·16(d)	4·40(d)	4·30(d)	4·57(d)	3·95(d)	e	e	e	e	4·57(d)	4·77(d)	4·05(d)
8, 9[f]	0·88(d) 0·95(d)	0·93(d)	0·97(d)	0·94(d) 0·97(d)	0·94(d) 0·97(d)	0·94(d) 0·97(d)	0·94(d) 0·97(d)	0·88(d) 1·03(d)	0·96(d) 0·99(d)	0·97(d)	0·93(d) 0·97(d)	0·97(d) 1·02(d)	0·93(d) 0·97(d)	0·97(d) 1·02(d)	g	g	0·98(d) 1·05(d)
10	1.41(s)	1·25(s)	1·23(s)	1·48(s)	1·45(s)	1·46(s)	1·40(s)	1·40(s)	1·43(s)	1·58(s)	1·77(s)	1·77(s)	1·92(s)	1·95(s)	2·17(s)	1·87(s)	1·87(s)
3-O$\underline{H}$	3·42(s)	3·87(s)	2·88(s)														
4-O$\underline{H}$	3·42(s)	3·87(s)		2·95(s)	2·95(s)	3·28(s)	3·28(s)										
4-OC$\underline{H}_3$			3·37(s)					3·27(s)	3·42(s)	3·32(s)							
	Assigned coupling constants, ± 0·5 Hz																
3–5[h]	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	<1·0					<1·0	1·5	<1·0
7–8, 7–9	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0	7·0			7·0

[a] Measured at 60 MHz in $CDCl_3$ unless noted otherwise. Abbreviations used: s, singlet; d, doublet.

[b] Measured in CCl_4.

[c] Configuration unassigned.

[d] Signal integrations were in agreement with all proton assignments.

[e] No signal from 3·20 to 8·30 ppm.

[f] No differentiation between these protons is made or implied.

[g] Chemical shift could not be estimated. Signals too complex.

[h] See text for these assignments.

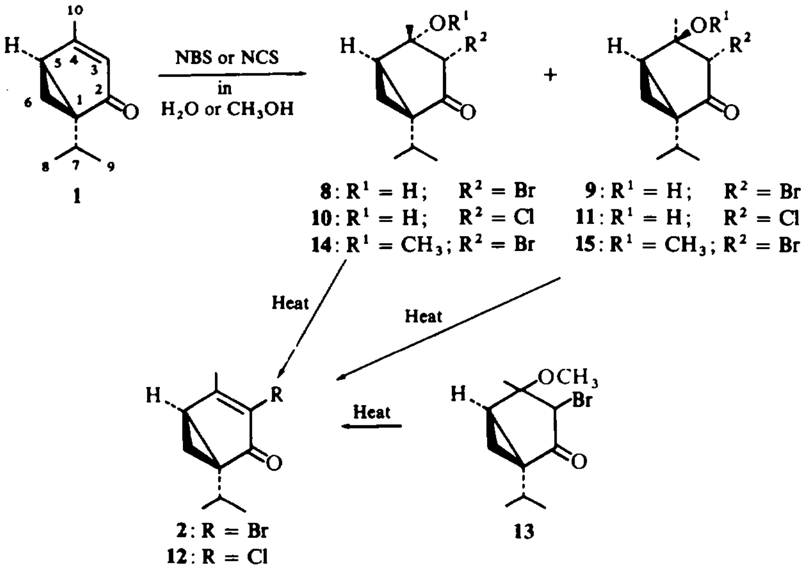
carbonyl group is expected to favor the back-side attack of methanol on the protonated oxirane ring at C-4.[11] The ORD curve of **7** is very similar to that of **6**,[4] both compounds showing a positive Cotton effect associated with the n-π^* transition near 284 mμ. For this same transition, the Cotton effect shown by **5** is negative.[4]

Reactions of N-*halosuccinimides with* (−)-*umbellulone* (**1**)

Both N-bromosuccinimide (NBS) and N-chlorosuccinimide (NCS), electrophilic reagents in polar solvents,[12–16] react smoothly with **1** suspended in water at room temperature. In each case, the crude reaction mixture was isolated and examined by IR and NMR. The latter revealed the presence in each of two halohydrins in the ratio of 1 : 3. In the NBS reaction, these were identified as (3*S*,4*S*)-3-bromo-4-hydroxydihydroumbellulone (**8**) and (3*S*,4*R*)-3-bromo-4-hydroxydihydroumbellulone (**9**), respectively (Chart 1 and Table 1); with NCS, (3*S*,4*S*)-3-chloro-4-hydroxydihydroumbellulone (**10**) and (3*S*,4*R*)-3-chloro-4-hydroxydihydroumbellulone (**11**), respectively (Chart 1 and Table 1).

Attempts to isolate each of these compounds were not successful. Heating the crude reaction mixture of **8** and **9** and of **10** and **11** resulted in the elimination of water from each of the four compounds and the respective formation of (−)-α-bromoumbellulone[4, 7, 8] (**2**) and (−)-α-chloroumbellulone[1] (**12**).

CHART 1



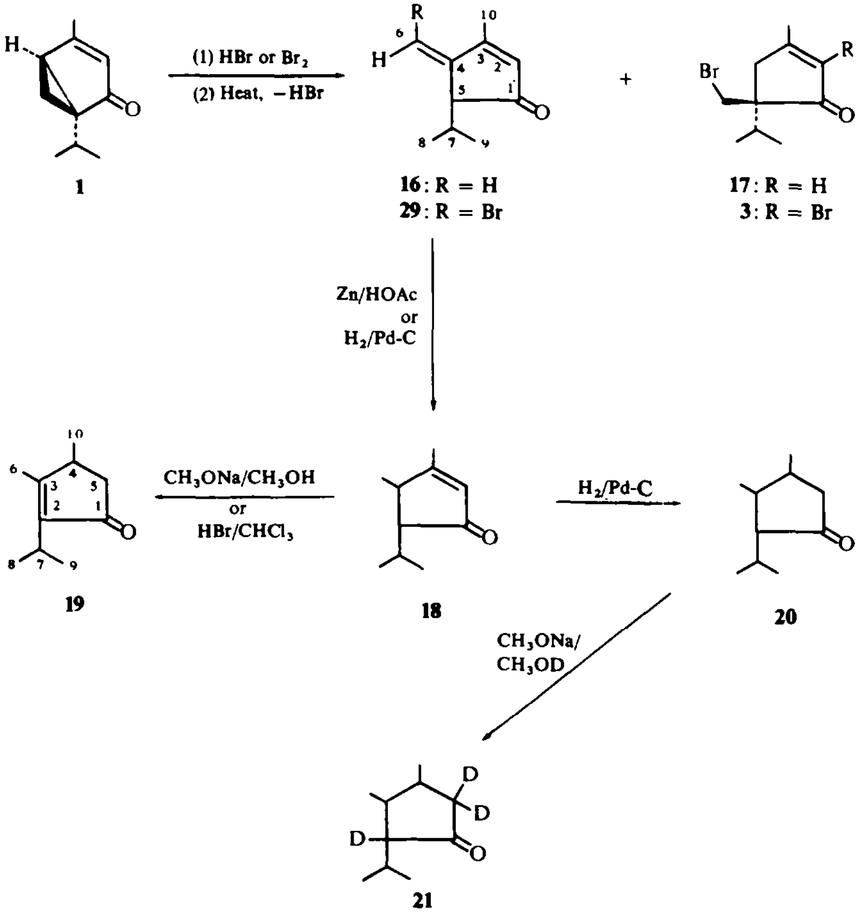
In **8**–**11**, the (3*S*) configuration is assigned assuming the addition of the entering nucleophile to a bridged chloronium or bromonium ion[17] at C-4. The (4*R*) configuration is assigned to **9** and **11**, the major product in the respective reactions, assuming a preferential *trans* addition of the entering nucleophile to the bridged ions.[17] In each of the latter, the halogen atom is *trans* to the cyclopropyl ring. The NMR spectra of **8**–**11** are compatible with these assignments.

NBS also reacts with **1** in boiling methanol. After isolation, the NMR spectrum of the crude reaction mixture indicated the presence of three methoxy bromo ketones in the ratio 1:3:6, all identified as 3-bromo-4-methoxydihydroumbellulones (**13–15**, respectively). Among other signals in the NMR spectrum (Table 1) of the crude mixture, there are observed three distinct MeO group singlets and three doublets corresponding to the respective C-3 protons.

A separation of the major component, **15**, from the others was accomplished by column chromatography on silica gel. Final purification of this compound, however, could not be accomplished because of its thermal instability. Standing at room temperature or heating resulted in demethanolation and the formation of (−)-α-bromoumbellulone (**2**). The other two components, **13** and **14**, were not separated from each other by chromatography on silica gel. GLC of the latter mixture as well as of the mixture of three components resulted in the formation of **2**.

The (3*S*,4*S*) and (3*S*,4*R*) configurations are assigned to **14** and **15**, respectively, in analogy with the steric course of the reaction of NBS and NCS in water with **1**.

CHART 2



1

16: R = H
29: R = Br

17: R = H
3: R = Br

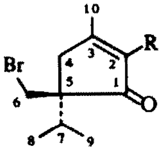
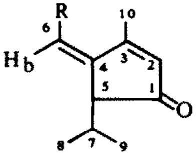
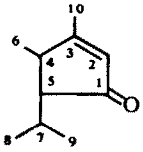
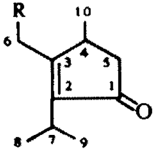
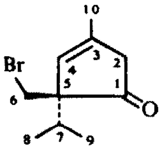
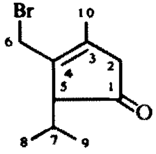
19

18

20

21

TABLE 2. SUMMARY OF NMR[a] DATA FOR SOME 2-CYCLOPENTEN-1-ONES

									
Substituent	**3**	**17**	**16**	**29**	**18**	**19**	**27**[b]	**26**[b]	**28**[b]
R	Br	H	H_a	Br	—	H	Br	—	—
Protons			Assigned chemical shifts,[c] ppm downfield from TMS = 0						
2	[d]	5·90(q)	5·27(q)[e]	5·34(d)	5·78(q)				1·93(s)
4	2·56(q)	2·47(q)						6·37(q)	
5			2·76(m)	2·95(m)					
6	3·53(s)	3·51(s)			1·20(d)	2·02(s)	4·23(d)[f] 4·34(d)[f]		2·77(d)[f] 3·14(d)[f]
6(H_a)			6·05(m)						
6(H_b)			5·43(q)[e]	5·56(d)					
8, 9[g]	0·83(d) 0·90(d)	0·84(d) 0·90(d)	0·94(d) 0·98(d)	0·92(d) 1·01(d)	0·80(d) 1·02(d)	1·18(d)	1·19(d)	0·90(d) 1·05(d)	1·17(d)
10	2·19(t)	2·13(m)	2·17(q)	2·25(d)	2·07(m)	1·16(d)	1·27(d)	2·27(m)	2·17(s)

	Assigned coupling constants, ±0·5 Hz[h]								
2–5			1·1	1·1					
2–6(H_a)			1·8[i]						
2–10		1·5			1·5				
4–6					7·0				
4–10	1·0	1·0				7·0	7·0	1·5	
5–6(H_b)			1·5	1·5					
5–10			0·6	0·8					
6(H_a)–6(H_b)			0·8[i]						
6α–6β							10·5		19·0
6(H_a)–10			1·3						
7–8, 7–9	7·0	7·0	7·0	7·0	6·5	7·0	7·0	7·0	7·0

---

[a] Measured at 60 MHz in $CDCl_3$ unless noted otherwise. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

[b] Measured in CCl_4.

[c] Signal integrations were in agreement with all proton assignments.

[d] No signals from 3·60 to 8·30 ppm.

[e] The signal assignments for the C-2 and C-6(H_b) protons are ambiguous and may be reversed.

[f] AB type doublet of doublets; calculated chemical shift.

[g] No differentiation between these protons is made or implied.

[h] For **16** and **29**, the assigned coupling constants are ±0·1 Hz.

[i] These assignments are ambiguous and may be 2–6(H_a), $J = 0{\cdot}8$ Hz; and 6(H_a)–6(H_b), $J = 1{\cdot}8$ Hz.

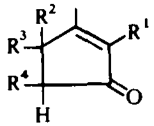
The very minor product **13**, for which the total configuration is unassigned, may arise by way of an enolization of **14** or **15**.

Reaction of hydrogen halides with (−)-*umbellulone* (**1**)

Hydrogen bromide reacts smoothly with **1** in ice-cold carbon tetrachloride. After removal of the solvent at room temperature, the NMR spectrum of the fuming, colorless oil indicated that a gross change in the carbon skeleton had occurred. On heating this oil at reduced pressure, a substantial quantity of hydrogen bromide is evolved, followed by the distillation of two distinct compounds. The lower boiling substance and larger fraction (71%) is identified as (±)-5-isopropyl-3-methyl-4-methylene-2-cyclopenten-1-one (**16**) and the higher boiling substance (18%), as (−)-(*R*)-5-(bromomethyl)-5-isopropyl-3-methyl-2-cyclopenten-1-one (**17**), the latter characterized earlier.[1]

The IR spectrum of **16** shows a CO band at 1690 cm^{-1} and two olefinic stretching bands at 1590 and 1635 cm^{-1}. Its NMR spectrum (Table 2) shows an i-Pr group as a doublet of doublets indicating the attachment of this group to a center of asymmetry.[18] There are also complicated signals for three vinylic protons and a broad signal for a methine proton. Although there is some ambiguity regarding the chemical shift assignments for the C-2 and C-6(H$_b$) vinylic protons, the complex splitting pattern was deduced through spin–spin decoupling experiments. The long-range coupling of the C-5 proton to those at C-10 through five σ bonds is unusual, but similar couplings have been reported.[19] The UV spectrum of **16** (Table 3) also confirms its assigned structure. By adding a 15 mμ increment for the Me group at C-3[1] and 35 mμ for the exocyclic double bond[20] to the base value of 214 mμ for 2-cyclopenten-1-one,[20] the calculated absorption max for the short wavelength transition of **16** is 264 ± 5 mμ, in good agreement with that found (Table 3). Finally, although **16** contains an asymmetric center, the isolated sample was optically inactive from 280 to 600 mμ, and hence the material is racemic.

Table 3. Summary of UV absorption data for some 2-cyclopenten-1-ones in methanol



Substituents	**16**	**18**	**19**	**29**
R^1	H	H	CH(CH$_3$)$_2$	H
R^2	CH$_2$	H	H	CHBr
R^3		CH$_3$	CH$_3$	
R^4	CH(CH$_3$)$_2$	CH(CH$_3$)$_2$	H	CH(CH$_3$)$_2$
		λ, mμ (ε)		
	325 (100)	308 (57)	306 (58)	330 (190)
	267 (14,000)	228 (14,000)	236 (14,000)	279 (11,000)

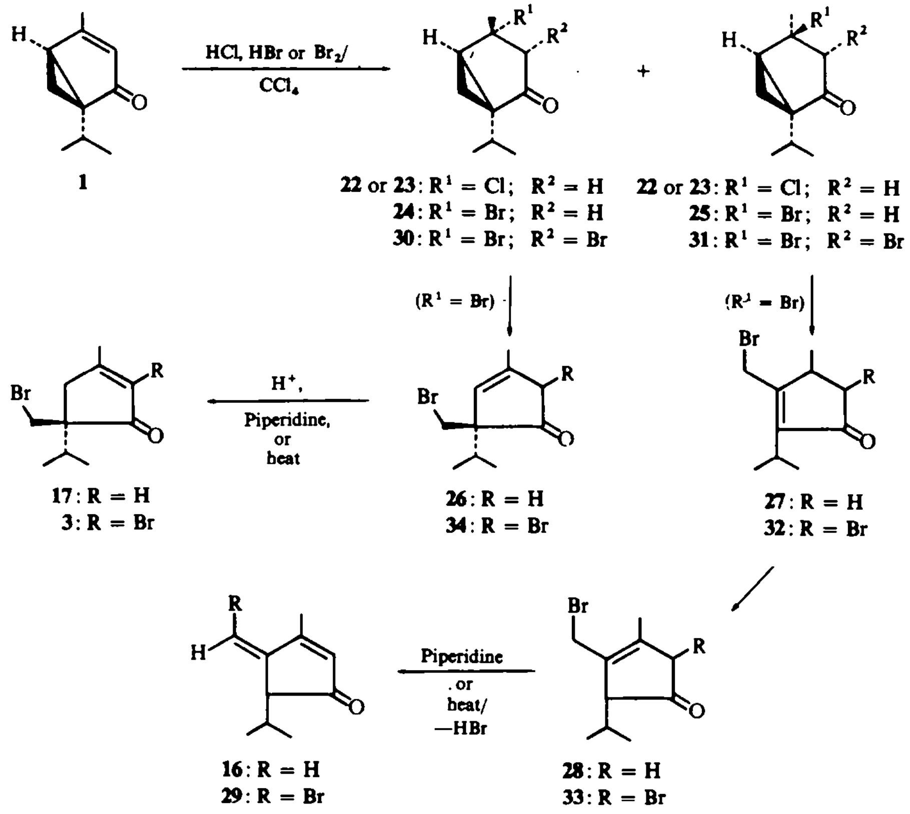
The reduction of **16** with zinc in acetic acid affords a mixture of two compounds, (±)-*cis* or *trans*-3,4-dimethyl-5-isopropyl-2-cyclopenten-1-one (**18**) and (±)-3,4-dimethyl-2-isopropyl-2-cyclopenten-1-one (**19**) in a ratio of 2:3, respectively. The two compounds were separated by chromatography on silica gel. Reduction of **16** with hydrogen using 10% Pd-C gives only **18**. The NMR (Table 2) and UV spectra (Table 3) for **18** and **19** are compatible with their assigned structures. For the latter spectra, the expected absorption maxima for the short wavelength transitions are 224 ± 5 and 236 ± 5 mμ, respectively.[20] The ketone **18** was further reduced with hydrogen using a 10% Pd-C catalyst. This reduction gives a single substance or a mixture of geometrical isomers with the 3,4-dimethyl-2-isopropylcyclopentanone structure (**20**). As expected for a cyclopentanone, this oil has an UV absorption spectrum with a max at 292 mμ (ε 25) and only end absorption at 210 mμ. Its NMR spectrum integrates for Me protons (0·8–1·3 ppm) and methylene-methine protons (1·4–2·8 ppm) in the ratio of 2:1, respectively. After treatment with sodium methooxide in MeOD, the oil has an NMR spectrum with unchanged Me signals but with reduced methylene-methine signals. These signals now integrate in the ratio of 4:1, respectively, showing the formation of 3,4-dimethyl-2-isopropylcyclopentanone-2,5,5-d_3 (**21**). Also, since the complex coupling pattern of the Me groups remains unchanged, the attachment of the Me groups must be at C-3, C-4 and C-7, thus eliminating structurally isomeric 2-cyclopenten-1-ones as possibilities for **18**. Finally, under both basic and acidic conditions **18** is isomerized to **19**. Compound **19** probably arises in the zinc–acetic acid reduction of **16** by way of isomerization of **18**.

A comparable reaction of hydrogen chloride with (−)-umbellulone (**1**) in ice-cold carbon tetrachloride was examined. If the ice-cold reaction mixture is examined with NMR before removal of the solvent, the spectrum clearly shows the formation of two 4-chlorodihydroumbellulones (**22** and **23**) (Chart 3), of which the respective configurations at C-4 are unassigned. Although the amount of **22** is larger than that of **23** the exact ratio could not be determined since the assigned NMR signals for each compound were overlapped. As the carbon tetrachloride solution stands at room temperature the NMR signals assigned to **22** and **23** are slowly replaced by those assigned to **1**. Also treatment of the solution with piperidine results in the rapid formation of **1**.

The reaction of hydrogen bromide with (−)-umbellulone (**1**) in ice-cold carbon tetrachloride was similarly examined. The immediate NMR spectrum of the reaction mixture shows the presence of (4*R*)-4-bromodihydroumbellulone (**24**) and (4*S*)-4-bromodihydroumbellulone (**25**) in the ratio of 2:3 (Table 1). It is assumed that the addition of hydrogen bromide to **1** proceeds largely by way of attack of the bromide ion on a π-complex,[17] the proton being co-ordinated to the C═C double bond of **1** on the side remote from the cyclopropyl ring. The bromide ion then adds *trans* to the co-ordinated proton,[21] and the predominant product of the hydrobromination reaction is assigned the (4*S*) configuration (**25**). That the assignment of these configurations to **24** and **25** is correct is considerably strengthened by the fact that, as discussed below, these are those respective configurations which are used in the most reasonable mechanisms to explain both the major and minor products eventually obtained in the hydrobromination reaction.

In the NMR spectrum, the signals assigned to **24** and **25** almost immediately begin to disappear, and after six hours at room temperature, the original spectrum has been

CHART 3



replaced by another. Easily distinguished are signals due to a trace of (−)-(*R*)-5-(bromomethyl)-5-isopropyl-3-methyl-2-cyclopenten-1-one (**17**) (Table 2). The other complex group of signals is assigned to a mixture of equal parts of **26** and **27** (Table 2). As the mixture stands at room temperature, this group of signals is replaced by a simpler one assigned to **28**. After four weeks at room temperature only signals assigned to **28** and to a trace of **17** were seen. During this time the solution had darkened and carbon tetrachloride insoluble material had formed. The spectrum remained unchanged for at least three more weeks. No signal assigned to **16** was observed.

When the reaction mixture in ice-cold carbon tetrachloride with NMR signals due to **24** and **25** is treated with piperidine, there is an immediate precipitation of piperidine hydrobromide. The other product from the reaction is (−)-umbellulone (**1**). Treatment of a similar mixture showing only a trace of **17** and about equivalent amounts of **26** and **27** also gave piperidine hydrobromide and **16** and **17** in a ratio of about 3 : 2. These results indicate that **24** rearranges at room temperature to **26** which on treatment with piperidine or heat isomerizes to **17**. Likewise, **25** rearranges to **27** which then isomerizes to **28**. On treatment with heat or piperidine the latter loses hydrogen bromide to form **16**. Since the NMR signals assigned to **26** disappear with the formation of only a trace of **17**, **26** must also decompose at room temperature to carbon tetrachloride insoluble material.

Reaction of halogens with (−)*-umbellulone* (**1**)

Addition of bromine to **1** in ice-cold carbon tetrachloride and evaporation of the solvent at room temperature gives a fuming, light yellow oil which on heating evolves hydrogen bromide and then on distillation affords two compounds. The lower boiling and larger fraction (61%) reported earlier[6] and discussed above as the unsaturated bromo ketone is now identified as (±)-*trans*-4-(bromomethylene)-5-isopropyl-3-methyl-2-cyclopenten-1-one (**29**) (Chart 2). The higher boiling substance (16%) is (−)-umbellulone dibromide[6] (**3**).

The IR spectrum of **29**, similar to that of **16**, shows CO absorption at 1715 cm^{-1} and two olefinic stretching bands at 1590 and 1640 cm^{-1}. The NMR spectrum (Table 2) displays a doublet for a vinylic Me group, signals for an i-Pr group attached to an asymmetric center,[18] two doublets for two vinylic protons and a broad multiplet in the methine proton region. The complex coupling pattern (Table 2) was elucidated by spin–spin decoupling experiments. The two vinylic protons are not mutually coupled thus locating the Br atom at C-6. Although the configuration of the C-4 to C-6 double bond could not be deduced unambiguously, it is tentatively assigned as shown in **29** on the basis that the C-6 proton is not coupled to those at C-10. The UV spectrum of **29** confirms its assigned structure. Adding increments of 15,[1] 35[20] and 17 mμ[1] for the C-3 Me group, the exocyclic double bond at C-4 and the Br atom at C-6, respectively, to the base balue of 214 mμ for 2-cyclopenten-1-one, the calculated absorption max is 281 ± 5 mμ, in good agreement with that found (Table 3). Finally, the isolated sample of **29** showed only a residual optical activity from 290 to 600 mμ. This small optical activity is accounted for by assuming a 0·5% contamination with (−)-α-bromoumbellulone (**2**).

The reduction of **29** with zinc in acetic acid, paralleling that of **16**, gives the same ratio (2 : 3) of (±)-*cis* or *trans*-3,4-dimethyl-5-isopropyl-2-cyclopenten-1-one (**18**) and (±)-3,4-dimethyl-2-isopropyl-2-cyclopenten-1-one (**19**).

The NMR spectrum, obtained immediately after the addition of bromine to (−)-umbellulone (**1**) in ice-cold carbon tetrachloride reveals the presence of two adducts. The NMR spectrum (Table 1) shows singlets for two Me groups and two doublets at 4·57 and 4·77 ppm. The latter two are assigned to the respective C-3 protons of (3*R*,4*S*)-3,4-dibromodihydroumbellulone (**30**) and (3*R*,4*R*)-3,4-dibromodihydroumbellulone (**31**) (Chart 3). The amount of the latter compound is the larger, but the exact ratio of the two could not be determined. Both **30** and **31** are assigned the (3*R*) configuration on the basis that the initial addition of a bromonium ion or its equivalent to **1** is expected to occur from the side remote from the cyclopropyl ring. Since the second stage of the bromination reaction should give rise to two bromo ketones with the *trans* dibromide predominating, the (4*S*) and (4*R*) configurations are assigned to **30** and **31**, respectively. The NMR spectra of **30** and **31** are compatible with these configurational assignments.

As the solution of **30** and **31** in carbon tetrachloride stands at room temperature, the NMR signals assigned to these compounds are slowly replaced by others. In this new spectrum can be seen signals due to a small amount of (−)-umbellulone dibromide

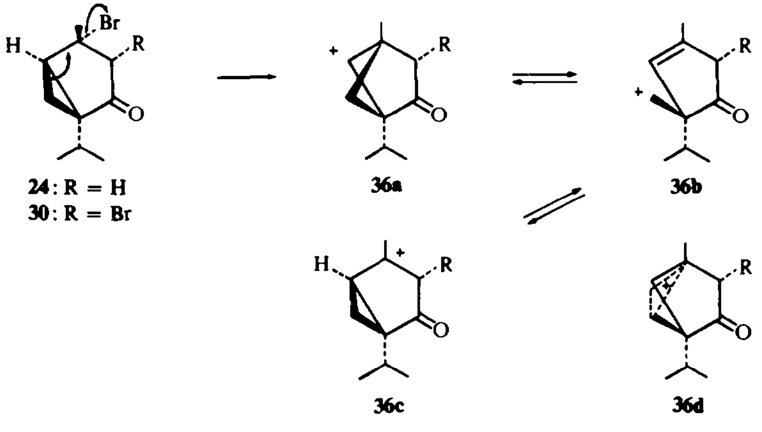
(3), but due to the complexity of the spectrum the other signals could not be assigned. However, in analogy to the hydrobromination reaction of **1** and because there were no signals for vinylic protons in the spectrum, it is assumed that the observed signals are due to a mixture of **32** and **33**. It is also assumed that the signals for **30** disappear as a result of rearrangement to **34**, which immediately isomerizes to a trace of **3** and decomposes to carbon tetrachloride insoluble material. As this mixture remains at room temperature, the complex set of signals begins slowly to diminish and another set, assigned earlier to (±)-*trans*-4-(bromomethylene)-5-isopropyl-3-methyl-2-cyclopenten-1-one (**29**), begins to appear. After several weeks, only signals for **29** and a small amount of **3** were visible.

Chlorine also reacts with (−)-umbellulone (**1**) in carbon tetrachloride and forms, on the basis of its NMR spectrum, a single 3,4-dichlorodihydroumbellulone (**35**). The configuration of this compound could not be assigned from its NMR spectrum and indeed may arise by a free radical process.[22] On standing at room temperature or on treatment with piperidine, the adduct loses hydrogen chloride and forms (−)-α-chloroumbellulone (**12**).

CONCLUSIONS

The initial reaction of N-bromo- and N-chlorosuccinimide in polar solvents and hydrogen chloride, hydrogen bromide and bromine in carbon tetrachloride with (−)-umbellulone (**1**) is an electrophilic addition at the C-3 double bond followed by the attack of a nucleophile at C-4 leading to two products, epimeric at C-4. The stabilities of these compounds are quite varied. The two keto diols **5** and **6** and the methoxy derivative **7** are stable at room temperature and during their isolation each was heated to at least 50°. The others on heating and those with chlorine or bromine at C-4 at room temperature undergo further reaction. Those with an OH group, a MeO group or a Cl atom at C-4 (**8–11**, **13–15**, **22**, **23** and **35**) lose the elements of water, methanol or hydrogen chloride and form the respective bicyclo[3.1.0]hex-3-en-2-one (**1**, **2** and **12**). These reactions presumably proceed by way of an ElcB mechanism or by way of a concerted E2 mechanism.[23] The dehydrohalogenation of **22–25**, **30**, **31** and **35** with piperidine also proceeds similarly.

CHART 4



When a Br atom is situated at C-4 (**24**, **25**, **30** and **31**) deep-seated rearrangements occur which lead finally to 2-cyclopenten-1-ones (**3**, **16**, **17** and **29**). This marked difference is ascribed to the relative ease of displacement of the substituents at C-4 which have the order Br > Cl > OH ≅ OCH_3[24] and to the effectiveness of bromide as a neighboring group.[25]

Thus **24** and **30** react by way of a carbonium ion (**36**), the formation of which results from a back-side displacement of the bromide ion (Chart 4) by participation of the cyclopropyl ring.[26] This carbonium ion may be a set of equilibrating, essentially classical cations (**36a**–**36c**) or a non-classical ion (**36d**).[27, 28] Attack of a bromide ion at C-6 (**36b** or **36d**) leads to **26** and **34** which then isomerize to **3** and **17**.

The reactions of **25** and **31** are possible accounted for by another process, a 1,3-shift of a bromide ion from C-4 to C-6, rupture of the C-1 to C-6 bond and a hydride transfer from C-5 to C-4 leading to **27** and **32**.

EXPERIMENTAL

M.ps were taken in capillary tubes and are corrected. B.ps are not corrected. Optical rotations at the sodium D-line were measured using 1-dm tubes, and unless otherwise noted, MeOH was the solvent. Elemental analyses were done by Galbraith Laboratories, Knoxville, Tennessee. Evaporations of solvents were done at reduced pressure without heating. IR spectra were obtained using a Beckman IR-10 spectrophotometer and were measured using KBr pellets (ν_{KBr}) or as capillary films (ν_{cap}) between KBr plates. UV spectra were measured in MeOH with a Cary Model 14 spectrophotometer using 1-cm cells. ORD curves were obtained with a Rudolph automatic recording spectropolarimeter, Model 260/658/850/810-614,* using the same conditions as outlined earlier.[1] The solvent was MeOH and the curves are reported as before.[4]

NMR spectra were measured with a Varian Model A-60 spectrometer† operating at 60 MHz. Unless noted otherwise, the spectra were measured as approximately 30% solns in $CDCl_3$, chemical shifts are reported in ppm downfield from TMS = 0, and coupling constants were estimated to ±0·5 Hz. Product ratios were determined by the careful integration of the respective spectra.

In order to use NMR in analyzing the reaction of HCl, HBr, Br_2 and Cl_2 with (−)-umbellulone (**1**) in CCl_4, the solns were prepared as outlined below for the reaction of Br_2 with **1**.

Br_2 was added dropwise to an ice-cold soln of 0·5 g (0·003 mole) of **1** in 1 ml of CCl_4 until a brown color persisted. The soln was immediately washed with dil $NaHSO_3$ aq and H_2O. It was dried ($MgSO_4$) and transferred to a chilled NMR tube. By keeping the tube in ice until immediately before measurement, the NMR spectrum of the initial bromination product could be obtained. Following measurement of this first spectrum, the tube was kept capped at room temperature, and the spectrum of the soln measured periodically.

(—)-*Umbellulone* (**1**)‡ had b.p. 52° (0·9 mm), n_D^{24} 1·4825, α_D^{26} −36·7° (neat, 1 dm), $[\alpha]_D^{25}$ − 32° (*c* 1·14) [lit.[7] $[\alpha]_D^{25}$ − 39·4° (neat)].

(—)-α-Bromoumbellulone (**2**) had m.p. 33–34°, $[\alpha]_D^{25}$ − 137° (*c* 1·55) [lit.[4] b.p. 120–125° (12 mm), m.p. 33–34°, $[\alpha]_D^{25}$ − 137° (*c* 1·55, MeOH)].

(—)-(3S)-*Epoxyumbellulone* (**4**) had m.p. 27–28°, $[\alpha]_D^{25}$ − 19° (*c* 1·01) [lit.[8] m.p. 25–26°, α_D^{25} − 20·4° (neat, 1 dm)]

(−)-(3S,4R)-3-*Hydroxy-4-methoxydihydroumbellulone* (**7**). A mixture of 2·91 g (0·0175 mole) of (**4**) and six drops of conc H_2SO_4 in 30 ml of dry MeOH was boiled for 30 min. The cooled soln was diluted with 20 ml of H_2O and thoroughly extracted with ether. The ethereal soln was dried ($MgSO_4$) and evaporation of the ether left 2·75 g of **7** (79%) as a yellow oil of at least 95% purity (NMR). The oil was chromatographed on

---

* We wish to thank the Department of Microbiology, Vanderbilt University, for the use of its spectropolarimeter, purchased with a grant (AI-06191) from the U.S. Public Health Service.

† We acknowledge the generosity of the National Science Foundation for a grant (GP-1683) to the Department of Chemistry for purchase of this instrument.

‡ We are grateful to Professor Richard H. Eastman, Stanford University, for a generous gift of this compound.

silica gel using hexane, benzene and $CHCl_3$ as eluants. The major fraction, a colorless oil, was eluted with $CHCl_3$. Molecular distillation of this material at 70° (2 mm) gave 1·62 g of **7** (47% based on **4**) as a colorless oil, n_D^{25} 1·4758, $[\alpha]_D^{25}$ − 49° (*c* 1·04), IR: ν_{cap}^{max} 1730 (C═O), 2930 (OMe), 3450 cm^{-1} (OH); UV: $\varepsilon_{282m\mu}^{max}$ 34, NMR: Table 1, ORD: (*c* 1·07) $[\phi]_{600}$ − 91°, $[\phi]_{589}$ − 95°, $[\phi]_{400}$ − 115°; (*c* 0·213) $[\phi]_{400}$ −170°, $[\phi]_{355}$ ±0°, $[\phi]_{309}$ +2090° (pk), $[\phi]_{295}$ ±0°, $[\phi]_{263}$ −5870° (tr), $[\phi]_{255}$ −5800° (pk), $[\phi]_{240}$ −6140°. (Found: C, 66·92; H, 9·43. $C_{11}H_{18}O_3$ requires: C, 66·64; H, 9·15%).

(3S,4S)-3-*Bromo-4-hydroxydihydroumbellulone* (**8**) *and* (3S,4R)-3-*bromo-4-hydroxydihydroumbellulone* (**9**). A hererogeneous mixture of 4·47 g (0·0298 mole) of **1**, 15·0 g (0·0843 mole) of NBS and 60 ml of H_2O was stirred at room temp for 15 hr. The excess NBS was destroyed by the addition of dil $NaHSO_3$ aq and the aq soln thoroughly extracted with ether. The ethereal soln was washed with H_2O and dried ($MgSO_4$). Evaporation of the solvent gave 5·74 g of a 1:3 mixture of **8** and **9** (79%) as a pale yellow oil of at least 95% purity (NMR), IR: ν_{cap}^{max} 1740 (C═O), 3480 cm^{-1} (OH); NMR: Table 1.

Heating of 3·63 g (0·0140 mole) of the 1:3 mixture of **8** and **9** at reduced press (4 mm) resulted in the complete dehydration of **8** and **9** and the distillation of 2·09 g of **2** (62%) as a pale yellow oil, b.p. 115–117° (4 mm), $[\alpha]_D^{25}$ −92° (*c* 1·71), contaminated with a small amount of succinimide (NMR). The IR and NMR spectra of this material were essentially identical to those of the authentic sample of **2** described above.

As described above, a sample of a 1:3 mixture of **8** and **9** was prepared directly from **1**. Passage of a 50% ethereal soln of this mixture through a GLC column (10-ft column of 30% silicone gum rubber SE 30 on Chromasorb W; inlet port temp, 270°; column temp, 200°) gave, aside from H_2O, only **2** in at least 95% purity (GLC). The latter substance was collected and was obtained as a colorless oil which crystallized on standing as white needles, m.p. 30–31°, $[\alpha]_D^{25}$ −138° (*c* 0·97). The IR and NMR spectra of this material were identical to those of the authentic sample of **2** described above.

(3S,4S)-3-*Chloro-4-hydroxydihydroumbellulone* (**10**) *and* (3S,4R)-3-*chloro-4-hydroxydihydroumbellulone* (**11**). A heterogeneous mixture of 3·03 g (0·0202 mole) of **1**, 10·5 g (0·079 mole) of freshly recrystallized NCS and 35 ml of H_2O was stirred at room temp for 20 hr. The excess NCS was destroyed by the addition of dil $NaHSO_3$aq and the aq soln thoroughly extracted with ether. The ethereal soln was washed with H_2O and dried ($MgSO_4$). Evaporation of the ether left 2·69 g of a 1:3 mixture of **10** and **11** (66%) as a pale yellow oil of at least 95% purity (NMR), IR: ν_{cap}^{max} 1740 (C═O), 3440 cm^{-1} (OH); NMR: Table 1.

Heating of this mixture of **10** and **11** at reduced press (8 mm) resulted in the incomplete dehydration of **10** and **11** and the distillation of a mixture of **10**, **11** and **12**, b.p. 135–140° (8 mm). Strong heating of this latter mixture at 190° followed by molecular distillation at 50° (0·3 mm) gave **12** as a yellow oil, $[\alpha]_D^{25}$ −86° (*c* 1·01). The IR and NMR spectra of this material were identical to those of the authentic sample of **12** described below.

(−)-*α-Chloroumbellulone* (**12**) had b.p. 68–70° (1·5 mm), n_D^{25} 1·5002, $[\alpha]_D^{25}$ − 115° (*c* 2·49) [lit.[1] b.p. 68–70° (1·5 mm), $[\alpha]_D^{25}$ −115° (*c* 2·49, MeOH)].

3-*Bromo-4-methoxydihydroumbellulone* (**13**), (3S,4S)-3-*bromo-4-methoxydihydroumbellulone* (**14**) *and* (3S,4R)-3-*bromo-4-methoxydihydroumbellulone* (**15**). A mixture of 1·96 g (0·0130 mole) of **1**, 7·0 g (0·039 mole) of NBS and 25 ml dry MeOH was boiled for one hr. The excess NBS was destroyed by the addition of dil $NaHSO_3$aq. The mixture was diluted with H_2O and thoroughly extracted with ether. The ethereal soln was washed with H_2O and dried ($MgSO_4$). Evaporation of the ether left 3·18 g of a 1:3:6 mixture of **13**, **14** and **15** (93%) as a pale yellow oil of at least 95% purity (NMR), IR: ν_{cap}^{max}1740 (C═O), 2855 cm^{-1} (OMe). A 2·95 g sample of this mixture was chromatographed on silica gel using hexane, benzene and $CHCl_3$ as eluting solvents. First eluted using benzene was 0·857 g of **2** (29%) of at least 95% purity (NMR) and next, using benzene–$CHCl_3$, 0·954 g of **15** (28%) as a pale yellow, unstable oil of at least 95% purity and uncontaminated with **13** or **14** (NMR), IR: ν_{cap}^{max} 1740 (C═O), 2845 cm^{-1} (OMe); UV: $\varepsilon_{278m\mu}^{max}$ 190, $\varepsilon_{212m\mu}^{max}$ 400; NMR: Table 1. In the chromatogram, using $CHCl_3$ as the eluting solvent, there was finally obtained 0·935 g of a 1:3 mixture of **13** and **14** (27%) as a pale yellow oil of at least 95% purity (NMR), IR: ν_{cap}^{max}1750 (C═O), 2850 cm^{-1} (OMe), NMR: Table 1.

A 1:3:6 mixture of **13**, **14** and **15** was prepared from **1** as described above. Passage of a 50% ethereal soln of the mixture through a GLC column (20-ft column of 30% silicone gum rubber SE 30 on Chromasorb W; inlet port temp, 285°; column temp, 235°) gave, aside from MeOH, only **2** in at least 95% purity (NMR). This latter substance was collected and was a colorless oil which crustallized on standing, m.p. 29–30°, $[\alpha]_D^{25}$ −127° (*c* 1·67). The IR and NMR spectra of this material were identical to those of the authentic sample of **2** described above.

GLC of a 50% ethereal soln of **15** or a 1:3 mixture of **13** and **14** using the same column and conditions as described above resulted in demethanolation to **2**, identified by its spectral properties.

(±)-5-*Isopropyl-3-methyl-4-methylene-2-cyclopenten-1-one* (**16**) *and* (−)-(R)-5-(*bromomethyl*)-5-*isopropyl-3-methyl-2-cyclopenten-1-one* (**17**). As reported earlier,[1] HBr was passed for 5 min through a stirred, ice-cold soln of 14·1 g (0·0939 mole) of **1** in 100 ml CCl_4. The pale brown soln was washed with 50 ml of H_2O and dried ($MgSO_4$). Evaporation of the solvent left a fuming, brown oil. On heating of this oil at reduced press (1·7 mm), first there was evolved a substantial amount of HBr followed by the distillation of two distinct fractions, A and B.

Fraction A was 10·0 g of **16** (71%) as a colourless oil, b.p. 74–75° (1·7 mm), n_D^{25} 1·5070, $[\alpha]_D^{25}$ ±0·3° (c 3·25), IR: ν_{cap}^{max} 1590 (C=C), 1635 (C=C), 1690 cm^{-1} (C=O); UV: Table 3, NMR: Table 2, ORD: (*c* 1·25) $[\phi]_{600}$ ±12°, $[\phi]_{589}$ ±12°, $[\phi]_{350}$ ±12°; (*c* 0·125) $[\phi]_{350}$ ±120°, $[\phi]_{280}$ ±120°. (Found: C, 79·74; H, 9·41. $C_{10}H_{14}O$ requires: C, 79·95; H, 9·39%).

Fraction B was 3·92 g of a pale yellow oil (18% based on pure **17**), b.p. 80–91° (1·7 mm), which partially crystallized on cooling. Recrystallization of this latter material from pet ether (b.p. 40–60°) and sublimation at 60° (0·3 mm) gave 1·51 g of **17** (7·0%), m.p. 85–86°, $[\alpha]_D^{25}$ −40° (*c* 1·40), NMR: Table 2, characterized earlier.[1]

(±)-cis *or* trans-3,4-*Dimethyl-5-isopropyl-2-cyclopenten-1-one* (**18**) and (±)-3,4-*dimethyl-2-isopropyl-2-cyclopenten-1-one* (**19**). A mixture of 2·21 g (0·0147 mole) of **16**, 12·0 g (0·183 g-atom) Zn dust, and 50 ml glacial HOAc was heated on a steam plate for 12 hr. The hot soln was filtered, and the filtrate diluted with 50 ml H_2O. The aq soln was made neutral by the addition of solid $NaHCO_3$ and then the soln thoroughly extracted with ether. The ethereal soln was washed with $NaHCO_3$ aq, then with H_2O and finally dired ($MgSO_4$). Evaporation of the ether left 1·38 g of a 2:3 mixture of **18** and **19** (62%) as a pale yellow oil of at least 95% purity (NMR). Separation of this mixture was achieved by column chromatography on silica gel with hexane, benzene and $CHCl_3$ as eluting solvents. With benzene, **19** was eluted. Evaporation of the solvent left 0·421 g (19%) of residue. Molecular distillation of this residue at 60° (1 mm) gave **19** as a colorless oil n_D^{25} 1·4741, IR: ν_{cap}^{max} 1640 (C=C), 1700 cm^{-1} (C=O); UV: Table 3, NMR: Table 2. (Found: C, 78·48; H, 10·30. $C_{10}H_{16}O$ requires: C, 78·89; H, 10·59%).

With $CHCl_3$, **18** was eluted. Evaporation of the solvent left 0·366 g (16%) of residue. Molecular distillation of this residue at 70° (1 mm) gave **18** as a colorless oil, IR: ν_{cap}^{max} 1630 (C=C), 1700 cm^{-1} (C=O); UV: Table 3, NMR: Table 2. (Found: C, 79·21; H, 10·81. $C_{10}H_{16}O$ requires: C, 78·89; H, 10·59%).

A soln of 0·992 g (6·60 mmoles) of **16** in 50 ml dry MeOH was reduced with H_2 over 0·764 g of 10% Pd=C. After uptake of one equiv of H_2 (163 ml at 25° and 1 atm) was complete, the mixture was filtered. Evaporation of the solvent gave 0·920 g of **18** (92%) as a colorless oil of at least 95% purity (NMR). The IR and NMR spectra of this material were identical to those of **18** characterized above.

A soln of 0·207 g (1·36 mmoles) of **18** in 3·5 ml MeOH containing 0·103 g (1·91 mmoles) NaOMe was boiled for 3 hr. The purple soln was then diluted with 5 ml of H_2O and thoroughly extracted with ether. The ethereal soln was dried ($MgSO_4$). Evaporation of the ether left 0·190 g of **19** as a pale yellow oil of at least 95% purity (NMR). The trace of **18** detected in the NMR spectrum of this oil was removed by column chromatography on silica gel. Elution with benzene and removal of the solvent left pure **19**, the IR and NMR spectra of which were identical to those of **19** characterized above.

In a similar way a soln of **18** in MeOH was saturated with HBr. The purple soln was then diluted with water and thoroughly extracted with ether. The ethereal soln was dried ($MgSO_4$). Evaporation of the ether gave a good return of **19** as a pale yellow oil of at least 95% purity (NMR). The IR and NMR spectra of this oil were identical to those of **19** characterized above.

(±)-3,4-*Dimethyl-2-isopropylcyclopentanone* (**20**). A soln of 0·222 g (1·46 mmoles) of **18** in 50 ml dry MeOH was reduced with H_2 over 0·159 g of 10% Pd=C. When one equiv of H_2 (30 ml at 25° and 1 atm) had reacted, the mixture was filtered. Evaporation of the solvent left 0·203 g of **20** (90%) as a colorless oil of at least 95% purity (NMR). Molecular distillation of this oil at 50° (0·4 mm) gave pure **20** as a colorless oil, IR: ν_{cap}^{max} 1740 cm⁻1 (C=O): UV: $\varepsilon_{292m\mu}^{max}$ 25, $\varepsilon_{210m\mu}^{cut\text{-}off}$ 84; NMR: 0·8–1·3 (12H; C-6, C-8, C-9 and C-10 protons), 1·4–2·8 ppm (6H; C-2, C-3, C-4, C-5 and C-7 protons). (Found: C, 77·92; H, 11·94. $C_{10}H_{18}O$ requires: C, 77·86; H, 11·76%).

(±)-3,4-*Dimethyl-2-isopropylcyclopentanone*-2,5,5-d_3 (**21**). A soln of 0·120 g (0·778 mmole) of **20** in 10 ml MeOD containing 0·100 g (1·85 mmoles) NaOMe was boiled for 1·5 hr. The mixture was diluted with 5 ml D_2O and extracted with ether. The ethereal soln was dried ($MgSO_4$). Evaporation of the ether left **21** as a colorless oil of at least 95% purity (NMR), NMR: 0·8–1·3 (12H; C-6, C-8, C-9 and C-10 protons), 1·4–2·4 ppm (3H; C-3, C-4 and C-7 protons).

4-*Chlorodihydroumbellulones* (**22** and **23**). HCl was passed for 3 min into an ice-cold soln of 0·510 g (3·40 mmoles) of **1** in 2 ml CCl_4. The soln was washed with H_2O and dried ($MgSO_4$), IR: $\nu_{CCl_4}^{max}$ 1740 cm^{-1} (C=O); NMR (CCl_4): Table 1, indicating that addition had occurred to form **22** and **23**.

As the soln above stood at room temp, the NMR spectrum of **22** and **23** was slowly replaced by that of **1**. When a portion of the above soln was treated with piperidine, a white crystalline solid immediately precipitated. The mixture was stirred for 1 hr, then acidified with dil HCl aq. The organic layer was separated and dried ($MgSO_4$). The NMR spectrum of this soln showed only signals previously assigned to **1**.

(−)-*Umbellulone dibromide* (**3**) *and* (±)-trans-*4-(bromomethylene)-5-isopropyl-3-methyl-2-cyclopenten-1-one* (**29**). To a stirred soln of 5·86 g (0·0390 mole) of **1** in 80 ml CCl_4 at −10° was slowly added 8·00 g (0·050 mole) of Br_2. The soln was washed with dil $NaHSO_3$ aq and H_2O and then dried ($MgSO_4$), IR: $\nu_{\mathrm{CCl_4}}^{\mathrm{max}}$ 1740 cm^{-1} (C=O), no absorption 1465 to 1740 cm^{-1}. Evaporation of the solvent left 11·45 g of a fuming, brown oil. On heating of this oil at reduced press (0·6 mm) there was a vigorous evolution of HBr and then the distillation of two fractions A and B. A black residue, 1·36 g, remained in the distillation pot.

Fraction A was 5·49 g of **29** (61 %), a pale yellow oil, b.p. 89–91° (0·6 mm), $[\alpha]_D^{25}$ −3·5 (*c* 7·0), IR; $\nu_{\mathrm{cap}}^{\mathrm{max}}$ 1590 (C=C), 1640 (C=C), 1715 cm^{-1} (C=O); UV: Table 3, NMR: Table 2, ORD: (*c* 7·0) $[\phi]_{600}$ −8°, $[\phi]_{589}$ −8°, $[\phi]_{388}$ ±0°, $[\phi]_{351}$ +40° (pk), $[\phi]_{337}$ ±0°, $[\phi]_{304}$ −320° (tr), $[\phi]_{290}$ −250° [lit.[6] b.p. 140–145° (20 mm)]. [Found: mol wt, 238 (osmometric in benzene). $C_{10}H_{13}BrO$ requires: mol wt, 229·12].

Fraction B was 1·97 g of **3** (16 %), b.p. 95–96 (0·5 mm), which at first was a pale yellow oil but which solidified on standing. Recrystallization of this material from cyclohexane gave 1·44 g of **3** (12 %) as white needles, m.p. 120–121°, $[\alpha]_D^{26}$ −6° (*c* 1·02), $[\alpha]_D^{22}$ +6·0° (*c* 3·0, $CHCl_3$) [lit.[6] m.p. 119–119·5°, $[\alpha]_D$ +6·4° (*c* 2·1, $CHCl_3$)], NMR: Table 2.

A mixture of 2·78 g (0·0121 mole) of **29**, 12·0 g (0·183 g-atom) Zn dust and 50 ml glacial HOAc was heated on a steam bath for 12 hr. Isolation of the product as outlined above for a similar reduction of **16** gave 1·45 g of a 2:3 mixture of **18** and **19** (79%) of at least 95% purity (NMR). The pure components, **18** and **19**, were separated by column chromatography on silica gel as outlined above and were identical in all respects to **18** and **19** characterized above.

3,4-Dichlorodihydroumbellulone (**35**). Cl_2 was passed for 5 min into a stirred, ice-cold soln of 3·44 g (0·0229 mole) of **1** in 40 ml of CCl_4. The light yellow soln was washed with dil $NaHSO_3$ aq, then with H_2O and dried ($MgSO_4$). Evaporation of the solvent at room temp left 4·48 g of **35** (88%) as a light yellow oil of at least 95% purity (NMR), IR: $\nu_{\mathrm{cap}}^{\mathrm{max}}$ 1750 cm^{-1} (C=O), NMR: Table 1. Heating of 3·76 g of this oil at reduced pressure (0·3 mm) resulted in some dehydrochlorination and distillation of 2·88 g of a mixture of **35** and **12**, b.p. 60–80° (0·3 mm), identified by NMR.

As described above, a sample of **35** was prepared directly from **1**. Passage of a 50% ethereal soln of the compound through a GLC column (20-ft column of 30% silicone gum rubber SE 30 on Chromasorb W: inlet port temperature, 275°; column temp, 250°) gave aside from HCl, only **12** in at least 95% purity (GLC and NMR). The substance was collected and was a colorless oil, n_D^{25} 1·5008, $[\alpha]_D^{25}$ −109° (*c* 0·85). The IR and NMR spectra of this material were identical to those of the authentic sample of **12** characterized above.

Acknowledgement—We wish to thank the National Science Foundation for a grant (GP-5772) supporting this work. R.T.G. also thanks the Monsanto Fund for financial aid.

REFERENCES

[1] Paper V: H. E. Smith, R. T. Gray, T. J. Shaffner and P. G. Lenhert, *J. Org. Chem.* **34**, 136 (1969).

[2] Taken from the Ph.D. dissertation of R.T.G., Vanderbilt University (June 1968).

[3] A preliminary report has appeared: H. E. Smith and R. T. Gray, *Chem. Commun.* 1695 (1968).

[4] R. T. Gray and H. E. Smith, *Tetrahedron* **23**, 4229 (1967).

[5] F. B. Power and F. H. Lees, *J. Chem. Soc.* **85**, 629 (1904).

[6] F. H. Lees, *Ibid.* **85**, 639 (1904).

[7] R. H. Eastman and A. Oken, *J. Am. Chem. Soc.* **75**, 1029 (1953).

[8] R. H. Eastman and J. C. Selover, *Ibid.* **76**, 4118 (1954).

[9] P. de Mayo, *The Chemistry of Natural Products* (Edited by K. W. Bentley) Vol. II; p. 110. Interscience, New York, N.Y. (1959).

[10] J. F. King and P. de Mayo, *Molecular Rearrangements* (Edited by P. de Mayo) Part 2; p. 807. Interscience, New York, N.Y. (1964).

[11] R. E. Parker and N. S. Isaacs, *Chem. Revs.* **59**, 737 (1959).

[12] C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.* **77**, 2549 (1955).

[13] D. R. Dalton, J. B. Hendrickson and D. Jones, *Chem. Commun.* 591 (1966).

[14] A. Jovtscheff, H. Reinheckel, K. Haage and R. Pomakowa, *Monatsch Chem.* **97**, 1620 (1966).

[15] F. L. Lambert, W. D. Ellis and R. J. Parry, *J. Org. Chem.* **30**, 304 (1965).

[16] S. F. Reed, Jr., *Ibid.* **30**, 2195 (1965).
[17] J. Hine, *Physical Organic Chemistry* (2nd Edition) Chap. 9, McGraw-Hill, New York, N.Y. (1962).
[18] T. S. Sorensen, *Canad. J. Chem.* **45**, 1585 (1967).
[19] K. Tori and M. Ohtsuru, *Chem. Commun.* 886 (1966).
[20] J. C. D. Brand and A. I. Scott, *Elucidation of Structures by Physical and Chemical Methods* (Edited by K. W. Bentley) Part I; p. 61, Interscience, New York, N.Y. (1963).
[21] G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.* **76**, 4121 (1954).
[22] M. L. Poutsma, *Ibid.* **87**, 4293 (1965).
[23] Ref. 17, Chapter 8; R. Baker, *Chem. Brit.* **4**, 250 (1968).
[24] Ref. 17, p. 184.
[25] S. Winstein and E. Grunwald, *J. Am. Chem. Soc.* **70**, 828 (1948).
[26] L. Birladeanu, T. Hanafusa, B. Johnson and S. Winstein, *Ibid.* **88**, 2316 (1966).
[27] K. L. Servis and J. D. Roberts, *Ibid.* **87**, 1331 (1965).
[28] P. von R. Schleyer and G. W. Van Dine, *Ibid.* **88**, 2321 (1966).