Stereochemical Course of the Photochemical Transformation of 3-Methylcar-4-en-2-one into Derivatives of 3,3,7-Trimethylocta-4,6-dienoic Acid

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Differentiation between the two vinylic methyl groups of methyl *trans*-3,3,7-trimethylocta-4,6-dienoate (IIa) by their nuclear Overhauser effect upon 6-H completes an elucidation of the stereochemical course of the photochemical transformation of 3-methylcar-4-en-2-one (Ia) into (IIa). The observed stereochemical course is rationalised by a non-concerted rearrangement of the diradical formed from (Ia) by α-cleavage, in which minimisation of non-bonded interactions is a controlling factor.

IN a recent paper[1] we have shown that the stereochemical assignments made by Baldwin and Krueger[2] for the photochemical transformation of 3-methylcar-4-en-2-one (Ia) into derivatives of 3,3,7-trimethylocta-4,6-dienoic acid (II; $R^1 = R^2 = Me$) were based on unreliable evidence. We showed that the stereochemical assignments for deuterium-labelled (I) were incorrect, and that those for the deuterium-labelled methyl ester of (IIa) were unreliable. After further n.m.r. studies on

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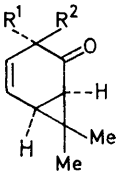
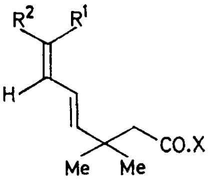
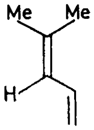
[1] A. J. Bellamy and W. Crilly, *J.C.S. Perkin II*, 1972, 395.

[2] J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 2396.

(IIa) and 4-methylpenta-1,3-diene (III) we now report that the stereochemical assignments made for deuterium-labelled (IIa) are incorrect.


(I)


(II)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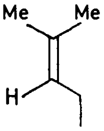
(IV)

a; $R^1 = R^2 =$ Me, X = OMe
b; $R^1 = CD_3$, $R^2 =$ Me, X = OMe
c; $R^1 =$ Me, $R^2 = CD_3$, X = OMe

In order to observe separate signals for each of the vinylic methyl groups in the n.m.r. spectrum (CCl_4 solution) of (IIa) it is necessary simultaneously to irradiate the olefinic proton at C(6). Under these conditions the vinylic methyl signals are separated by 1·6 Hz (δ 1·734 and 1·718 p.p.m.). One possible method of assigning these absorptions is by an NOE experiment.[3] Irradiation at the absorption frequency of the methyl group *cis* to 6-H should produce increased intensity in the 6-H absorption, whereas irradiation at the absorption frequency of the *trans*-methyl group should produce little change in the intensity of the 6-H absorption. However, the very small chemical shift difference between the two vinylic methyl groups makes such an experiment difficult.

NOE measurements for (IIa), (III), and (IV)

Sample	Internal standard	Ratio of olefinic proton absorption and internal standard absorption		
		A *	B *	C *
4% (IIa) in C_6D_6	CH_2Cl_2	0·590 ± 0·025	0·635 ± 0·037	0·682 ± 0·034
2% (III) in C_6D_6	CH_2Cl_2	1·731 ± 0·061	1·799 ± 0·087	1·993 ± 0·045
2% (IV) in CCl_4	$CHCl_2{\cdot}CHCl_2$	0·991 ± 0·029	1·061 ± 0·018	1·165 ± 0·043

Compound	Enhancement of olefinic proton absorption on irradiation of: High-field methyl absorption (B/A × 100–100)	Significance † level	Low-field methyl absorption (C/A × 100–100)	Significance ‡ level
(IIa)	7·6 ± 7·8%	(0·75%)	15·6 ± 7·6%	(1·2%)
(III)	3·9 ± 6·2%	(7·2%)	15·1 ± 4·8%	(<0·1%)
(IV)	7·0 ± 3·6%	(<0·1%)	17·6 ± 5·5%	(<0·1%)

* A; irradiation at 50 Hz away from any absorption. B; irradiation of high-field methyl absorption. C; irradiation of low-field methyl absorption. † Probability of enhancement being zero.[4] ‡ Probability of enhancement being equal to that observed on irradiation of high-field methyl absorption.[4]

The NOE experiment became feasible with benzene as the solvent, since the chemical shift difference between the two vinylic methyl groups increased to 2·9 Hz and simultaneous irradiation of 6-H was unnecessary in order to observe two signals.* With a 4% (w/v) solution of (IIa) in [$^2H_6$]benzene and a low irradiating power (see Experimental section) we observed a 15·6 ± 7·6% increase in the 6-H absorption on irradiating the low-field methyl absorption (δ 1·642 p.p.m.) and a 7·6 ± 7·8% increase in the 6-H absorption on irradiating the high-field methyl absorption (δ 1·613 p.p.m.). (The probability of the two enhancements being equal is 1·2%, and the probability of the smaller enhancement being equal to zero is 0·75% [4]). Since the largest increase † occurred when the irradiating frequency was centred on the low-field methyl absorption, this methyl group must be *cis* to 6-H [R^2 in (II)]. Thus, in benzene solution, the absorptions at δ 1·642 and 1·613 p.p.m. are assigned to the vinylic methyl groups *cis* and *trans* to 6-H respectively. To relate these assignments to the absorptions observed in CCl_4 solution we ran spectra of (IIa) in several C_6H_6–CCl_4 mixtures. There was no 'cross-over' of the two absorptions, therefore the absorptions at δ 1·734 and 1·718 p.p.m. are assigned to the vinylic methyl groups *cis* and *trans* to 6-H respectively. These assignments are the reverse of those made by Baldwin and Krueger.[2]

Our reasons for doubting the previous assignments for (IIa) [2] arose from our studies [1] with the model compound (III). By a chemical method we showed that for (III) in CCl_4 solution, the low-field methyl absorption (δ 1·754 p.p.m.) was due to the methyl group *cis* to 3-H, and the high-field methyl absorption (δ 1·734 p.p.m.) was due to the methyl group *trans* to 3-H. Using the NOE method already described for (IIa), we have now confirmed our assignments for (III). In [$^2H_6$]benzene irradiation of the low-field methyl absorption (δ 1·591 p.p.m.) increased the 3-H absorption by 15·1 ± 4·8%, while irradiation of the high-field methyl absorption (δ 1·542 p.p.m.) increased the 3-H absorption by 3·9 ±

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* An NOE study of the conformation of 2-acetylfurans, in which the separation between the two irradiation frequencies was 5—6 Hz, has recently been reported by K.-I. Dahlquist and A. R. Hornfeldt, *Tetrahedron Letters*, 1971, 3837.

† This is not a maximum NOE as the irradiating power level was kept low to minimise simultaneous irradiation of the high-field methyl absorption. The 7·6% increase in the 6-H absorption on irradiating the high-field methyl absorption is probably due to unavoidable overlap of the irradiating band with the low-field methyl absorption.

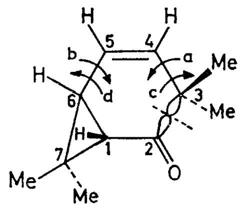
[3] (*a*) R. A. Bell and J. K. Saunders, *Canad. J. Chem.*, 1970, **48**, 1114; (*b*) G. E. Bachers and T. Schaefer, *Chem. Rev.*, 1971, **71**, 617.

[4] For tests of significance see: O. L. Davies, 'Statistical Methods in Research and Production,' Oliver and Boyd, Edinburgh, 1947, ch. 4.

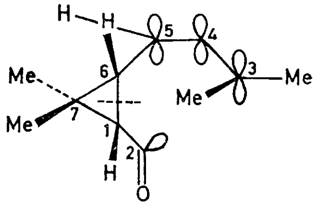
6·2%. (The probability of the two enhancements being equal is <0·1%, and the probability of the smaller enhancement being equal to zero is 7·2%[4]). Therefore, the low-field methyl absorption is due to the methyl group *cis* to 3-H. Extrapolation to CCl_4 solution by measuring the two absorptions in C_6H_6–CCl_4 mixtures showed that the absorptions at δ 1·754 and 1·734 p.p.m. are due to the vinylic methyl groups *cis* and *trans* to 3-H respectively.

Similar NOE experiments with 2-methylpent-2-ene (IV) in CCl_4 solution showed that the low-field methyl absorption (δ 1·649 p.p.m.) is due to the methyl group *cis* to 3-H (17·6 ± 5·5% NOE) and the high-field methyl absorption (δ 1·575 p.p.m.) is due to the methyl group *trans* to 3-H (7·0 ± 3·6% NOE).

We are now able to say that the stereochemical assignments made by Baldwin and Krueger[2] for (Ib) and (Ic) and for (IIb) and (IIc), should *both* be reversed. This double reversal means that the reported[2] stereochemical course for the photochemical transformation (I) $\longrightarrow$ (II) is still correct, *i.e.* (Ib) $\longrightarrow$ (IIb), (Ic) $\longrightarrow$ (IIc). We feel that the stereochemical course is that which would be expected if minimisation of non-bonded interaction were the major controlling factor during the rearrangement. Assuming the rearrangement to be initiated by cleavage of C(2)–C(3), *i.e.* α-cleavage (λ > 300 nm), giving an alkyl-acyl diradical,[5] C(2) and C(3) could move apart in a variety of ways by rotation of C(3)–C(4) and C(5)–C(6): (i) if rotation of C(3)–C(4) and C(5)–C(6) occur as depicted in (V) by the arrows a or c, and d respectively, C(3), or the methyl groups attached to C(3), is forced into collision with the *endo*-methyl group at C(7); (ii) if rotation of C(3)–C(4) and C(5)–C(6) occur as shown by c and b respectively, the *endo*-methyl group at C(3) is forced into collision with C(2); (iii) if rotation of C(3)–C(4) and C(5)–C(6) occur as shown by a and b respectively, no serious non-bonded interactions are encountered. Furthermore this mode would produce the allyl radical C(3)–C(4)–C(5) with the minimum rotation of C(3)–C(4).



(V)



(VI)

After rotation of C(3)–C(4) and C(5)–C(6) as described in (iii), the diradical would be in the preferred conformation for cleavage of the cyclopropane,[6] shown in (VI). This allows good overlap of C(1)–C(6) with the adjacent atomic orbitals at C(2) and C(5). Cleavage of C(1)–C(6) would complete the rearrangement, generating a keten function from C(1)–C(2) and a *trans*-double bond from C(5)–C(6).

Rearrangement as depicted in (V) by the arrows a and b therefore appears the most favourable course for minimisation of non-bonded interaction and produces the observed stereochemical change for the conversion of (I) $\longrightarrow$ (II). Our rationalisation favours a non-concerted rearrangement.

EXPERIMENTAL

N.m.r. spectra were determined using a Varian HA100 spectrometer (δ in p.p.m.). 4-Methylpenta-1,3-diene (III) was prepared as previously described.[1] 2-Methylpent-2-ene (IV) was prepared in a similar manner by dehydration of 2-methylpentan-2-ol in dimethyl sulphoxide at 165°. The two olefins produced were separated by preparative g.l.c. (30% S.E. 30; 50°).

Methyl trans-*3,3,7-Trimethylocta-4,6-dienoate* (IIa).—3-Methylcar-4-en-2-one[1] (2·6 g) in ether (550 ml) and methanol (7·5 ml) at 15° under nitrogen was irradiated (450 W Hanovia medium-pressure mercury-arc lamp—Pyrex filter) until all the starting material had reacted as judged by t.l.c. and g.l.c. The solvent was evaporated and the crude ester was purified by preparative g.l.c. (15% Carbowax 20M, 7 ft × ¼ in, 150°). The ester had $\nu_{max.}$ (film) 1734, 1660, and 1243 cm^{-1}; δ (CCl_4) 6·03 (2d, 5-H, $J_{4,5}$ 15 Hz, $J_{5,6}$ 10 Hz), 5·63 (broad d, 6-H, $J_{5,6}$ 10 Hz, $J_{6,Me}$ 1 Hz), 5·46 (d, 4-H, $J_{4,5}$ 15 Hz), 3·52 (s, OMe), 2·17 (s, 2-H_2), 1·68 (broad s, vinylic Me_2), and 1·09 (s, 3-Me_2). Simultaneous irradiation of the 6-H resonance at δ 5·63 p.p.m. resolved the vinylic methyl absorption at δ 1·68 p.p.m. into two singlets (δ 1·734 and 1·718 p.p.m.).

General NOE Procedure.—The procedure described by Bell and Saunders[3a] was followed. The solutions were filtered and degassed, and Me_4Si was used as an internal lock. A suitable internal standard was added to each solution. The strength of the second r.f. field was measured on an oscilloscope. As the difference in the chemical shifts of the two vinylic methyl absorptions, which had to be irradiated separately, was very small, the concentration of the solutions was kept low (2—4% w/v), and the strength of the second r.f. field was kept below that required to produce a maximum NOE so that the frequency range of the irradiating band was as narrow as possible. The most suitable power level was found to be 28 mV. This gave a reasonable enhancement in the olefinic proton absorption when applied to the *cis*-methyl absorption, and a smaller enhancement when applied to the *trans*-methyl absorption. Ideally, the enhancement from irradiation of the *trans*-

	(IIa) (4% w/v)		(III) (2% w/v)	
Solvent (C_6H_6 : CCl_4, v/v)	Low-field Me (δ)	High-field Me (δ)	Low-field Me (δ)	High-field Me (δ)
5 : 0	1·642	1·613	1·591	1·542
4 : 1	1·658	1·628	1·632	1·587
3 : 2	1·678	1·649	1·660	1·619
2 : 3	1·697	1·672	1·691	1·657
1 : 4	1·712	1·692	1·726	1·698
0 : 5	1·734	1·718	1·762 †	1·740 †

† These values differ slightly from those given in the Discussion (from ref. 1) which are for a 1M solution.

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[5] N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 1972 **5**, 92.

[6] W. G. Dauben and R. E. Wolf, *J. Org. Chem.*, 1970, **35**, 2361, and references therein.

methyl absorption should be negligible, but the power level required for this would also give a much smaller enhancement from the *cis*-methyl group.

An average of ten integrals were recorded for the olefinic proton and the internal standard for each irradiation position.

Mixed Solvent Measurements with (IIa) *and* (III).—The chemical shifts of the two vinylic methyl absorptions were measured with simultaneous irradiation of 6-H and 3-H respectively.

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