The Photochemical Transformation of 3-Methylcar-4-en-2-one into Derivatives of 3,3,7-Trimethylocta-4,6-dienoic Acid. Revised Stereochemical Assignments

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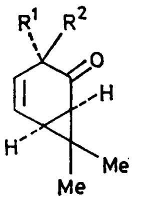
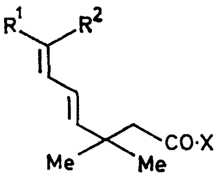
The stereochemical assignments made by Baldwin and Krueger for the photochemical transformation of 3-methylcar-4-en-2-one into derivatives of 3,3,7-trimethylocta-4,6-dienoic acid have been reinvestigated and revised. The stereochemistry of alkylation of eucarvone to give 3-alkylcar-4-en-2-one derivatives was found to occur as expected, from the least hindered face of the intermediate anion. Differentiation between the two methyl groups of 4-methylpenta-1,3-diene by n.m.r. spectroscopy (chemical shift difference 0·02 p.p.m.) was accomplished by utilising the thermal [1,5] hydrogen migration in 5,5,5-trideuterio-4-trideuteriomethylpenta-1,3-diene.

THE photochemical transformation of 3-methylcar-4-en-2-one (Ia) into derivatives of 3,3,7-trimethylocta-4,6-dienoic acid (II), first reported by Bellamy and Whitham,[1] has been further studied by Baldwin and Krueger [2] to determine the stereochemical changes involved in this reaction, *viz.* the stereochemical relation between the methyl groups at C(3) in the ketone (Ia) and the vinylic methyl groups in the derivatives (IIa) or (IIb). However, the stereochemical assignments in deuterium-labelled starting material and product made by the latter workers appeared to us to be unreliable and we have therefore re-examined these assignments. In this paper we present evidence which demonstrates that the stereochemical assignments for the labelled starting material should be reversed, and that those for the labelled product are uncertain.



(I)

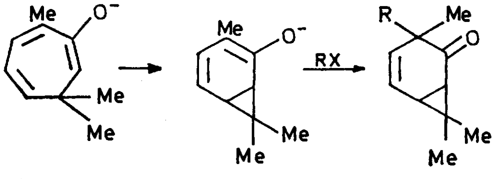
a; $R^1 = R^2 = Me$
b; $R^1 = PhCH_2$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = PhCH_2$
d; $R^1 = CD_3$, $R^2 = Me$
e; $R^1 = Me$, $R^2 = CD_3$



(II)

a; $R^1 = R^2 = Me$, $X = C_6H_{11}NH$
b; $R^1 = R^2 = Me$, $X = MeO$
c; $R^1 = Me$, $R^2 = CD_3$, $X = MeO$
d; $R^1 = CD_3$, $R^2 = Me$, $X = MeO$

To determine the stereochemical origin of the vinylic methyl groups in the ester (IIb), Baldwin and Krueger prepared 3-methylcar-4-en-2-one stereospecifically labelled with a trideuteriomethyl group. This was accomplished by (*a*) alkylation of the enolate ion of eucarvone (2,6,6-trimethylcyclohepta-2,4-dienone) with trideuteriomethyl iodide, and (*b*) alkylation of 2-trideuteriomethyl-6,6-dimethylcyclohepta-2,4-dienone with unlabelled methyl iodide. Formation of 3-methylcar-4-en-2-one probably occurs by alkylation of the enolate ion of car-3-en-2-one (3,7,7-trimethylbicyclo[4,1,0]hept-3-en-2-one), the valence tautomer of the enolate ion of eucarvone (see Scheme 1).[3a]



SCHEME 1

The n.m.r. spectrum (CCl_4 solution) of unlabelled 3-methylcar-4-en-2-one shows four singlets for the methyl absorptions, at δ 1·25, 1·07, 1·03, and 0·95 p.p.m. from tetramethylsilane. Alkylation of unlabelled eucarvone with trideuteriomethyl iodide gave methylcarenone which gave no signal at δ 1·07 p.p.m., whereas alkylation of labelled eucarvone with unlabelled methyl iodide gave methylcarenone which gave no signal at δ 1·03 p.p.m. Thus the n.m.r. signals with the smallest chemical shift difference are those due to the methyl groups at C(3). Baldwin and Krueger assigned the signals at δ 1·07 and 1·03 (1·02 in ref. 2) p.p.m. to the *endo*- and *exo*-methyl groups, respectively, because the *endo*-methyl group lies near the plane of the carbonyl group.

If this assignment is correct, then alkylation of the bicyclic ion (IV) must occur exclusively from the most hindered face of the molecule. We think this extremely unlikely when one face of the enolate ion is unhindered and the other is hindered by one of the methyl groups at C(7). Thus, we feel that stereochemical assignment on the basis of such a small chemical shift difference is unreliable, especially when other considerations are overwhelmingly opposed to it. In any case, these assignments are inconsistent with those made for 2,2-dimethyl-4-t-butylcyclohexanone, in which the absorption at highest field is assigned to the equatorial methyl group.[4]

We have now demonstrated that alkylation does in fact occur from the least hindered face of the enolate ion by comparative n.m.r. studies using 3-methyl- (Ia) and

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[1] A. J. Bellamy and G. H. Whitham, *J. Chem. Soc.*, 1964, 4035.

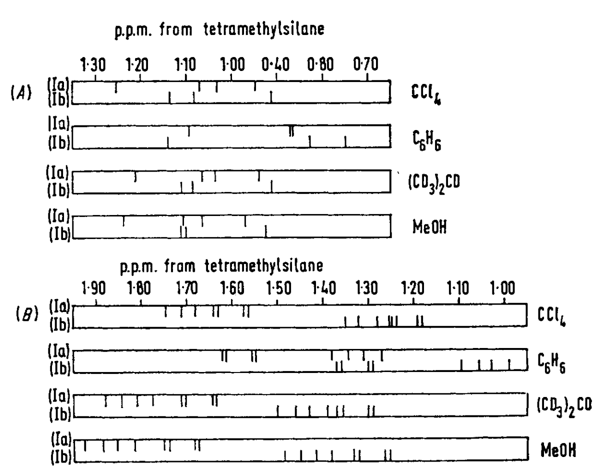
[2] J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 2396.

[3] (*a*) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Amer. Chem. Soc.*, 1956, **78**, 180; (*b*) E. J. Corey and H. J. Burke, *ibid.*, p. 174.

[4] B. J. L. Huff, F. N. Tuller, and D. Caine, *J. Org. Chem.*, 1969, **34**, 3070.

3-benzyl-car-4-en-2-one (Ib). If alkylation with benzyl chloride occurred from the most hindered face of the ion, compound (Ic) would be the product, with the benzyl group *cis* to the cyclopropane ring, whereas if alkylation occurred from the least hindered face, compound (Ib) would be the product, with the benzyl group *trans* to the cyclopropane ring. In the n.m.r. spectrum of compound (Ic) we might expect the phenyl group to shield the *endo*-methyl group at C(7), but in compound (Ib) there should be no such effect.

Preliminary examination of the n.m.r. spectra of CCl_4 solutions of 3-methyl- and 3-benzyl-car-4-en-2-one shows that the chemical shifts of the methyl absorptions are very similar in both compounds. However, the chemical shifts of the cyclopropyl protons at C(1) and C(6) in benzylcarenone are 0·40 p.p.m. upfield from those in methylcarenone. A more quantitative evaluation of these effects was obtained by comparison of the chemical shifts of absorption due to both methyl groups and cyclopropyl protons in four solvents extrapolated to infinite dilution (Figure).



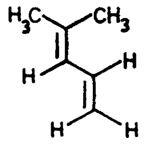
Methyl (*A*) and cyclopropyl (*B*) proton n.m.r. absorptions of 3-methyl- (Ia) and 3-benzyl-car-4-en-2-one (Ib)

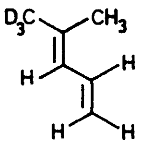
These observations argue strongly in favour of (Ib) being the structure of 3-benzylcar-4-en-2-one, and against structure (Ic). In structure (Ic) the phenyl group would be unable to adopt a position in which it would shield the cyclopropyl protons. In contrast, structure (Ib) can adopt a conformation in which the cyclopropyl protons lie directly above the plane of the aromatic ring.* Furthermore, in this conformation the *exo*-methyl group at C(7) is also likely to be shielded, but to a smaller extent as it is further removed from the phenyl group. It follows from Baldwin and Krueger's results that the methyl groups at C(7) are those with the largest chemical shift difference *i.e.* 1·251 and 0·949 p.p.m. in CCl_4 (the methyl absorptions in methylcarenone are virtually independent of concentration). We assign these absorptions to the *exo*- and *endo*-methyl groups at C(7) respectively, since the *endo*-methyl group lies above the planes of both the double bond and the carbonyl group, and would therefore be the most shielded. The methyl group at C(7), which has the largest upfield shift on passing from methylcarenone to benzylcarenone, is in fact the one which absorbs at δ 1·251 p.p.m., the *exo*-methyl group at C(7), as anticipated (Δ 0·116 p.p.m.).†

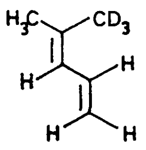
The assignment of structure (Ib) to 3-benzylcar-4-en-2-one strongly suggests that alkylation of the enolate ion (IV) occurs, as expected, from the least hindered face of the molecule. Thus, alkylation with trideuteriomethyl iodide would give compound (Id), and not (Ie) as previously reported.[2] Similarly, alkylation of 2-trideuteriomethyl-6,6-dimethylcyclohepta-2,4-dienone with undeuteriated methyl iodide would give compound (Ie) and not (Id).‡

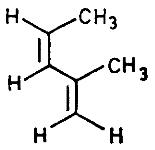
The configurational assignments for the photocleavage products (IIc) and (IId) are also based on rather unreliable evidence. The vinylic methyl groups in the undeuteriated diene (IIb) absorb at δ 1·734 and 1·718 p.p.m. (CCl_4 solution) in the n.m.r. spectrum. The signal at lowest field was assigned to the methyl group *trans* to 6-H on the basis that it would be more deshielded by the unsaturated system than the *cis*-methyl group.[2]

To test this argument we have studied the n.m.r. spectrum of 4-methylpenta-1,3-diene (V). The two methyl groups in the diene (V) absorb at δ 1·754 and 1·734 p.p.m. (CCl_4 solution). To observe the two singlets it is necessary to spin-decouple 3-H.


(V)


(Vd)


(Ve)


(VI)

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* The methylene protons above the plane of the aromatic ring in paracyclophanes show an upfield shift, relative to cyclohexane, of 0·53, 0·8, and 1·2 p.p.m. for [12]-,[5a] [10]-,[5a,5b] and [9]-paracyclophane,[5b] respectively.

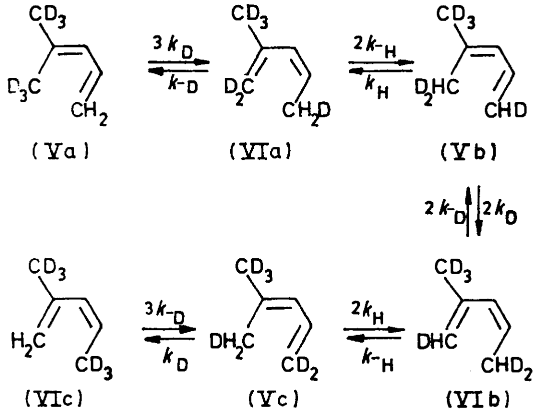
† The results of approximate shielding calculations (C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1, p. 595) support our interpretation of the observed n.m.r. spectra of compounds (Ia) and (Ib), although we do not wish to place too much emphasis on these as the exact conformation of the phenyl group in compound (Ib) is uncertain.

‡ These conclusions are valid even if the bicyclic ion (IV) is not an intermediate in the formation of compound (I) from the monocyclic ion (III), *i.e.* if ring bridging and alkylation occur simultaneously.

[5] (*a*) J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846; (*b*) D. J. Cram and M. Goldstein, *ibid.*, 1963, **85**, 1063.

One possible way to distinguish between the two methyl absorptions is by an NOE experiment.[6] Irradiation at the absorption frequency of the methyl group *cis* to 3-H should give increased intensity to the 3-H absorption, whereas irradiation at the absorption frequency of the *trans*-methyl group should give little change in the intensity of the 3-H absorption. However, such an experiment is difficult to perform at present owing to the very small chemical shift difference between the two methyl absorptions. We therefore turned to a chemical means of distinguishing between them.

Frey and Ellis have shown that 4-methylpenta-1,3-diene, on heating in the gas phase, equilibrates with *cis*-2-methylpenta-1,3-diene (VI) by a reversible, unimolecular [1,5] migration of hydrogen.[7] Only the methyl group *cis* to the carbon chain (*trans* to 3-H) would be involved in this reaction, and we have therefore studied this reaction using 4-methylpenta-1,3-diene with both methyl groups fully deuteriated. In the course of the equilibration of this molecule (Scheme 2), the *cis*-methyl group would incorporate ^{1}H atoms from C(1), ^{2}H atoms being transferred to C(1), and would therefore absorb in the ^{1}H n.m.r. spectrum; the *trans*-methyl group would remain fully deuteriated and would not appear in the n.m.r. spectrum.* The [1,5] migration of hydrogen in *cis*-penta-1,3-diene has been studied by use of deuterium labelling in a similar manner.[8]



SCHEME 2

5,5,5-Trideuterio-4-trideuteriomethylpenta-1,3-diene (Va) was heated in the gas phase at 250° during five half-lives ($t_{\frac{1}{2}}$ 56 min at 250° was calculated from data given by Frey and Ellis,[7] assuming a primary kinetic isotope effect of 4·4 for all [1,5] hydrogen transfer steps; $k_{\mathrm{H}}/k_{\mathrm{D}} = 1{\cdot}15 \exp 1400/RT$ for *cis*-penta-1,3-diene [8]). After this time the product was a mixture of compounds (V) (90·4%) and (VI) (9·6%). The mixture of compounds (Va), (Vb), and (Vc) was isolated by preparative g.l.c. and analysed by ^{1}H n.m.r. spectroscopy. With simultaneous irradiation of the 3-H proton, the methyl absorption of the mixture appeared as five lines at δ 1·729, 1·708, 1·686, 1·667, and 1·643 p.p.m. This analysed for a 1 : 1 : 1 triplet for compound (Vc), centred at δ 1·708 p.p.m., and a 1 : 2 : 3 : 2 : 1 quintet for (Vb), centred at δ 1·686 p.p.m. The geminal ^{1}H–^{2}H coupling constant was *ca.* 2·1 Hz in both compounds (Vb) and (Vc) (*cf.* 2·3—2·4 Hz for $-\mathrm{CHD{\cdot}CO}-$, $-\mathrm{CO{\cdot}CH_2D}$, and $-\mathrm{CO{\cdot}CHD_2}$ in partially deuteriated butan-2-one [9a]), and the chemical shift difference was 0·022 p.p.m.

Simulation of Scheme 2 on an analogue computer using the known rate constants for [1,5] hydrogen migration in this system,[7] and a primary kinetic isotope effect of 4·4,[8] gave a plot of the concentrations of all six species against time. From these data we calculated the abundance of each species after five half lives [(Va) (12·6), (Vb) (54·2), (Vc) (23·8), (VIa) (3·2), (VIb) (5·5), and (VIc) (0·9%)]. After complete equilibration (ten half-lives) the abundance of each species was (Va) (9·2), (Vb) (53·8), (Vc) (26·7), (VIa) (3·2), (VIb) (6·0), and (VIc) (1·1%) (assuming no isotope effect on the ground-state energies). Using these data for the relative abundance of compound (Vb) and (Vc) after five half-lives *i.e.* 2·28 : 1, the relative intensities of the five lines in the ^{1}H n.m.r. spectrum should be (from low to high field) 3·6, 4·6, 5·6, 2·0, and 1·0. The observed spectrum was in fair agreement with these values, although exact integration was not possible.

To relate the chemical shifts observed for the methyl absorption in compounds (Vb) and (Vc) to the methyl absorption in undeuteriated 4-methylpenta-1,3-diene, it is necessary to correct for the isotopic shifts caused by deuterium, both geminal and in the adjacent trideuteriomethyl group, in compounds (Vb) and (Vc).

It is known that successive substitution of deuterium for hydrogen in a methyl group causes an upfield shift in the signals of the remaining proton(s), and that the shift caused by the second deuterium atom is equal to that caused by the first.[9] It therefore follows that since compound (Vb) absorbs at higher field by 0·022 p.p.m. than compound (Vc), 4-trideuteriomethyl-*cis*-penta-1,3-diene (Vd) would absorb at 0·022 p.p.m. downfield from compound (Vc) *i.e.* at δ 1·730 p.p.m.

In order to compensate for the effect of the adjacent trideuteriomethyl group on the chemical shift we prepared a mixture of 4-trideuteriomethyl-*cis*-penta-1,3-diene (Vd) and 4-trideuteriomethyl-*trans*-penta-1,3-diene (Ve) (see Experimental section). With simultaneous irradiation of the 3-H, the methyl absorption of the mixture appeared as two singlets at δ 1·753 and 1·730 p.p.m. ($\mathrm{CCl_4}$ solution). At the same concentration in $\mathrm{CCl_4}$, and with simultaneous irradiation of 3-H, the

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* Interconversion of the two methyl groups in 4-methylpenta-1,3-diene is unlikely to occur to a significant extent under our reaction conditions since $<2\%$ of *trans*-2-methylpenta-1,3-diene was formed during equilibration for 10 half-lives.[7] See also H. M. Frey, A. M. Lamont, and R. Walsh, *Chem. Comm.*, 1970, 1583.

[6] R. A. Bell and J. K. Saunders, *Canad. J. Chem.*, 1970, **48**, 1114 and references therein.

[7] H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 1965, 4770.

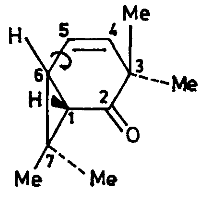
[8] W. R. Roth and J. Konig, *Annalen*, 1966, **699**, 24.

[9] (*a*) O. S. Tee and J. Warkentin, *Canad. J. Chem.*, 1965, **43**, 2424; (*b*) G. J. Martin, M.-T. Quemeneur, and M. L. Martin, *Bull. Soc. chim. France*, 1970, 4082; (*c*) P. Laszlo and Z. Welvart, *ibid.*, 1966, 2412.

diene (V) absorbs at δ 1·754 and 1·734 p.p.m. Thus, the trideuteriomethyl group causes upfield shifts of 0·001 and 0·004 p.p.m.* Using these values, the absorption of the *cis*-methyl group in undeuteriated 4-methylpenta-1,3-diene (V) is calculated to occur at δ 1·731 or 1·734 p.p.m., in excellent agreement with the observed value for compound (V) (δ 1·734 p.p.m.). The singlet at δ 1·754 p.p.m. in the spectrum of the diene (V) must therefore be due to the methyl group which is *trans* to the carbon chain.

These assignments are the reverse of those given by Baldwin and Krueger [2] for compound (IIb). Although compound (IIb) contains an ester group, the latter is well removed from the vinylic methyl groups and any intramolecular shielding or deshielding effect due to the ester group is expected to be very small.† Any intermolecular effect will also be small.‡ Thus the assignments made by Baldwin and Krueger for the ester (IIb) may also need to be reversed. However, the presence of an alkyl substituent, *i.e.* C(3) in the ester (IIb), which is absent in the diene (V) may have a small, but in this case significant, effect upon the position of the methyl group absorption. The decision is therefore less unambiguous in this case than for methylcarenone (Ia).

While the results of Baldwin and Krueger [2] show conclusively that the transformation of compound (Ia) into the ester (IIb) occurs in a highly stereoselective manner, and that rotation about C(5)–C(6) has to occur in the direction shown in (VII) [rotation of C(6) relative to C(5)] to produce a *trans*-double bond in compound (IIb), the direction of rotation about C(3)–C(4), *i.e.* conrotatory or disrotatory with respect to movement in the C(5)–C(6) bond, depends, respectively, upon whether their configurational assignments in the ester (IIb) are correct, or need to be reversed.



(VII)

EXPERIMENTAL

N.m.r. spectra were determined using a Varian HA100 spectrometer (δ in p.p.m.). G.l.c. analyses were performed on a column (50 m × 0·25 mm i.d. capillary) coated with Apiezon L, except where otherwise stated.

Alkylation of Eucarvone.—Eucarvone [3b] (5·9 g, 0·033 mol) was added dropwise under nitrogen to a stirred suspension of sodium hydride (1·67 g, 0·066 mol) in dry dioxan (23 ml), and the mixture was heated under reflux during 2 h. After cooling to 20°, dry alkyl halide (0·05 mol) was added and stirring was continued during a further 2 h. The excess of sodium hydride was destroyed by careful addition of acetic acid, the mixture was poured into brine (200 ml), and the product was extracted with ether (2 × 50 ml). The ethereal solution was washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated to give the crude product.

Alkylation with methyl iodide gave a mixture consisting mainly of 3-methylcar-4-en-2-one and 2,6,6,7-tetramethylcyclohepta-2,4-dienone (4 : 1). The products were separated by preparative g.l.c. (15% Carbowax 20M; 6 ft × $\frac{1}{4}$ in; 100°; He carrier gas).

The 3-methylcarenone had $\nu_{max.}$ (film) 1695 cm^{-1}, δ (CCl_4) 5·72 (two q, 5-H as the X part of an ABX system, $J_{4,5}$ 10·0 Hz), 5·48 (d, 4-H), 1·66 (m, 2H, 1- and 6-H as the AB part of an ABX system, $J_{1,6}$ 6·8, $J_{5,6}$ 4·0, $J_{1,5}$ 0·8 Hz), 1·24, 1·06, 1·03, and 0·95 (four s, 3-,3-,7-, and 7-CH_3).

2,6,6,7-Tetramethylcyclohepta-2,4-dienone had $\nu_{max.}$ 1660 cm^{-1}, $\lambda_{max.}$ (EtOH) 304 nm (*cf.* eucarvone, ref. 3*b*), δ (CCl_4) 6·35 (m, 3-H), 5·75 (m, 4- and 5-H), 2·42 (q. 7-H, $J_{7,Me}$ 7·4 Hz), 1·90 (d, 2-CH_3, $J_{3,Me}$ 1·3 Hz), 1·05 (d, 7-CH_3, $J_{7,Me}$ 7·4 Hz), 1·11 and 1·04 (two s, 2 × 6-CH_3) (*cf.* eucarvone [11]).

Alkylation with benzyl chloride gave 3-benzylcar-4-en-2-one (4·5 g, 48%), b.p. 92—94° at 0·06 mmHg (lit.,[3b] 117—119° at 1 mmHg), $\nu_{max.}$ (film) 1690, 1608, and 1006 cm^{-1} (lit.,[3b] 1695, 1611, and 1004 cm^{-1}), $\lambda_{max.}$ (EtOH) 290 nm (log ε 2·00) [lit.,[3b] 290 nm (log ε 2·05)], δ (CCl_4) 7·1 (m, 5H, phenyl), 5·8 (two q, 5-H as the X part of an ABX system, $J_{4,5}$ 10·0 Hz), 5·38 (d, 4-H, $J_{4,5}$ 10·0 Hz), 2·88 and 2·50 (two d, 2H, CH_2Ph, J_{gem} 13·0 Hz), 1·28 (m, 2H, 1- and 6-H as the AB part of an ABX system), and 1·20, 1·11, and 0·99 (three s, 3-CH_3 and 2 × 7-CH_3), as the only product.

Preparation of 4-*Methylpenta*-1,3-*diene by Dehydration of* 2-*Methylpent*-4-*en*-2-*ol.*—2-Methylpent-4-en-2-ol was prepared by the addition of allylmagnesium bromide to acetone.[12] The product (71%), b.p. 44° at 27 mmHg (lit.,[12] 46—46·5° at 30 mmHg), was shown to be pure by g.l.c.

The alcohol (2·0 g) was dehydrated by heating a solution in dimethyl sulphoxide (10 ml) under reflux during 14 h.[13] The dehydration products were then distilled from the reaction mixture and collected in a receiver at −80°. Analysis by g.l.c. (40°; bis-2-methoxyethyl adipate) showed the product to be a mixture of four dienes (in order of elution), 2-methylpenta-1,4-diene (31·8), *cis*-2-methylpenta-1,3-diene (1·4), *trans*-2-methylpenta-1,3-diene (23·9), and 4-methylpenta-1,3-diene (42·9%).

trans-2-Methylpenta-1,3-diene was removed from the mixture by the formation of its adduct with maleic anhydride.[7,14] The mixture (0·8 g) in dioxan (10 ml) at 0°

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* In compounds (IIb)—(IId) the shifts are 0·002 and 0·006 p.p.m.[2]

† For methyl *cis*-2,6-dimethylhepta-3,5-dienoate, in which the ester group can get close to the vinylic methyl groups, the latter absorb at δ 1·78 and 1·71 p.p.m. whereas for the *trans*-isomer, in which the ester group is well removed, they absorb as a single peak at δ 1·70 p.p.m. (5-H was not simultaneously irradiated).[10]

‡ Admixture of an equimolar quantity of methyl 3-methylbutanoate with 4-methylpenta-1,3-diene causes a downfield shift in both methyl signals of 0·002—0·003 p.p.m.

[10] P. M. Collins and H. Hart, *J. Chem. Soc.* (*C*), 1967, 1197.

[11] A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, 1968, **90**, 2347.

[12] H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, 1942, **7**, 326.

[13] V. J. Traynelis, W. L. Hergenrother, J. R. Livington, and J. A. Valicenti, *J. Org. Chem.*, 1962, **27**, 2377; V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *ibid.*, 1964, **29**, 123.

[14] G. B. Bachman and C. G. Goebel, *J. Amer. Chem. Soc.*, 1942 **64**, 787.

was treated with maleic anhydride (1·0 g) and a trace of hydroquinone during 3 days. The solvent and remaining dienes were distilled from the mixture and separated by preparative g.l.c. (30% SE 30 at 80°; 20 ft × $\frac{1}{4}$ in).

The n.m.r. spectrum (CCl_4) of 2-methylpenta-1,4-diene showed the following absorptions: δ 5·7 (m, 4-H), 5·0 (two m, 5-H_2), 4·67 (m, 1-H_2), 2·70br (d, 3-H_2, $J_{3,4}$ 7 Hz), and 1·70 (m, 2-Me).

The n.m.r. spectrum (CCl_4) of 4-methylpenta-1,3-diene showed the following absorptions: δ 6·4 (two overlapping t, 2-H, $J_{2,3}$ 10·5, $J_{1,2}$ 17 and 10·5 Hz), 5·74br (d, 3-H, $J_{2,3}$ 10·5 Hz, further coupled to Me group), 4·9 (m, 1-H_2), and 1·82br (s, Me). Simultaneous irradiation of 3-H at δ 5·74 resolved the methyl absorption into two singlets at δ 1·754 and 1·734. The spectrum was identical with that given by a sample of 4-methylpenta-1,3-diene prepared by a different route.[7,14]

5,5,5-*Trideuterio*-4-*trideuteriomethylpenta*-1,3-*diene*.—The method of synthesis was identical with that for the undeuteriated diene already described. However, dehydration of $[^{2}H_6]$-2-methylpent-4-en-2-ol, prepared from allylmagnesium bromide and $[^{2}H_6]$acetone, gave a different ratio of products [2-methylpenta-1,4-diene (16·6), *cis*-2-methylpenta-1,3-diene (1·8), *trans*-2-methylpenta-1,3-diene (20·5), and 4-methylpenta-1,3-diene (61·1%)]. 2-Methylpenta-1,4-diene and 4-methylpenta-1,3-diene were isolated as before.

The n.m.r. spectrum (CCl_4) of 1,1-dideuterio-2-trideuteriomethylpenta-1,4-diene differed from that of the undeuteriated compound in that absorption due to the methyl group at C(2) and the protons at C(1) was absent, and that due to the protons at C(3) now appeared as a doublet of triplets ($J_{3,4}$ 7·0, $J_{3,5}$ 1·2 Hz). The n.m.r. spectrum (CCl_4) of 5,5,5-trideuterio-4-trideuteriomethylpenta-1,3-diene showed no methyl absorption, and 3-H appeared as a sharper doublet.

Thermal Rearrangement of 5,5,5-*Trideuterio*-4-*trideuteriomethylpenta*-1,3-*diene*.—The reaction vessel (240 ml), containing the deuteriated diene (0·240 g), was cooled to −196° and sealed at 0·1 mmHg pressure. The diene was heated at 250—260° during five half-lives (see Discussion section). Analysis of the product by g.l.c. showed two components, *cis*-2-methylpenta-1,3-diene (9·6%) and 4-methylpenta-1,3-diene (90·4%), with a trace of *trans*-2-methylpenta-1,3-diene. The products were separated by preparative g.l.c. as described previously.

The n.m.r. spectrum (1M in CCl_4) of the separated 4-methylpenta-1,3-diene showed the following absorptions: δ 6·4 (m, 4-H), 5·7 (d, 3-H), 4·9 (m, 5-H_2), and 1·7 (m, Me) (ratio 1·00 : 1·00 : 0·97 : 1·31). The chemical shifts of the lines in the multiplet due to the methyl protons were δ 1·739, 1·724, 1·718, 1·701, 1·695, 1·680, 1·663br, and 1·640. On simultaneous irradiation of the H-3 absorption at δ 5·7, the multiplet collapsed to five lines at δ 1·729, 1·708, 1·686, 1·667, and 1·643. The intensity ratios were in agreement with the expected values (see Discussion section). Undeuteriated 4-methylpenta-1,3-diene, at the same concentration in CCl_4 and with simultaneous irradiation at δ 5·7, showed two singlets at δ 1·754 and 1·734 for the methyl groups.

Preparation of cis- *and* trans-4-*Trideuteriomethylpenta*-1,3-*diene*.—Trideuteriomethylmagnesium iodide [0·056 mol; from $[^{2}H_3]$methyl iodide (0·06 mol)] in ether (150 ml) was treated with anhydrous cadmium chloride (0·028 mol) and the mixture was stirred at 25° for 1 h before addition of acetyl chloride (0·037 mol) with cooling and stirring. The mixture was stirred for a further 1 h at 25° before addition of allylmagnesium bromide [from allyl bromide (0·2 mol)] in ether (150 ml). After being stirred for 1 h, the mixture was hydrolysed by pouring on to ice–dilute hydrochloric acid and the product was isolated. The products, 4-methylpent-1-en-4-ol(87%) and 4-methylhepta-1,6-dien-4-ol (13%) were separated by preparative g.l.c. (30% SE 30; 120°). The n.m.r. spectrum of the purified 4-trideuteriomethylpent-1-en-4-ol was as expected, the methyl absorption appearing as a single sharp line, integrating for three protons.

The purified alcohol (2·0 g) was dehydrated by heating in dimethyl sulphoxide (10 ml) at 160° during 16 h.[13] Analysis of the hydrocarbon distillate by g.l.c. (40°; bis-2-methoxyethyl adipate) showed four components, 2-methylpenta-1,4-diene (27·0), *cis*-2-methylpenta-1,3-diene (1·0), *trans*-2-methylpenta-1,3-diene (30·5), and 4-methylpenta-1,3-diene (41·5%).

The 4-methylpenta-1,3-diene was separated from the other products as previously described. Its n.m.r. spectrum (1M in CCl_4) was identical with that described earlier for undeuteriated 4-methylpenta-1,3-diene. Simultaneous irradiation of 3-H caused the broad methyl signal to resolve into two singlets at δ 1·755 and 1·730.

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