



The infrared and nuclear magnetic resonance spectra of the triacetyl derivatives were essentially identical. Triacetylquinide, VIII, is readily converted to quinic acid by heating in aqueous potassium hydroxide solution followed by ion-exchange chromatography to yield the free acid.⁵

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Chemical Shifts of Axial and Equatorial α -Protons in the N.m.r. of Steroidal α -Haloketones

Sir:

The discovery¹ that axial hydrogens are more highly shielded than corresponding equatorial ones increased the use of n.m.r. chemical shift data in structural studies of cyclohexane systems. Interpretations of this differential shielding have been proposed^{2,3a,c,d} and scattered examples of exceptions to the rule have been reported.^{1b,4} We have found that a carbonyl group adjacent to a monohalogenated carbon in ster-

oidal α -haloketones has the net effect of deshielding the remaining α -hydrogen when it is axial and of shielding it when it is equatorial. The effects are pronounced enough to reverse the usual axial-equatorial relationship and therefore are of practical importance for stereochemical studies as well as of theoretical interest.

The compounds examined were seventeen steroidal α -haloketones, which include the complete set of stereoisomeric 6-monohalo-5 α -cholestan-7-ones (halogen = F, Cl, Br, I). Because of the relative rigidity of ring B, this set is of value for correlation of stereochemistry with chemical shifts, with vicinal coupling constants and their dependence on the nature of attached substituents, with long range shielding and deshielding effects, etc. Table I lists the chemical shifts in deuteriochloroform (in p.p.m. downfield from tetramethylsilane) for the hydrogen on the halogen-bearing carbon. The values for five epimeric pairs

TABLE I

Number	Compound ^a	H conformation ^b	Chemical shift, δ , p.p.m. ^c
1	6 α -Fluoro-5 α -cholestan-7-one	a	4.51
2	6 β -Fluoro-5 α -cholestan-7-one	e	4.40
3	6 α -Chloro-5 α -cholestan-7-one	a	4.43
4	6 β -Chloro-5 α -cholestan-7-one	e	4.01
5	6 α -Bromo-5 α -cholestan-7-one	a	4.63
6	6 β -Bromo-5 α -cholestan-7-one	e	4.13
7	6 α -Iodo-5 α -cholestan-7-one	a	4.91
8	6 β -Iodo-5 α -cholestan-7-one	e	4.37
9	3 β -Bromo-5 α -cholestan-2-one	a	4.61
10	3 α -Bromo-5 α -cholestan-2-one	e	4.28
11	3 α -Iodo-5 α -cholestan-2-one	e	4.60
12	7 α -Bromo-5 α -cholestan-6-one	e	4.17
13	4 α -Bromo-2 α -methylcholestan-5 α -3-one	a	4.64
14	4 β -Bromo-5 β -cholestan-3-one	a	5.03
15	2 α -Chloro-5 α -cholestan-3-one	a	4.65
16	2 α -Bromo-5 α -cholestan-3-one	a	4.80
17	2 α -Iodo-5 α -cholestan-3-one	a	4.97
18	6 α -Bromo-5 α -cholestane	a	3.99
19	6 β -Bromo-5 α -cholestan-3 β -ol acetate	e	4.27
20	6 α -Chloro-5 α -cholestane	a	3.74
21	3 β -Bromo-5 α -cholestane	a	3.90
22	3 α -Bromo-5 α -cholestane	e	4.63
23	Cyclohexyl fluoride	a	4.28
24	Cyclohexyl fluoride	e	4.72
25	Cyclohexyl chloride	a	3.73
26	Cyclohexyl chloride	e	4.43
27	Cyclohexyl bromide	a	3.92
28	Cyclohexyl bromide	e	4.64
29	Cyclohexyl iodide	a	4.08
30	Cyclohexyl iodide	e	4.83

^a 1, m.p. 160–161°, α –18°; 2, m.p. 100.5–101°, α –80°; 3, m.p. 143–143.5°, α –8°; 4, m.p. 108.5–109°, α +33°; 5, m.p. 153.5–154°, α –7°; 6, m.p. 106–106.5°, α +68°; 7, m.p. 148.5–149°, α +1°; 8, m.p. 99–99.5°, α +114°. All new haloketones gave satisfactory analytical data and were characterized by infrared and ultraviolet absorption, by optical rotations measured in chloroform and at the sodium D line by optical rotatory dispersion, by chemical transformations, and by the n.m.r. coupling constants cited in this paper. Their syntheses will be described in a forthcoming publication. Compounds 9, 10 and 11 were kindly supplied by Professor C. Djerassi [C. Djerassi, H. Wolf and E. Bunnenberg, *J. Am. Chem. Soc.*, **85**, 324 (1963)]. Compounds 12–22 were prepared according to reported procedures. Data for the cyclohexyl halides (23–30) are those recorded by A. J. Berlin and F. R. Jensen [*Chem. Ind. (London)*, 998 (1960)] in their study of conformational equilibria at low temperatures in carbon disulfide solution. ^b Conformations (a = axial; e = equatorial) refer to the hydrogen attached to the halogenated carbon. ^c The n.m.r. spectra of compounds 1–22 were recorded in deuteriochloroform at 60 Mc./sec. (Varian A-60 spectrometer). Chemical shifts (δ) are recorded in p.p.m. as displacements downfield from tetramethylsilane, used as internal reference. All entries in Tables I and II represent averages of several scans.

(1) (a) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957); (b) *ibid.*, **80**, 6098 (1958).

(2) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

(3) (a) L. M. Jackman, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, Chapter 7; (b) p. 52; (c) J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961); **37**, 34, 192 (1962); (d) R. F. Zurcher, *Helv. Chim. Acta*, **44**, 1755 (1961).

(4) (a) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961); (b) A. S. Matlack, J. C. W. Chien and D. S. Breslow, *J. Org. Chem.*, **26**, 1455 (1961); (c) E. Campaigne, N. F. Chamberlin and B. E. Edwards, *ibid.*, **27**, 135, 4718 (1962); (d) J. Tadanier and W. Cole, *ibid.*, **27**, 4610, 4624 (1962).

(1-10) reveal that the signal for the epimer with an equatorial hydrogen appears at higher field than that for the epimer with axial hydrogen.⁵ The individual chemical shifts shown by the remaining α -haloketones (11-17) are also consistent with this "reversal" of the usual axial-equatorial relationship. That this reversal is not primarily due to distant anisotropic effects of the ring system is suggested by the numerous examples of steroidal compounds (alcohols, acetates, etc.) that observe the normal axial-equatorial order⁶ and is confirmed by the two pairs of non-ketonic bromo-compounds 18, 19; and 21, 22. In each of these two pairs the axial proton signal adopts its usual position upfield from the equatorial proton signal. The following analysis shows that the anomalous order for the α -haloketones is caused largely by the presence of a ketone group next to the halogenated carbon.

Aliphatic protons adjacent to a ketone group are ordinarily at lower fields than those in the corresponding non-ketonic analogs. For example, the methylene proton signal is at 1.25 p.p.m. in *n*-pentane and at 2.39 p.p.m. in pentanone-3.^{3b} In cyclohexane the signal is at 1.44 p.p.m., and in cyclohexanone the α -methylenes absorb at 2.25 p.p.m.^{3b,7} The chemical shifts for reference cyclohexyl halides with axial hydrogens (23, 25, 27, 29) and for non-ketonic steroid halides with axial hydrogens (18, 20, 21) may be compared to those for steroid α -haloketones with axial hydrogens (1, 3, 5, 7, 9, 13-17). This comparison shows that the presence of a carbonyl group moves the adjacent axial proton signal downfield. Some specific values for these displacements are 0.64 p.p.m. for 18 \rightarrow 5; 0.71 p.p.m. for 21 \rightarrow 9; 0.69 p.p.m. for 20 \rightarrow 3.

In contrast, an equatorial proton on a halogenated carbon is shifted upfield by introduction of the adjacent carbonyl group (*cf.* 24 with 2; 26 with 4; 22 with 10; 19 with 6; 19 with 12; 30 with 8). Whatever factors are responsible for this net upfield shift, they are of sufficient magnitude to overcome the deshielding normally produced by a carbonyl acting on α -hydrogens. Furthermore, an equatorial α -hydrogen is close to the nodal plane of the carbonyl π -system where deshielding might be expected due to the anisotropy of the carbonyl group.^{3a,8}

The dependence of vicinal coupling constants (J_{HH}) on dihedral angle is well documented, but little is known on how they vary with the nature of attached substituents.⁹ The $J(aa)$ and $J(ea)$ coupling constants listed in Table II for the set of α -haloketones 1-8 are

TABLE II
C₆-C₅ COUPLING CONSTANTS (C.P.S.)

	Compound number							
	1	2	3	4	5	6	7	8
$J_{HH}(aa)$	10.4 ^a		11.4		11.8		11.9	
$J_{HH}(ea)$		1.2 ^a		2.4		2.8		4.3

^a The geminal HF coupling constant was 51.2 c.p.s. in 1 and 53.9 c.p.s. in 2.

pertinent. On the assumption that the compounds with equatorial halogens (1, 3, 5, 7) have the same ring geometry, there is a slight increase in J_{aa} in the series

(5) Another epimeric pair that fits these observations is 2 β - and 2 α -fluoroandrostan-3,17-dione, whose C-3 hydrogen signals in deuteriochloroform are at 4.76 and 4.98 p.p.m. (δ scale), respectively [N. L. Allinger, M. A. Darroge, M. A. Miller and B. Waegell, *J. Org. Chem.*, **28**, 780 (1963)].

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fluorine \rightarrow iodine. In the corresponding series with an axial halogen (2, 4, 6, 8) the $J(ea)$ values show a similar increasing trend. But because of possible steric interaction of a C-6 axial halogen with the angular methyl group at C-10 the $J(ea)$ values may reflect some ring distortion superposed on a substituent effect.

The chemical shift data in Table I are also of interest in view of disagreement between theoretical predictions^{3a,c} and recent experimental findings¹⁰ on the effect of an alkyl group located in a 1:3 diaxial relationship to a proton. Not enough model compounds are available for a full analysis, but the variations in signals (Table I) for protons of a given conformational type (*i.e.*, axial or equatorial) indicate a deshielding effect for the 1:3 diaxial arrangement (or its equivalent).

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The Photochemical Conversions of Stilbenes to 9,10-Dihydrophenanthrenes

Sir:

Recent speculation¹⁻⁴ about the photochemical conversion of *cis*-stilbene (IIa) to phenanthrene (Va) has centered on the formation of a tertiary allylic dihydrophenanthrene (IVa) as intermediate, although this has not been isolated. Stegemeyer¹ found that the initial rate of phenanthrene formation was finite in the case of *cis*-stilbene (IIa) but zero in the case of *trans*-stilbene (Ia). He suggested that the intermediate IIIa was an excited state of *cis*-stilbene which cyclized and dehydrogenated in a concerted process to give phenanthrene.

Both Schaffner² and Mallory³ and their co-workers held the view that the reaction proceeded through the intermediate IVa which was dehydrogenated in a dark reaction by molecular oxygen or by other hydrogen acceptors present. Mallory³ and Moore⁴ have independently shown that phenanthrene is not formed on photolysis of degassed dilute solutions of stilbene. Moore⁴ obtained evidence for the intermediate IVa by observing its electronic spectrum and he proposed that this intermediate (IVa) was formed from an excited singlet state of *cis*-stilbene (IIIa) which is not available to *trans*-stilbene.

We have studied the photolysis of two stilbene systems: *trans*- $\alpha\beta$ -dicyanostilbene (Ib) and diphenylmaleinimide (Iic) and have isolated two stable 9,10-dihydrophenanthrenes (VIb and VIc) related to the intermediates (IVa) previously postulated. Both these compounds (VIb and VIc) are unchanged on further irradiation.

trans- $\alpha\beta$ -Dicyanostilbene (Ib, 3.9×10^{-2} M) was photolyzed in chloroform solution for 15 hr. in a Pyrex vessel surrounding a water-cooled Hanovia 400-w. medium pressure mercury lamp. Fractional crystallization of the product from benzene gave 9,10-phenan-

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