

## Photochemistry of 7-syn-Isobutylnorborn-2-en-2-yl Methyl Ketone. Intramolecular Hydrogen Abstraction in an $\alpha,\beta$ -Unsaturated Ketone with Geometrically Equivalent $\alpha$ - and $\beta$ -Carbon Atoms

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Preparation and photolysis of 7-syn-isobutylnorborn-2-en-2-yl methyl ketone (7) and its deuteriated isomer (8) are described. Irradiation of (7) in its  $n,\pi^*$  band ( $\lambda > 3\ 400\ \text{\AA}$ ) leads to two volatile isomers (11) (55%) and (13) (10%), whilst (8) gives (11d) and (13d). The same products were obtained on irradiation of (7) and (8) in the  $\pi,\pi^*$  band ( $\lambda > 2\ 500\ \text{\AA}$ ), along with two additional ketones, the photoreduction product (16) and the dienone (25). These results indicate that isomerization of (7) occurs through hydrogen abstraction by the  $\beta$ -carbon atom of the enone system, but not the  $\alpha$ -carbon atom. Thus minimization of stereochemical and geometric differences between  $\alpha$  and  $\beta$  carbons relative to the abstractable hydrogen does not suffice to elicit abstraction at both centres. The structure of the bexane photoproduct (13) was secured through independent synthesis from olefinic ester (38a). Synthesis of (7), (8), and (13) made use of the novel reaction of a norbornene with trichloroacetyl isocyanate to form an unsaturated nitrile [as (31)  $\longrightarrow$  (34) and (38)  $\longrightarrow$  (39)].

INVESTIGATIONS in recent years have demonstrated that irradiation of several types of  $\alpha,\beta$ -unsaturated ketones leads to inter- or intra-molecular abstraction of hydrogen by the  $\beta$ -carbon atom of the enone system, with formation of a radical pair or biradical which goes on to form various disproportionation and/or coupling products [see equation (1)].<sup>1-3</sup> Quenching and sensitization studies suggest in several cases that this abstraction proceeds from a readily accessible triplet state. There are also instances of a formally analogous reaction involving intramolecular

hydrogen transfer to the  $\alpha$ -carbon atom of enone systems [equation (2)]. Not only are fewer examples of this second process available, but there appears to be less uniformity of mechanism here. Thus the conversion of taxinine and several of its derivatives [see (1)] into isomers of type (2) is reported<sup>4</sup> to be a sensitizable triplet reaction,<sup>†</sup> while cyclization of  $\gamma$ -dimethoxymethylcyclohexenones, as exemplified by the transformation of (3) into (4), occurs neither from the lowest  $\pi,\pi^*$  and  $n,\pi^*$  triplet states nor from the first singlet ( $n,\pi^*$ ) state, but rather from a reactive state either identical with, or reached from, the second singlet ( $\pi,\pi^*$ ) state.<sup>5</sup> Furthermore, a concerted [ $\sigma_2s + \pi_2s$ ] pathway was favoured<sup>4</sup> for the taxinine isomerization,<sup>‡</sup> but

<sup>†</sup> For another photoisomerization interpreted as a triplet process involving intramolecular hydrogen transfer to the  $\alpha$ -carbon of an enone see B. Gioia, A. Marchesini, G. D. Andreotti, G. Bocelli, and P. Sgarabotto, *J.C.S. Perkin I*, 1977, 410.

<sup>‡</sup> For this reason equation (2) cannot be regarded as completely general.

<sup>1</sup> W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, 1967, **89**, 5474; D. Belluš, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, 1969, **52**, 971; R. Reinfried, D. Belluš, and K. Schaffner, *ibid.*, 1971, **54**, 1517; W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, 1971, **93**, 5513; A. B. Smith, III, and W. C. Agosta, *ibid.*, 1973, **95**, 1961; J. A. Turner, V. Iyer, R. S. McEwen, and W. Herz, *J. Org. Chem.*, 1974, **39**, 117; A. Marchesini, U. M. Pagnoni, and A. Pinetti, *Tetrahedron Letters*, 1973, 4302.

<sup>2</sup> S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, 1972, **94**, 7797.

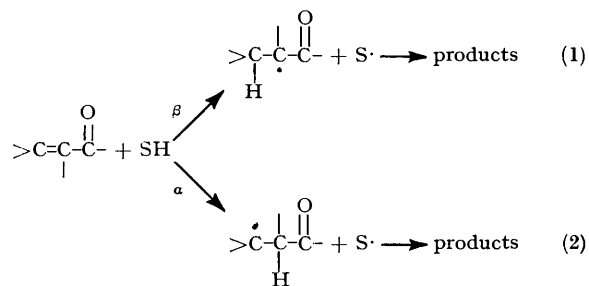
<sup>3</sup> A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, 1974, **96**, 3289.

<sup>4</sup> T. Kobayashi, M. Kurono, H. Sato, and K. Nakanishi, *J. Amer. Chem. Soc.*, 1972, **94**, 2863.

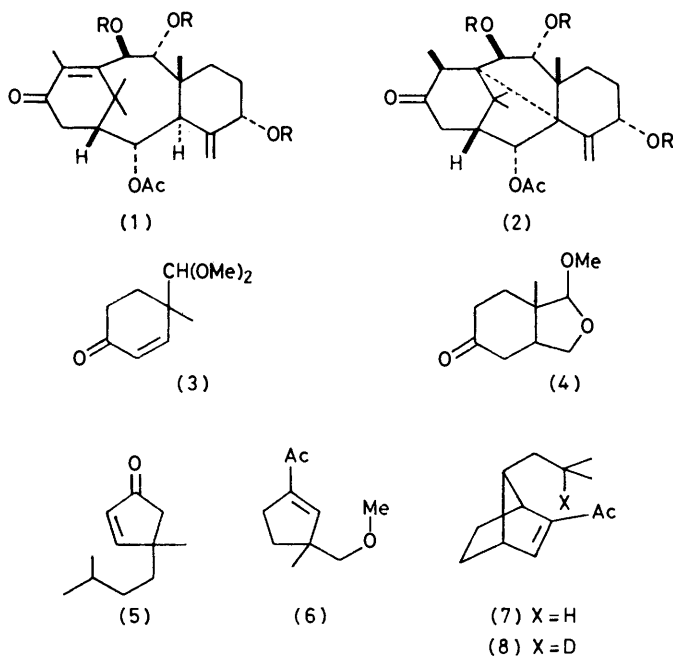
<sup>5</sup> J. Gloor and K. Schaffner, *Helv. Chim. Acta*, 1974, **57**, 1815; F. Nobs, U. Burger, and K. Schaffner, *ibid.*, 1977, **60**, 1607.

biradical intermediates have been advanced in the cyclization of (3) and related systems.<sup>5</sup>

An interesting and important question exists concerning the factors favouring photochemical hydrogen



transfer to the  $\alpha$ - or  $\beta$ -carbon atom of a particular enone. With one exception,\* there are no known cases in which abstraction by both centres has been shown to occur in a single molecule, although both processes may be geometrically feasible. In many of the examples of these two processes, however, there are steric or entropic factors that appear to favour transfer to one site or the



other. For example, we have studied intramolecular abstraction by the  $\beta$ -carbon atom in various cyclopentenones and 1-acylcyclopentenones, such as (5)<sup>2</sup> and (6),<sup>3</sup> which were specifically designed to favour this process by location of abstractable hydrogen in a 1,5-relationship to the  $\beta$ -carbon atom.† Similarly the polycyclic structure of the taxinine system (1) holds a transferable hydrogen quite close to the  $\pi$ -lobe of the  $\alpha$ -carbon atom in the

\* Herz *et al.*<sup>6</sup> have described the photochemistry of a cyclopentenone that appears to give both products. Unfortunately, the product of hydrogen abstraction by the  $\alpha$ -carbon atom is non-crystalline and available only in small amount.

† For evidence that a 1,5-relationship is indeed more favourable than 1,4 or 1,6, see ref. 7.

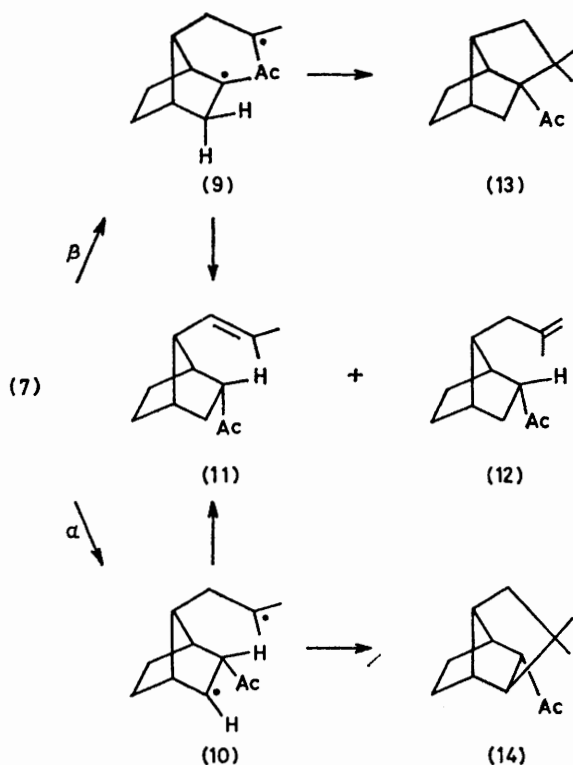
ground state. No doubt an important role also may exist for other factors, such as the availability of competing processes and the relative stability of intermediate species, in determining whether products are formed through abstraction by the  $\alpha$ - or the  $\beta$ -carbon atom, or indeed whether any such abstraction occurs at all. In view of the present uncertainty of mechanism, and with an interest in improving our ability to predict the course of such processes in other systems, we have sought in the present study to determine whether geometric and entropic factors alone can control the site of hydrogen abstraction. For this purpose we have prepared 7-*syn*-isobutylbicyclo[2.2.1]hept-2-en-2-yl methyl ketone (7) and its monodeuteriated derivative (8). In the favoured conformation of this compound the tertiary hydrogen of the isobutyl side-chain is essentially equidistant from the  $\alpha$ - and  $\beta$ -carbon atoms of the enone system [C(2) and C(3)]. Furthermore, in the ground state the acetyl group should remain preferentially in the *s-trans* or *s-cis* planar conformation to maximize overlap with the olefinic double-bond, and in this orientation it should have little steric interaction with the isobutyl group. The ketone (7) then provides a substrate in which the geometric and entropic differences between abstraction by  $\alpha$ - and  $\beta$ -carbon atoms are reduced to a minimum, and intramolecular photochemical hydrogen abstraction in such a system should be of particular interest. Below we describe first the photochemistry of (7) and (8) at both long and short wavelengths, and then the various preparative transformations connected with this study.

The significant question is whether photolysis of (7) results in abstraction of the readily available tertiary side-chain hydrogen by the  $\alpha$ - or the  $\beta$ -carbon atom, or both. These possibilities are summarized below. Transfer of hydrogen to the  $\beta$ -carbon would yield the intermediate biradical (9), while the corresponding transfer to the  $\alpha$ -position leads to (10). Disproportionation of either of these intermediates could yield (11) and/or (12), but intramolecular coupling would lead to a unique brexane derivative in each case, (13) from (9), and (14) from (10). We first examined the photolysis of (7) at long wavelengths and isolated the volatile photoproducts formed. Irradiation of (7) in benzene solution in its  $n,\pi^*$  band (0.0027 M,  $\lambda > 3400 \text{ \AA}$ ) furnished *ca.* 65% of two volatile isomers in the ratio 85:15. For the major product structure (11) follows from spectroscopic properties recorded in the Experimental section and from the chemical evidence summarized below. Base-catalysed equilibration of (11) led to partial inversion to give its *exo*-substituted epimer (15). Selective hydrogenation of each of these isobutenyl ketones gave the corresponding isobutyl compounds (16) and (17), respectively. Authentic samples of (16) and (17) were available through hydrogenation of (7), and samples prepared by the two routes were identical. The

<sup>6</sup> W. Herz, V. S. Iyer, M. G. Nair, and J. Saltiel, *J. Amer. Chem. Soc.*, 1977, **99**, 2704.

<sup>7</sup> S. Ayrál-Kaloustian, S. Wolff, and W. C. Agosta, *J. Amer. Chem. Soc.*, 1977, **99**, 5984.

*endo*-stereochemistry of the acetyl group in (11) is that expected if this photoisomer is formed by intramolecular hydrogen transfer from (9) or (10) as indicated above; this assignment of stereochemistry is also consistent with the fact that hydrogenation of (7) gave a 9 : 1 mixture of (17) and (16), respectively. This requires preferential *endo*-addition of hydrogen to (7), and it is known that in similar catalytic reduction of 2,7,7-trimethylnorborn-2-ene (18) the ratio of *endo* to *exo* addition of hydrogen is also 9 : 1.<sup>8</sup> In both (7) and (18) *exo*-approach to the double bond is hindered by the *syn*-7-alkyl substituent. Further confirmation of the stereochemistry of the acetyl group in these four ketones came from the chemical shifts to the *endo*- and *exo*-protons at C(2) adjacent to the carbonyl group. Treatment of both the isobutyl and the isobutenyl ketones with sodium carbonate in hot methan[<sup>2</sup>H]ol gave the corresponding tetradeuteriated ketones (19a), (20a) and (19b), (20b) with no difficulty. Comparison of the n.m.r. spectra of the deuteriated and non-deuteriated ketones then allowed straightforward identification of the signals due to the C(2) protons. The *exo*-proton of (11) appears well downfield from the

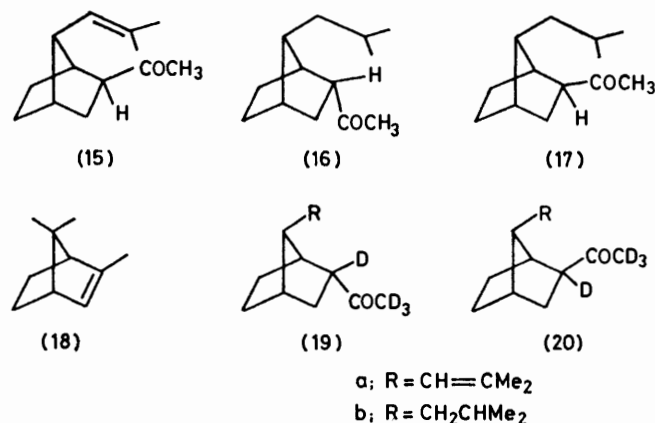


*endo*-proton of (15) ( $\delta$  2.92 vs. 2.02 p.p.m.), and the same relationship obtains for these signals in (16) and (17) ( $\delta$  2.85 vs. 2.14 p.p.m.). These differences conform to the general rule that *exo*-protons at C(2) in norbornanes resonate downfield from the corresponding *endo*-protons.<sup>9</sup>

\* We thank Professor Greene for a copy of the i.r. spectrum of (21).

<sup>8</sup> H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Amer. Chem. Soc.*, 1973, **95**, 2209.

Structure (13) for the minor isomer formed from (7) rests on several observations. The replacement of typical isopropyl methyl group absorption in the n.m.r. spectrum of (7) ( $\delta$  0.79, d,  $J = 7$  Hz, 6H) by two methyl



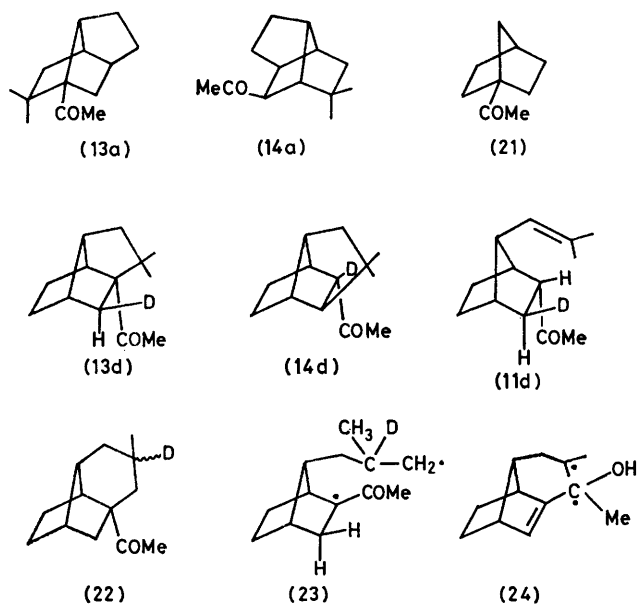
singlets ( $\delta$  0.97 and 1.06) signalled a new carbon-carbon bond to the side-chain tertiary centre. The unusually low frequency of carbonyl absorption (1 692  $\text{cm}^{-1}$ ) in the i.r. spectrum suggested the  $\alpha$ -trisubstituted ketone structure of (13) rather than the  $\alpha$ -disubstituted structure of (14). [Alternative perspectives of (13) and (14) are shown in (13a) and (14a).] For comparison, the carbonyl band of methyl 1-norbornyl ketone (21)<sup>9,10</sup> appears at 1 697  $\text{cm}^{-1}$ , while the four 2-acetylnorbornanes (11) and (15)–(17) all have carbonyl absorption at 1 710–1 712  $\text{cm}^{-1}$ . Further support for (13) over (14) came from treatment of the ketone with sodium carbonate in refluxing ethan[<sup>2</sup>H]ol. No epimerization occurred, and only three atoms of hydrogen were exchanged for deuterium. The only observable change in the n.m.r. spectrum of the product was disappearance of the acetyl methyl signals ( $\delta$  1.99, s, 3 H). Finally the n.m.r. spectrum of the deuteriated product formed on photolysis of (8) (see below) is more easily reconciled with (13) than (14). This substance should be either (13d) or (14d), with the deuterium label now appearing either on the  $\beta$ - or the  $\alpha$ -carbon atom. Comparison of the n.m.r. spectra of deuteriated and non-deuteriated products indicated that the signal for the hydrogen replaced by deuterium is at  $\delta$  1.95 and must have a coupling constant  $J > 9$  Hz. These values are quite reasonable for the geminally coupled methylene proton of (13), but unlikely for the tertiary proton adjacent to the carbonyl group in (14). Rigorous proof of structure (13) rests on an alternative stepwise synthesis of this tricyclic ketone as described in a subsequent paragraph.

In order to determine the origin the major photo-

<sup>9</sup> J. I. Musher, *Mol. Phys.*, 1963, **6**, 93; W. D. Kumler, J. N. Shoolery, and F. V. Brucher, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 2533; T. J. Flautt and W. F. Erman, *ibid.*, 1963, **85**, 3212; K. Tori, Y. Hamashima, and A. Takamizawa, *Chem. Pharm. Bull.*, 1964, **12**, 924; P. V. Demarco, D. Doddrell, and E. Wenkert, *Chem. Comm.*, 1969, 1418.

<sup>10</sup> F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, 1963, **28**, 55.

product (11), we turned to photolysis of the deuteriated isobutyl ketone (8). Irradiation of (8) under the conditions used for (7) gave a mixture of 55% of four volatile products in the ratio 74 : 12 : 8 : 6. The major product, deuteriated (11), was shown by n.m.r. spectral comparisons to contain one deuterium atom located solely at C-3, as shown in (11d). This indicates that, within the error limits of n.m.r. integration (<5%), all (11) is formed by way of (9). The second product, noted above, was (13d). The third product is tentatively assigned structure (22) on the basis of its spectral properties;



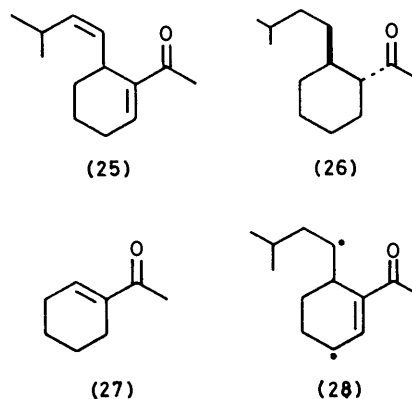
too little of the fourth product was obtained for characterization, but from its n.m.r. spectrum it appeared to be a mixture. The difference in products formed from (7) and from (8) can be accounted for by the operation of deuterium kinetic-isotope effect which retards abstraction from the tertiary centre in (8).<sup>\*</sup> Under these circumstances a small amount of competitive abstraction from one of the isopropyl methyl groups could lead to (23), which could then collapse to (22).

Conceivably the isomerization of (7) to (11) and (13) could be explained alternatively by a pathway involving abstraction of hydrogen by carbonyl oxygen with rearrangement of the resulting biradical (24) to (9). We consider this most improbable, however. Not only is the geometry available for this abstraction relatively unfavourable, but the required rearrangement (24) to (9) seems unlikely. Furthermore, photolysis of (7) in benzene saturated with deuterium oxide yielded (11) and (13) with no measurable (n.m.r. and mass spectra) incorporation of deuterium. Previous experience with carbonyl-abstraction processes indicates that the hydroxyl proton of (24) should undergo exchange with solvent deuterium oxide under these conditions,<sup>11</sup> so that sub-

sequent rearrangement would then furnish deuteriated products.

As mentioned previously, other abstractions by the  $\beta$ -carbon atom of enones are known to be triplet reactions. Sensitization and quenching experiments suggest the same is true for the conversion of (7) into (11) and (13). Photolysis of (7) in the presence of 12.7 equivalents of acetophenone showed that these isomerizations could be efficiently sensitized, and irradiation with varying low concentrations of 2,3-dimethylbuta-1,3-diene demonstrated that they could be efficiently quenched.

We next examined the photochemistry of (7) and (8) at short wavelengths. As noted above,  $\gamma$ -dimethoxymethylcyclohexenones such as (3) undergo hydrogen transfer to the  $\alpha$ -carbon atom only on irradiation in the  $\pi, \pi^*$  band; for this reason it was particularly interesting to determine the behaviour of (7) under these conditions. Appropriate photolysis of (7) in cyclohexane solution (0.0099M,  $\lambda > 2500 \text{ \AA}$ ) furnished 75% of four volatile products in the ratio 48 : 26 : 17 : 9. The two minor products were the photoreduced ketone (16), which presumably arises by hydrogen abstraction from solvent cyclohexane, and the dienone (25). The environment of the double bonds in (25) was deduced from spectroscopic data, and hydrogenation of (25) gave *trans*-2-isopentylcyclohexyl methyl ketone (26). This reduction product was identical with an authentic sample prepared through conjugate addition of isopentylmagnesium bromide to cyclohex-1-enyl methyl ketone (27). Gas chromatographic and spectroscopic data indicated that both preparations of (26) furnished a single isomer, and no change in properties was apparent after treatment with hot methanolic sodium carbonate. For these reasons (26) is assigned the *trans*-geometry shown. The photochemical formation of (25) provides



a mechanistic problem which is currently under investigation. It is possible that this dienone is the result of a direct homolytic cleavage of the  $\gamma, \delta$ -bond of (7) [see (28)] and subsequent disproportionation. The failure to detect formation of any of the *trans*-isopentyl isomer of (25), however, implies that some more complex

<sup>\*</sup> For a previous example of an isotope effect in intramolecular hydrogen abstraction by carbon see ref. 2.

<sup>11</sup> R. A. Cormier and W. C. Agosta, *J. Amer. Chem. Soc.*, 1974, **96**, 618.

process may be responsible for this rearrangement.\*

The two major products from (7) were those of immediate concern for the present study. These were (11) and (13), just as in the previously described long wavelength irradiation. Furthermore, irradiation of (8) at short wavelength gave once again (11d) and (13d). Thus there is no evidence for hydrogen abstraction by the  $\alpha$ -carbon atom on either  $n,\pi^*$  or  $\pi,\pi^*$  irradiation of (7).

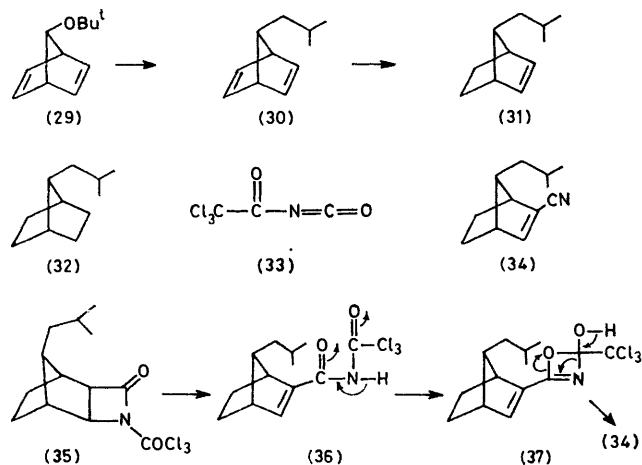
Isomerization of (7) exclusively by way of  $\beta$ -carbon abstraction of hydrogen indicates that minimization of stereochemical and geometric factors does not suffice to elicit competitive abstraction by both  $\alpha$ - and  $\beta$ -carbon atoms of the enone system. Until a better understanding of these processes is available, it will remain uncertain whether or not this result also means that  $\beta$ -carbon abstraction is generally favoured and that  $\alpha$ -abstraction will occur only in special, still undefined circumstances.

**Preparative Experiments.**—The title compound (7) was available in four steps from 7-t-butoxynorbornadiene (29). Treatment of (29) with isobutylmagnesium iodide in refluxing benzene for three days gave the corresponding isobutyl-substituted diene (30) in 94% yield. This reaction of (29) has been used previously with phenyl and methyl Grignard reagents.<sup>13</sup> Hydrogenation of (30) in hexane at 0 °C yielded largely the desired mono-olefin (31) along with a small amount of 7-isobutylbornane (32).

A quite effective method was developed for introduction of the acetyl group into (31). Reaction of this olefin with three equivalents of trichloroacetyl isocyanate (33)<sup>14</sup> in hot *p*-xylene for five days followed by dilution of the reaction mixture with ether and washing with aqueous base, gave the unsaturated nitrile (34) directly in 70–89% yield. We suggest that this transformation probably proceeds through formation of the [2 + 2] adduct (35), which opens to the unsaturated imide (36). Disproportionation of (36) *via* (37) could then lead to the nitrile (34) and trichloroacetic acid.† The formation of both (35) and (36) has good precedent in the addition of trichloroacetyl isocyanate (33) to various enol ethers and enol thioethers.<sup>15</sup> With these reactive olefins both [2 + 2] and [4 + 2] cycloaddition products, as well as unsaturated imides, are formed under quite mild conditions. The suggested thermal conversion of imide (36)

into (34) also has ample precedent.<sup>16</sup> Finally (34) was converted into the desired unsaturated ketone (7) on reaction with methylmagnesium bromide.

Synthesis of the deuteriated substrate (8) required repetition of the steps outlined above using [2-<sup>2</sup>H]-isobutyl iodide in preparation of the Grignard reagent initially required for reaction with (29). This iodide was available from [2-<sup>2</sup>H]isobutyl alcohol<sup>2</sup> by way of the derived tosylate.



For proof of structure of the tricyclic photoproduct (13) we carried out an independent synthesis by way of a new route to this ring system. This began with *syn*-norborn-2-en-7-ylmethyl acetate (38a),<sup>17</sup> which is available from the corresponding alcohol (38b).<sup>18</sup> Reaction of (38a) with trichloroacetyl isocyanate (33) under the conditions described for preparation of (34) furnished the unsaturated nitrile (39a) in high yield; ‡ subsequent hydrogenation gave the mixture of the cyano-acetates (40a). Hydrolysis of the ester, followed by oxidation of (40b), first with chromium trioxide–pyridine complex in methylene chloride<sup>19</sup> and then with Jones' reagent,<sup>20</sup> gave the cyano-acids (41b) and (42b). These were conveniently characterized as the corresponding methyl esters (41c) and (42c), which were separated and purified by preparative vapour phase chromatography (v.p.c.). The stereochemistry of the two nitriles could be reliably assigned from the position and coupling of the proton at C-2 in their <sup>1</sup>H n.m.r. spectra. In one case this signal appears at  $\delta$  3.14 ( $W_{1/2} = 23$  Hz), while in the other it

\* For formally related reactions in other systems see ref. 12.

† For further information and application of this transformation to other systems see B. Byrne, C. A. Wilson, II, and W. C. Agosta, *Tetrahedron Letters*, 1976, 2189.

‡ Exploratory experiments showed that (33) also reacted well with the methyl ether (38c), which was prepared from the alcohol (38b) and methyl iodide. Subsequent reactions of the methoxynitrile (39c), however, were less satisfactory than those of (39a). Preparation of (38c) and (39c) is described in the Experimental section.

<sup>12</sup> R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *J. Amer. Chem. Soc.*, 1973, **95**, 4346 and references therein.

<sup>13</sup> P. R. Story and S. R. Fahrenholtz, *J. Org. Chem.*, 1963, **28**, 1716.

<sup>14</sup> A. J. Speziale and L. R. Smith, *J. Org. Chem.*, 1962, **27**, 3742; 1963, **28**, 1805.

<sup>15</sup> L. R. Smith, A. J. Speziale, and J. E. Fedder, *J. Org. Chem.*, 1969, **34**, 633; J. L. Chitwood, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, 1971, **36**, 2228; B. A. Arbuzov, N. N. Zobova, and F. B. Balabanova, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, 2056; B. A. Arbuzov, N. N. Zobova, and I. I. Andronova, *ibid.*, 1974, 1566.

<sup>16</sup> F. Becke and T. F. Burger, *Annalen*, 1968, **716**, 78; D. A. Klein, *J. Org. Chem.*, 1971, **36**, 3050.

<sup>17</sup> R. K. Bly and R. S. Bly, *J. Org. Chem.*, 1966, **31**, 1577.

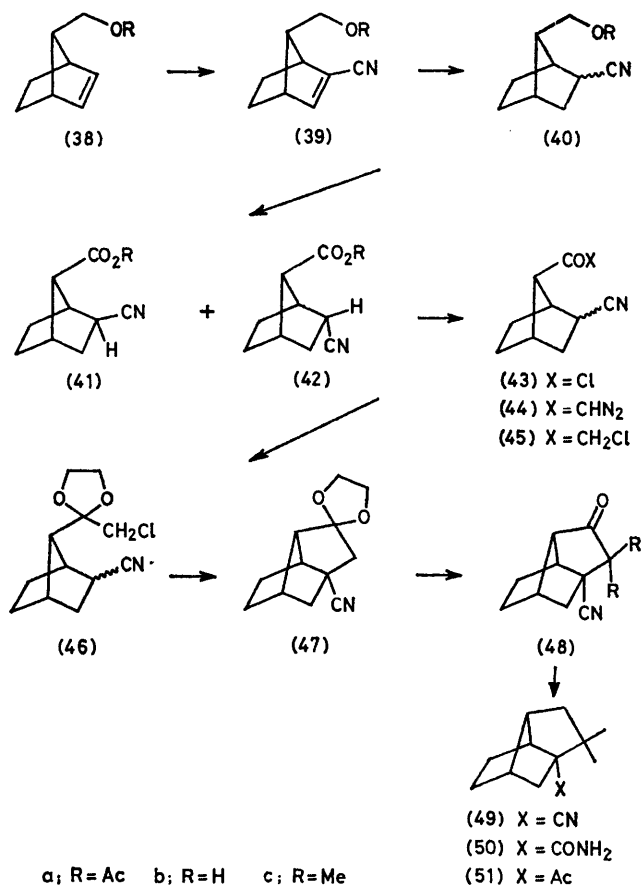
<sup>18</sup> J. A. Berson, J. J. Gajewski, and D. S. Donald, *J. Amer. Chem. Soc.*, 1969, **91**, 5550; R. R. Sauers and R. M. Hawthorne, *J. Org. Chem.*, 1964, **29**, 1685; R. K. Bly and R. S. Bly, *ibid.*, 1963, **28**, 3165.

<sup>19</sup> R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 1970, **35**, 4000.

<sup>20</sup> A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemm, *J. Chem. Soc.*, 1953, 2548; C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, 1956, **21**, 1547.

is at  $\delta$  2.84 ( $W_{1/2} = 6$  Hz). In line with previous experience<sup>9</sup> noted above the broader signal at lower field was taken to be that of the *exo*-proton of (42c).

The purified mixture of acids (41b) and (42b) was then converted *via* the acyl chloride (43) and diazoketone (44) into the chloro-ketone (45), all following well known procedures. Reaction of (45) with an excess of ethylene glycol in hot benzene containing toluene-*p*-sulphonic acid furnished the acetal (46)\*. Subsequent treatment of (46) with lithium hexamethyldisilazane † in benzene resulted in smooth cyclization to the cyano-acetal (47). This intramolecular alkylation is an example of the halogeno-acetal cyclization developed by



Stork and his co-workers,<sup>21</sup> and in the present application it provides convenient access to functionalized derivatives of the bixane system.<sup>22</sup> Deacetalization in aqueous methanolic hydrochloric acid then yielded the

\*  $\alpha$ -Halogeno-ketones typically yield acetals under ordinary conditions without difficulty: M. Kühn, *J. Prakt. Chem.*, 1940, **156**, 103. The ketone (45) required excess of glycol and recycling for good conversion to (46).

† This was prepared as described by U. Wannagat and H. Niederprüm, *Chem. Ber.*, 1961, **94**, 1540.

‡ For other examples of this rather rare transformation, see M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Non-metallic Substances,' Prentice-Hall, New York, 1954, pp. 870–871, and references cited therein.

<sup>21</sup> G. Stork, J. O. Gardner, R. K. Boeckman, jun., and K. A. Parker, *J. Amer. Chem. Soc.*, 1973, **95**, 2014; G. Stork and R. K. Boeckman, jun., *ibid.*, 1973, **95**, 2016.

oxo-nitrile (48b) in an overall yield of 41% from (41b) and (42b).

In our hands the most effective conditions (82% yield) for conversion of (48b) into the desired dimethyl ketone (48c) were two separate monomethylations with methyl iodide on the lithium enolate preformed by reaction of the ketone with lithium di-isopropylamide in tetrahydrofuran containing hexamethylphosphoric triamide. The phosphoramidate was added both to accelerate alkylation of the enolate anion<sup>23</sup> and to reduce the nucleophilicity of lithium di-isopropylamide.<sup>24</sup> Wolff-Kishner reduction of (48c) using hydrazine and potassium hydroxide in hot diethylene glycol then furnished a mixture of nitrile (49) and the related amide (50).

We explored various reactions for conversion of these products into the desired methyl ketone (51). The nitrile could be conveniently hydrolysed to the amide in hot base, but the amide (50) itself proved to be quite resistant to further hydrolysis in base with or without added hydrogen peroxide or on exposure to aqueous sodium peroxide.<sup>25</sup> On treatment with methylmagnesium bromide the amide failed to give the desired methyl ketone, although this is a long known reaction of hindered amides,<sup>26</sup> and instead was cleanly dehydrated to the nitrile (49).‡ Direct treatment of the nitrile with methyl-lithium, on the other hand, furnished the desired methyl ketone (51) without difficulty. Comparison of the i.r. and 220-MHz n.m.r. spectra and v.p.c. retention time of this material with those of the minor photoproduct (13) indicated that these compounds were identical.

#### EXPERIMENTAL

**Materials and Equipment.**—All v.p.c. was carried out using a Varian Aerograph Model A-90-P3 with one of the following columns: A, 30% SE-30, 20 ft  $\times$  0.25 in, stainless steel; B, 25% DEGS, 20 ft  $\times$  0.25 in, aluminium; C, 10% Carbowax 20M, 5 ft  $\times$  0.25 in, aluminium; D, 15% XF-1150, 5 ft  $\times$  0.25 in, stainless steel; E, 25% QF-1, 25 ft  $\times$  0.25 in, aluminium; F, 25% SDEGS, 27 ft  $\times$  0.25 in, aluminium; G, 25% QF-1, 5 ft  $\times$  0.25 in, aluminium; H, 25% XF-1150, 6 ft  $\times$  0.25 in, aluminium. Columns A–E, G, and H were prepared using Chromosorb W; for column F Chromosorb P was used. N.m.r. and i.r. spectra were obtained in CCl<sub>4</sub> unless otherwise noted. N.m.r. spectra were measured on a Varian model HR-220 (220 MHz) or a Model T-60 (60 MHz) spectrometer. I.r. spectra were measured on a Perkin-Elmer model 237B spectrophotometer. Boiling points are uncorrected; melting points are corrected. Photochemical experiments were carried out either with a Hanovia model L medium-pressure mercury-vapour lamp (450 W) in a quartz immersion well using a

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<sup>24</sup> J. L. Herrmann, G. R. Kieczkowski, and R. H. Schlessinger, *Tetrahedron Letters*, 1973, 2433. See also B. H. Toder, S. J. Branca, R. K. Dieter, and A. B. Smith, III, *Synth. Comm.*, 1975, **5**, 435.

<sup>25</sup> H. L. Vaughn and M. D. Robbins, *J. Org. Chem.*, 1975, **40**, 1187.

<sup>26</sup> F. C. Whitmore, C. I. Noll, and V. C. Meunier, *J. Amer. Chem. Soc.*, 1939, **61**, 683, and references cited therein.

uranium-glass (Corning #3320) filter ( $\lambda > 3400 \text{ \AA}$ ) or with Rayonet 2 573  $\text{\AA}$  lamps ( $\lambda > 2500 \text{ \AA}$ ) in a Rayonet reactor. All new compounds were obtained as colourless oils unless otherwise noted.

**7-Isobutylbicyclo[2.2.1]hept-2,5-diene (30).**—Isobutylmagnesium iodide was prepared from magnesium (3.0 g, 0.123 g-atom) and isobutyl iodide (22.6 g, 123 mmol) in dry ether (80 ml) under a nitrogen atmosphere. As the ether was removed by distillation, dry benzene (160 ml) was added slowly. Solvent was distilled until a head temperature of 79 °C was attained, and the mixture was cooled. In one portion 7-t-butoxynorbornadiene (10.333 g, 63 mmol) was added; the mixture was heated at reflux for three days and then quenched, with 1.1 equiv. of saturated aqueous  $\text{NH}_4\text{Cl}$ . The benzene layer was decanted, the precipitate was washed with benzene, and organic layers were combined. Distillation of solvent through a 40-cm Vigreux column and then distillation of the residue (b.p. 115 °C, 120 mmHg) gave (30) (8.49 g, 57.4 mmol, 94%). V.p.c. on column A at 140 °C (flow rate 120 ml/min) gave an analytical sample: i.r. 3 050, 2 945s, 2 890, 2 860, 2 830, 1 545, 1 465, 1 385, 1 365, 1 315, 720, and 650  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  0.81 (d,  $J = 6.5$  Hz, 6 H), 1.13 (dd,  $J_1 = J_2 = 7$  Hz, 2 H), 1.32 (m, 1 H), 2.49br (t,  $J = 7$  Hz, 1 H), 3.21 (m, 2 H), 6.65 (dd,  $J_1 = J_2 = 2$  Hz, 2 H), 6.78 (dd,  $J_1 = J_2 = 2$  Hz, 2 H); mass spectrum  $m/e$  148.128 4 ( $M^+$ , calc. for  $\text{C}_{11}\text{H}_{16}$ , 148.125 2).

**syn-7-Isobutylbicyclo[2.2.1]hept-2-ene (31).**—A mixture of dry hexane (225 ml) and 5% palladium on carbon (0.600 g) was cooled to 0 °C and thrice purged with hydrogen, with alternate evacuation; a solution of (30) (8.850 g, 60 mmol) in dry hexane (25 ml) was then injected. At atmospheric pressure, 1.1 equiv. of hydrogen (1 478 ml, 66 mmol) was consumed. Reaction progress was monitored by v.p.c. using column A at 140 °C (flow rate 60 ml/min). Work-up in the usual fashion and simple distillation of the residue (b.p. 115 °C, 90 mmHg) gave (31) and (32) (7.789 g, 52 mmol, 87%) in the ratio 87 : 13. V.p.c. using the above conditions gave analytical samples: (31) i.r. 3 095, 2 980s, 2 900s, 1 540, 1 465, 1 375, 1 360, 1 325, 1 250, 1 090, and 995  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  0.81 (d,  $J = 6.5$  Hz, 6 H), 0.92 (m, 2 H), 1.06 (dd,  $J_1 = J_2 = 7.5$  Hz, 2 H), 1.38 (m, 1 H), 1.62 (m, 3 H), 2.55 (m, 2 H), 5.88 (dd,  $J_1 = J_2 = 2$  Hz, 2 H); mass spectrum  $m/e$  150.140 6 ( $M^+$ , calc. for  $\text{C}_{11}\text{H}_{18}$ , 150.140 8). Compound (32): i.r. 2 970s, 2 900s, 1 470, 1 465, 1 455, 1 375, 1 360, 1 240, and 850  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  0.88 (d,  $J = 6.5$  Hz, 6 H), 1.05—1.20 (m, 6 H), 1.43—1.65 (m, 6 H), 1.85 (m, 2 H) (Found: C, 86.7; H, 13.15. Calc. for  $\text{C}_{11}\text{H}_{20}$ : C, 86.76; H, 13.24%).

**syn-7-Isobutylbicyclo[2.2.1]hept-2-en-2-carbonitrile (34).**—To a 250-ml flask were carefully added under a stream of nitrogen trichloroacetyl isocyanate (33) (19.14 g, 101.5 mmol), (31) (6.00 g, 40 mmol), and *p*-xylene (50 ml). The solution was heated to reflux under nitrogen for 5 days. After cooling to room temperature the reddish brown solution was poured into aqueous sodium hydroxide (3 M; 200 ml) and extracted with ether (5  $\times$  50 ml). The combined organic extracts were washed with aqueous hydrochloric acid (10%, 1  $\times$  50 ml) and brine (1  $\times$  50 ml) and dried ( $\text{MgSO}_4$ ). After concentration of the organic extracts by distillation (max. temp. 140 °C), the crude product was chromatographed on silica gel (200 g) with ether-hexane (1% to 10%). Fractions containing nitrile ( $R_F$  0.48 on silica gel, 20% ether-hexane) were combined and concentrated by distillation through a Vigreux column. This afforded

pure (34) (6.24 g, 35.6 mmol, 89%). Yields varied from 70—89% in various preparations. V.p.c. on column B gave an analytical sample: i.r. (thin film) 3 050, 2 940s, 2 920s, 2 865s, 2 210s, 1 580, 1 465, 1 380, 1 365, 1 315, 885, and 840  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  0.85 (2d, each  $J = 6.5$  Hz, 6 H), 1.00—1.25 (m, 4 H), 1.40 (m, 1 H), 1.82 (m, 3 H), 2.82 (m, 1 H), 2.88 (m, 1 H), and 6.67 (d,  $J = 3$  Hz, 1 H); mass spectrum  $m/e$  175.135 0 ( $M^+$ , calc. for  $\text{C}_{12}\text{H}_{17}\text{N}$ , 175.136 0).

**syn-7-Isobutylbicyclo[2.2.1]hept-2-en-2-yl Methyl Ketone (7).**—Under nitrogen 3M-methylmagnesium bromide (5.8 ml, 17.4 mmol, 4 equiv.) was slowly added to a solution of (34) (0.760 g, 4.35 mmol) in dry ether (50 ml). The resulting solution was stirred for 17 h. During 30 min the reaction solution was then added to rapidly stirred, cold 0.4M-HCl (300 ml), and the mixture was then heated at reflux for 1 h. Usual work-up with ether and bulb-to-bulb distillation (150 °C, 10 mmHg) gave (7) (0.504 g, 2.62 mmol, 60%). V.p.c. on column B at 195 °C (60 ml/min) gave an analytical sample: i.r. 3 035, 2 945s, 2 910s, 2 860s, 1 662s, 1 580s, 1 465, 1 365s, 1 270, and 1 260  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  0.79 (d,  $J = 7$  Hz, 6 H), 0.85—1.12 (m, 4 H), 1.38 (m, 1 H), 1.65—1.88 (m, 3 H), 2.15 (s, 3 H), 2.76 (m, 1 H), 3.04 (m, 1 H), and 6.70 (d,  $J = 2.5$  Hz, 1 H); mass spectrum  $m/e$  192.151 9 ( $M^+$ , calc. for  $\text{C}_{13}\text{H}_{20}\text{O}$ , 192.151 3); u.v. (cyclohexane) 238 nm ( $\epsilon$  10 248) and 327 (48.3).

**[2- $^2\text{H}$ ]Isobutyl Iodide.**—[2- $^2\text{H}$ ]Isobutyl alcohol <sup>2</sup> was converted into the tosylate using toluene-*p*-sulphonyl chloride and pyridine in the usual fashion. A portion of this (15.5 g, 68 mmol) was dissolved in dry, freshly distilled hexamethylphosphoramide (350 ml), and dry sodium iodide (40.6 g, 270 mmol) was added. The solution was purged with nitrogen and stirred at 25 °C for 3 days. It was then added to water (1 l) containing sodium bisulphite (0.5 g). The product was extracted into pentane (4  $\times$  200 ml) and isolated by distillation (b.p. 65 °C, 50 mmHg), yield 92%: i.r. 2 950s, 2 915s, 2 855s, 2 110, 1 460s, 1 380, 1 365, 1 235, 1 217, 1 190s, 1 185s, and 1 134  $\text{cm}^{-1}$ .

**Deuteriated syn-7-Isobutylbicyclo[2.2.1]hept-2-en-2-yl Methyl Ketone (8).**—This ketone was prepared as described for (7), but using the deuteriated iodide (38) in the first step. Spectroscopic measurements indicated that the intermediates differed from the undeuteriated compounds only in the presence of 1 deuterium atom in the tertiary position of the side-chain. Spectral data for (8): i.r. 3 045, 2 950s, 2 920s, 2 865, 1 665s, 1 585, 1 470, 1 370, 1 275, and 1 260  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  0.83 (s, 6 H), 0.87—1.12 (m, 4 H), 1.64—1.88 (m, 3 H), 2.13 (s, 3 H), 2.78br (s, 1 H), 3.07br (s, 1 H), and 6.60 (d,  $J = 3$  Hz, 1 H); mass spectrum  $m/e$  193.157 0 ( $M^+$ , calc. for  $\text{C}_{13}\text{H}_{19}\text{DO}$ , 193.157 6).

**Photolysis of (7) at Long Wavelength.**—A solution of (7) (1.038 g, 5.4 mmol) in benzene (Baker, thiophen free) (2 l) was purged with nitrogen for 45 min, followed by irradiation ( $\lambda > 3400 \text{ \AA}$ ) for 2 h. Progress of reaction was followed by v.p.c. on column B at 195 °C (60 ml/min flow rate). When starting material was no longer visible, photolysis was stopped, and solvent was removed *in vacuo*. V.p.c. on column E at 200 °C (60 ml/min flow rate) gave analytical samples of (11) and (13) in the ratio 85 : 15. Spectral data for (11): i.r. 3 035, 2 940s, 2 900, 2 860, 1 710s, 1 470, 1 460, 1 440, 1 375, 1 355, 1 305, 1 185, 1 165, and 1 125  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  1.03—1.64 (m, 5 H), 1.67 (d,  $J = 1$  Hz, 3 H), 1.71br (s, 3 H), 1.80 (dd,  $J_1 = 4.5$  Hz,  $J_2 = 13$  Hz, 1 H), 1.96 (m, 1 H), 2.02 (s, 3 H), 2.30 (m, 1 H), 2.48br (d,  $J = 8$  Hz, 1 H), 2.92br (m, 1 H), and 5.27br (d,  $J = 8$  Hz, 1 H); mass

spectrum  $m/e$  192.151 2 ( $M^+$ , calc. for  $C_{13}H_{20}O$ , 192.151 3). Spectral data for (13): i.r. 2 945s, 2 860s, 1 692s, 1 465, 1 385, 1 365, 1 350, 1 257, and 1 145  $cm^{-1}$ ; n.m.r.  $\delta$  0.91 (m, 1 H), 0.97 (s, 3 H), 1.06 (s, 3 H), 1.30 (m, 2 H), 1.35 (m, 2 H), 1.50 (dd,  $J_1 = 11$  Hz,  $J_2 = 5$  Hz, 1 H), 1.66 (m, 1 H), 1.81 (m, 1 H), 1.92br (s, 1 H), 1.98 (m, 1 H), 1.99 (s, 3 H), and 2.68 (m, 1 H); mass spectrum  $m/e$  192.152 2 ( $M^+$ , calc. for  $C_{13}H_{20}O$ , 192.151 3).

*Epimerization of (11) in Methanol*.—Compound (11) (20 mg),  $Na_2CO_3$  (100 mg), and methanol (50 ml) were refluxed in a nitrogen atmosphere for 18 h. Usual work-up with water and methylene chloride followed by v.p.c. on column E at 200 °C (60 ml/min flow rate) gave (11) and (15) (56 : 43). Spectral data for (15): i.r. 2 945s, 2 860s, 1 712s, 1 455, 1 445, 1 375, 1 355, 1 263, 1 210, 1 175, and 1 065  $cm^{-1}$ ; n.m.r.  $\delta$  1.24 (m, 4 H), 1.55 (s, 6 H), 1.62 (m, 1 H), 1.97 (s, 3 H), 2.02 (m, 2 H), 2.17 (m, 2 H), 2.43 (d,  $J = 3$  Hz, 1 H), and 4.78 (d,  $J = 7$  Hz, 1 H); mass spectrum  $m/e$  192.152 6 ( $M^+$ , calc. for  $C_{13}H_{20}O$ , 192.151 3).

*Epimerization of (11) in Methan[ $^2H$ ]ol*.—Compound (11) (20 mg),  $Na_2CO_3$  (100 mg), and methan[ $^2H$ ]ol (50 ml, >98% D) were refluxed for 18 h. Products were isolated as in the above described experiment. N.m.r. data for (19a) and (20a) were closely comparable to those for (11) and (15) respectively, except that in the spectrum of (19a) signals at 2.02 (s, 3 H) and 2.92br (m, 1 H) were absent, and in the spectrum of (20a) signals at 1.97 (s, 3 H) and 2.02 (m, 1 H) were absent.

*Hydrogenation of (7)*.—Compound (7) was hydrogenated at 1 atm in methanol with 5% palladium on carbon. Work-up and v.p.c. on column E gave (16) and (17) (1 : 9). Isomer (16): i.r. (thin film) 2 940s, 2 860s, 1 710s, 1 465, 1 380, 1 355, 1 190, 1 170, and 1 135  $cm^{-1}$ ; n.m.r.  $\delta$  0.917, 0.924 (2d,  $J = 6$  Hz for each, 6 H), 1.08 (m, 1 H), 1.22 (m, 3 H), 1.32—1.69 (m, 4 H), 1.78 (m, 2 H), 1.82 (m, 1 H), 2.02 (s, 3 H), 2.26 (m, 1 H), and 2.85 (m, 1 H); mass spectrum  $m/e$  194.167 2 ( $M^+$ , calc. for  $C_{13}H_{22}O$ , 194.167 0). Isomer (17): i.r. (thin film) 2 940s, 2 860s, 1 710s, 1 465, 1 380, 1 360, 1 355, 1 210, 1 175, and 1 065  $cm^{-1}$ ; n.m.r.  $\delta$  0.84 with d,  $J = 6.5$  Hz at 0.817 and d,  $J = 6.5$  Hz at 0.847 (m, 8 H), 1.17—1.67 (m, 7 H), 2.00 (m, 1 H), 2.06 (s, 3 H), 2.14 (m, 2 H), 2.44 (m, 1 H); mass spectrum  $m/e$  194.165 6 ( $M^+$ , calc. for  $C_{13}H_{22}O$ , 194.167 0).

*Hydrogenation of (11) and (15)*.—Using the conditions described above, (11) and (15) were hydrogenated to (16) and (17), respectively. Spectral data were identical to those of samples prepared from (7).

*Epimerization of (16) in Methan[ $^2H$ ]ol*.—Ketone (16) was epimerized as described above for (11). The products (19b) and (20b) (72 : 28) gave n.m.r. spectra closely comparable to those given above for (16) and (17) respectively, except that in the spectrum of (19b) signals at 2.02 (s, 3 H) and 2.85 (m, 1 H) were absent, and in the spectrum of (20b) the signal at 2.06 (s, 3 H) was absent and the multiplet at 2.14 was reduced from 2 H to 1 H.

*Deuteration of (13) in Ethan[ $^2H$ ]ol*.—The ketone (13) (32 mg),  $Na_2CO_3$  (100 mg), and ethan[ $^2H$ ]ol (50 ml), were heated at reflux under nitrogen for 20 h and the reaction product was isolated as described above. V.p.c. on column E at 200 °C (60 ml/min flow rate) gave deuterated (13), the n.m.r. spectrum of which was identical with that of (13) except for the absence of signal at 1.99 (s, 3 H).

*Photolysis of (7) at Long Wavelength in Benzene-Deuterium Oxide*.—In benzene (72 ml) saturated with  $D_2O$  the ketone (7) (72 mg) was irradiated as described above. Analytical

samples of (11) and (13), obtained as previously described, showed no incorporation of deuterium by n.m.r. or mass spectral analysis.

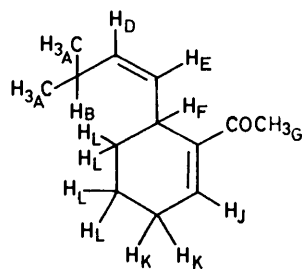
*Photolysis of (8) at Long Wavelength*.—A solution of (8) (0.840 g, 4.35 mmol) in benzene (2 l) was purged with nitrogen for 45 min and then irradiated through uranium glass for 8 h. Progress of the reaction was followed by v.p.c. on column B at 195 °C (60 ml/min flow rate). When no starting material remained, photolysis was stopped, and solvent was removed *in vacuo*. V.p.c. on column E 200 °C (60 ml/min flow rate), gave analytical samples of (11d) (68.5%), (13d) (12.7%), and (22) (13.2%), the remaining 5.6% being an unidentified material. Compound (11d): i.r. 3 035, 2 940s, 2 900s, 2 170, 1 710s, 1 470, 1 450, 1 385, 1 375, 1 360s, 1 280, and 1 180s, 1 125  $cm^{-1}$ ; n.m.r.  $\delta$  1.11 (m, 1 H), 1.26 (m, 1 H), 1.40 (m, 1 H), 1.45—1.62 (m, 1 H), 1.67 (d,  $J = 1$  Hz, 3 H), 1.71 (d,  $J = 1$  Hz, 3 H), 1.80 (m, 1 H), 1.96 (m, 1 H), 2.02 (s, 3 H), 2.30 (m, 1 H), 2.48br (d,  $J = 8$  Hz, 1 H), 2.92 (m, 1 H), 5.27 (ddd,  $J = 8$  Hz,  $J_2 = J_3 = 1$  Hz, 1 H), signal at 2.92 ( $CHCOCH_3$ ) indicates >97% protium at this position; mass spectrum  $m/e$  193.155 5 ( $M^+$ , calc. for  $C_{13}H_{19}DO$ , 193.156 7). Compound (13d): i.r. 2 940s, 2 850s, 2 200, 1 692s, 1 465, 1 385, 1 365, 1 350s, 1 250, and 1 145  $cm^{-1}$ ; n.m.r.  $\delta$  0.91 (m, 1 H), 0.97 (s, 3 H), 1.06 (s, 3 H), 1.17—1.73 (m, 7 H), 1.81 (m, 1 H), 1.92br (s, 1 H), 1.99 (s, 3 H), and 2.68 (m, 1 H); signal at 1.98 (m, 1 H) absent; mass spectrum  $m/e$  193.158 0 ( $M^+$ , calc. for  $C_{13}H_{19}DO$ , 193.156 7). Compound (22): i.r. 2 940s, 2 860s, 2 130, 1 700s, 1 475, 1 465, 1 450, 1 375, 1 360s, 1 245, 1 235, 1 160, and 1 140  $cm^{-1}$ ; n.m.r.  $\delta$  0.84 (m, 1 H), 0.88 (s, 3 H), 1.08br (d,  $J = 13.5$  Hz, 1 H), 1.14 (AB,  $J_{AB} = 4$  Hz,  $\Delta\nu_{AB} = 2.3$  Hz, 2 H), 1.35br (dd,  $J_1 = 4.5$  Hz,  $J_2 = 13.5$  Hz, 1 H), 1.44 (m, 2 H), 1.78 (d,  $J = 10.5$  Hz, 1 H), 1.92 (m, 3 H), 2.01 (m, 1 H), 2.04 (s, 3 H), 2.23 (m, 1 H); mass spectrum  $m/e$  193.155 7 ( $M^+$ , calc. for  $C_{13}H_{19}DO$ , 193.156 7).

*Photolysis of (7) at Short Wavelength*.—A solution of (7) (1.003 g, 5.22 mmol) in cyclohexane (525 ml) was purged with nitrogen for 20 min and irradiated through quartz glass for 40 min ( $\lambda > 2500$  Å). Reaction progress was monitored by v.p.c. on column F (198 °C, 100 ml/min). Concentration under reduced pressure, bulb-to-bulb distillation, and purification of the product mixture (750 mg) by v.p.c. on column F followed by column E (198 °C, 85 ml/min) gave four products (11), (13), (25), and (16) in the ratios of 48 : 26 : 17 : 9, respectively. Compounds (11), (13), and (16) were identical by i.r., n.m.r., and v.p.c. comparisons with samples prepared as described above. Compound (25): i.r. (thin film) 2 950, 2 930, 2 865, 1 672, 1 633, 1 345, 1 230, 962, 785, and 755  $cm^{-1}$ ; n.m.r.  $\delta$  0.93 (d,  $J = 6$  Hz, 6 H,  $H_A$ ), 1.40—1.77 (m, 4 H,  $H_L$ ), 1.98—2.22 [m (2.16, s,  $H_G$ ), 6 H,  $H_B$ ,  $H_K$ ], 3.30br (1 H,  $H_F$ ), 5.13—5.34 (m,  $W_{1/2} = 8$  Hz, 2 H,  $H_D$ ,  $H_E$ ), 6.73 (dd,  $J_1 = J_2 = 4$  Hz, 1 H,  $H_J$ ); double irradiation revealed the following couplings:  $H_B$  ( $H_G$ ,  $H_K$ ) to  $H_A$ ;  $H_B$  ( $H_G$ ,  $H_K$ ) to  $H_D$ ,  $H_E$ ;  $H_F$  to  $H_D$ ,  $H_E$ ;  $H_K$  ( $H_B$ ,  $H_G$ ) to  $H_J$ ; mass spectrum  $m/e$  192.148 4 ( $M^+$ , calc. for  $C_{13}H_{20}O$ , 192.151 3); u.v. (ethanol) 226 nm ( $\epsilon$  6 340).

*Hydrogenation of (6-Isopent-cis-1-enyl)-1-cyclohex-1-enyl Methyl Ketone (25)*.—The dienone (25) (2.95 mg, 0.015 mmol) was reduced in ethanol in one atmosphere of hydrogen using 5% palladium on charcoal (31.6 mg). After 20 min the uptake of hydrogen ceased (1.3 ml). Charcoal was removed by filtration through Celite, and solvent was distilled through a 10-cm Vigreux column. Brief concentration under reduced pressure afforded (26) (2.5 mg,



0.010 5 mmol, 70%), identical by i.r. and 220 MHz n.m.r. spectroscopy with an authentic sample.



(25a)

*trans*-2-Isopentylcyclohexyl Methyl Ketone (26).—To a flame-dried 100 ml flask equipped with condenser, drying tube, pressure-equalized addition funnel, gas-inlet tube, and magnetic stirring bar were added magnesium turnings (607 mg, 25 g-atom) and ether (10 ml). A small portion of an ethereal solution of 1-bromo-3-methylbutane (3.78 g, 25 mmol) was added under nitrogen, and reaction was initiated by brief heating. The remaining bromide was added so as to maintain a gentle ether reflux. After an additional 30 min of stirring, copper(I) iodide (48 mg, 0.25 mmol) was added and the dark-blue solution was cooled in an ice-water bath. An ethereal solution (20 ml) of 1-acetylcyclohexene (1.242 g, 10 mmol) was added during 20 min. The solution was subsequently stirred 3.25 h while the cooling bath attained room temperature. After the reaction mixture had been cooled to 5 °C, a saturated aqueous solution (50 ml) of ammonium chloride was rapidly added. The aqueous layer was separated and extracted with ether (3 × 25 ml). The combined ethereal extracts were washed with brine (1 × 25 ml) and dried (MgSO<sub>4</sub>). Concentration under reduced pressure and distillation afforded a light yellow oil: 1.496 g (77%); b.p. 118–120 °C/30 Torr. A sample purified by vapour-phase chromatography on column F (185 °C, 100 ml/min, 16 min) gave the following spectral data: i.r. 2 925, 2 850, 1 710, 1 465, 1 445, 1 365, 1 350, 1 240, and 1 165 cm<sup>-1</sup>; n.m.r. δ 0.84 and 0.88 (2 d, *J* = 6.5 Hz for each, 6 H), 0.92–1.35 (m, 8 H), 1.39–1.63 (m, 3 H), 1.68–1.93 (m, 4 H), and 2.06 (s, 3 H) (Found: C, 79.55; H, 12.4. Calc for C<sub>13</sub>H<sub>24</sub>O: C, 79.53; H, 12.32%).

*Treatment of the Ketone (26) with Base*.—Refluxing an anhydrous methanolic solution (25 ml) of (26) (40 mg) for 18 h with sodium carbonate (100 mg) afforded (26) unchanged as shown by i.r. and 220 MHz n.m.r. spectroscopy and v.p.c. retention time.

*Sensitized Photolysis of the Ketone (7)*.—Benzene solutions of (7) (0.005 33M) and (7) containing acetophenone (0.005 33M and 0.067 6M, respectively) were irradiated 5 min in a merry-go-round device using 360-nm lamps in a Rayonet reactor. Concentration of each solution under reduced pressure and analysis by v.p.c. showed 30% and 56% conversion, respectively, to products. The ratio of products was approximately the same in each case.

*Photolysis of (7) with 2,3-Dimethylbuta-1,3-diene*.—Irradiation for 30 min as described above of benzene solutions of (7) (0.005 7M) in the presence of varying concentrations of 2,3-dimethylbuta-1,3-diene and analysis by v.p.c. gave the following results: ([Q], Φ<sub>0</sub>/Φ<sub>Q</sub> for each product) 1.05mm 0.95; 6mm, 0.91; 1.2mm, 0.68. These data yield a linear Stern-Volmer plot with *k*τ = 38 l mol<sup>-1</sup>.

*Photolysis of (8) at Short Wavelength*.—A degassed solution (15 min) of (8) (20 mg) in cyclohexane (20 ml) was irradiated (10.0 min) in a quartz test tube using the Rayonet apparatus described above equipped with 254-nm lamps. Concentration of the solution under reduced pressure afforded a colourless oil (16 mg). Analysis of the product mixture by i.r. and v.p.c. on column F (190 °C, 100 ml/min) showed 97% conversion of (8) into four major products: deuteriated (16) (47%), deuteriated (25) (26%), and (11d) and (13d) (25% combined). These last two products were separated by rechromatography on column E, as described above, and identified by spectral comparisons with (11d) and (13d) obtained on long wavelength photolysis of (8).

*syn*-7-Methoxymethylbicyclo[2.2.1]hept-2-ene (38c).—To a stirred suspension of ether-washed sodium hydride (300 mg, 50% in mineral oil, 6 mmol) in dimethoxyethane (DME) (6 ml) was added the alcohol (38b)<sup>18</sup> (531 mg, 4.3 mmol) in DME (2 ml). After the mixture was stirred 30 min at room temperature, methyl iodide (850 mg, 6 mmol) in DME (2 ml) was added. After the mixture had been stirred 3 h, ether (25 ml) was added, and sodium iodide was filtered off. The organic solution was dried (MgSO<sub>4</sub>) and concentrated by distillation to give the ether (38c) (389 mg, 2.82 mmol, 65%). An analytical sample was afforded by preparative v.p.c. on column B (127 °C, 100 ml/min): i.r. (CCl<sub>4</sub>) 3 051, 2 955, 2 862, 1 460, 1 327, 1 110s, 980, 865, and 708s cm<sup>-1</sup>; n.m.r. (CCl<sub>4</sub>) δ 0.8–1.1 (m, 2 H), 1.5–2.0 (m, 3 H), 2.70 (m, 2 H), 3.10 (s, 3 H), 3.14 (d, *J* = 7.0 Hz, 2 H), and 5.83 (m, 2 H). (Found: C, 78.3; H, 10.4. Calc. for C<sub>9</sub>H<sub>14</sub>O: C, 78.21; H, 10.21%).

*7-Methoxymethylbicyclo[2.2.1]hept-2-ene-2-carbonitrile (39c)*.—A solution of the ether (38c) (630 mg, 4.25 mmol) and trichloroacetyl isocyanate (2.39 g, 12.7 mmol) in dry *p*-xylene (10 ml) was sealed in a Carius tube under a high flow of nitrogen and then heated at 140 °C for 88 h. The cooled solution was added to 3M-sodium hydroxide (50 ml) and extracted with ether (5 × 25 ml). The combined organic extracts were washed with 10% hydrochloric acid (25 ml) and saturated brine (50 ml), dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. Bulb-to-bulb distillation (105 °C at 0.5 Torr) gave the nitrile (39c) (620 mg, 3.80 mmol), 90%, as a colourless oil: i.r. (CCl<sub>4</sub>) 2 972, 2 918, 2 870, 2 213, 1 580, 1 447, 1 311, 1 115br, 980, 873, 840, and 705 cm<sup>-1</sup>; n.m.r. (CCl<sub>4</sub>) δ 1.1–1.4 (m, 2 H), 1.6–2.2 (m, 3 H), 2.97br (2 H), 3.16 (d, *J* = 7.0 Hz, 2 H), 3.22 (s, 3 H), and 6.70br (d, *J* = 3 Hz, 1 H); mass spectrum, *m/e* 163.096 8 (*M*<sup>+</sup>, calc. for C<sub>10</sub>H<sub>13</sub>NO, 163.099 6) (Found: C, 73.35; H, 7.95; N, 8.40. Calc. for C<sub>10</sub>H<sub>13</sub>NO: C, 73.59; H, 8.03; N, 8.58%).

*syn*-7-Acetoxyethylbicyclo[2.2.1]hept-2-ene-2-carbonitrile (39a).—A mixture of the unsaturated acetate (38a) (1.473 g, 8.86 mmol) and trichloroacetyl isocyanate (5.01 g, 26.6 mmol) in anhydrous *p*-xylene (16 ml) was heated to reflux under a nitrogen atmosphere for 3.5 days. The reaction was cooled, poured into 3M-NaOH and extracted three times with ether. The organic extracts were combined, washed with 5% aqueous NaOH and brine, and dried over MgSO<sub>4</sub>. The ether was distilled off at atmospheric pressure and *p*-xylene at 8 mmHg (aspirator); distillation of the residue from eight such reactions yielded 9.635 g (70%), b.p. 100–110 °C (0.5 mmHg). Further purification was achieved on column G (200 °C); i.r. 2 970m, 2 950m, 2 875m, 2 220m, 1 747s, 1 580w, 1 447w, 1 368s, 1 230s, 1 088w, 1 030s, 875w, and 840w cm<sup>-1</sup>; n.m.r. (60 MHz) δ 6.70 (dd, *J* = 0.5, 3.0 Hz, 1 H), 3.88 (d, *J* = 7 Hz, 2 H),

3.00br (s, 2 H), 2.20—0.95 (m with s at 1.98, 8 H) (Found: C, 68.95; H, 6.65; N, 7.25. Calc. for  $C_{11}H_{13}NO_2$ : C, 69.09; H, 6.85; N, 7.33%).

exo- and endo-2-Cyanobicyclo[2.2.1]heptane-syn-7-carboxylic Acids (41b) and (42b).—The unsaturated acetoxy-nitrile (9.505 g, in 1 g and two ca. 4 g batches) (39a) was hydrogenated in methanol (ca. 20 ml/g) with 5% Pd/C (ca. 90 mg/g) as catalyst. V.p.c. analysis of aliquots indicated when the reaction should be terminated. The reaction mixtures were combined and most of the methanol was removed by distillation. The residue was taken up in ether, washed twice with  $H_2O$ , and dried. After removal of solvent, 8.751 g (91%) of a mixture of nitriles (indicated by v.p.c.) was obtained: i.r. 2 955s, 2 870m, 2 238w, 1 745s, 1 367m, 1 225s, 1 115m, and 1 027m  $cm^{-1}$ .

The crude saturated acetoxy-nitrile (8.751 g) was dissolved in MeOH and cooled to 0 °C. With stirring, 0.25 M- $K_2CO_3$  (120 ml) was added and the ice-bath was removed. After 1.5 h, v.p.c. analysis on column G (200 °C) indicated the absence-acetate. Some of the methanol was removed *in vacuo* and the residue was poured into  $H_2O$  (250 ml) and extracted four times with ether. The organic extracts were combined, washed twice with  $H_2O$  and once with brine, and then dried. Removal of the ether *in vacuo* gave 3.982 g. Continuous extraction of the aqueous phases for 2 days with ether yielded another 3.277 g; i.r. 3 620w, 3 450br, 2 955s, 2 875m, 2 240m, 1 080m, and 1 037m  $cm^{-1}$ .

The crude cyano-alcohols (302.4 mg, 2 mmol) were oxidized to the aldehyde with chromium trioxide-pyridine complex according to published procedures.<sup>19</sup> Standard work-up gave 220.4 mg (74%). Separation of these aldehydes could be effected by v.p.c. on column A (160 °C). The first eluted, major (ca. 70%) aldehyde had i.r. 2 955s, 2 875m, 2 810w, 2 715m, 2 245m, 1 722s, 1 455w, and 1 300w  $cm^{-1}$ ; n.m.r. (60 MHz)  $\delta$  9.77 (s, 1 H) and 3.16—1.08br (m, 10 H); the second eluted aldehyde had i.r. 2 955s, 2 875s, 2 805w, 2 820w, 2 240m, 1 725s, 1 472m, and 1 458m  $cm^{-1}$ ; n.m.r. (60 MHz)  $\delta$  9.96br (s, 1 H) and 3.07—1.00br (m, 10 H).

The crude cyano-aldehydes (220.4 mg) were taken up in acetone (10 ml) and treated with an excess of Jones' reagent<sup>20</sup> for 2 h at 10—15 °C. Standard work-up yielded 223.8 mg (92%). Esterification with diazomethane allowed v.p.c. separation of the epimers on column G (170 °C). The first eluted, major cyano-ester was identified as (42c): i.r. 2 960s, 2 948s, 2 875m, 2 238m, 1 737s, 1 460m, 1 432m, 1 300m, 1 210m, 1 198s, and 1 175m  $cm^{-1}$ ; n.m.r. (220 MHz)  $\delta$  3.61 (s, 3 H), 3.14 (sym 12 line m, 1 H), 2.68 (m, 1 H), 2.57 (m, 1 H), 2.52 (m, 1 H), 2.22 (sym 12 line m, 1 H), 2.02—1.92 (m, 1 H), and 1.84—1.44 (m, 4 H) (Found: C, 67.35; H, 7.3; N, 7.55. Calc. for  $C_{10}H_{13}NO_2$ : C, 67.02; H, 7.31; N, 7.82%).

The second eluted ester was identified as (41c): i.r. 2 950s, 2 875s, 2 240m, 1 737s, 1 450w, 1 430m, 1 325w, 1 302m, 1 290m, 1 218s, 1 190s, 1 132m, 1 040w, and 1 025m  $cm^{-1}$ ; n.m.r. (60 MHz)  $\delta$  3.67 (s, 3 H), 2.84br (s, 1 H), and 2.73—0.97br (m, 9 H) (Found: C, 67.25; H, 7.45; N, 7.6. Calc. for  $C_{10}H_{13}NO_2$ : C, 67.02; H, 7.31; N, 7.82%).

8-Oxotricyclo[4.3.0.0<sup>3,7</sup>]nonane-1-carbonitrile (48b).—To a benzene solution (12 ml) of the cyano-acids (1.652 g, 10 mmol), magnetically stirred and cooled in an ice-bath, was added oxalyl chloride (5 ml). After stirring at 0 °C for 15 min, the ice-bath was removed, and the mixture was stirred for an additional 55 min. An i.r. spectrum of an aliquot indicated no remaining acid. Unchanged reagent

and benzene were removed *in vacuo* and the residue was immediately added with the aid of ether to a large excess of ethereal diazomethane cooled to 0 °C. The mixture was allowed to warm to 25 °C overnight. The ether was removed by distillation; an i.r. spectrum of the residue showed bands at 2 245, 2 110, and 1 640  $cm^{-1}$ .

The crude cyano-diazo-ketone was taken up in ether (80 ml), cooled to 0 °C, and treated dropwise with conc. aqueous HCl (3 ml). The mixture was stirred for 0.5 h after addition of the acid. The reaction was washed with  $H_2O$  and brine and dried. Removal of solvent gave 2.512 g of product; i.r. 2 968s, 2 875m, 2 245w, 1 733s, and 1 712s  $cm^{-1}$ .

A mixture of the cyano-chloro-ketone (2.512 g), ethylene glycol (2.5 ml), toluene-*p*-sulphonic acid (ca. 85 mg), and benzene (35 ml) was heated at reflux overnight with removal of the  $H_2O$ . An i.r. spectrum of the residue obtained after standard work-up indicated incomplete acetalization. Two additional identical cycles were necessary to transform (45) fully into (46) (2.394 g, crude).

To a solution of hexamethyldisilazane (12.9 g, 80 mmol) in benzene (80 ml), magnetically stirred and cooled to 0 °C under a nitrogen atmosphere, was added phenyl-lithium (80 mmol). The crude cyano-chloro-acetal (2.694 g) was added in benzene (20 ml) and the mixture was heated at reflux for 4 h. The reaction mixture was cooled and acetic acid (5 ml) and water (50 ml) were added. After separation of the benzene layer, the aqueous phase was extracted with ether. The organic phases were combined, washed with dilute aqueous HCl, saturated aqueous  $NaHCO_3$ , and brine, and dried. Solvent was removed by distillation; v.p.c. analysis of the residue on column G (185 °C) indicated essentially one peak and none of the starting materials. Involatile materials were removed by bulb-to-bulb distillation, yield ca. 3.00 g (b.p. 150 °C, 0.5 mmHg).

The cyano-acetal (47) was dissolved in methanol (60 ml) and 10% aqueous HCl (30 ml) was added. The mixture was stirred for 1 h at 25 °C after which it was diluted with  $H_2O$  (200 ml) and extracted with ether ( $\times$  4). The extracts were combined, washed with  $H_2O$ , saturated aqueous  $NaHCO_3$ , and brine and then dried. Removal of solvent by distillation gave 2.650 g of a residue which was further purified by chromatography on 100-g of deactivated Woelm neutral  $Al_2O_3$  (8%  $H_2O$ ). The cyano-ketone (48b) [751 mg; 41% from the cyano-acids (41b) and (42b)] was eluted with ether-pentane (1 : 1). Further purification was accomplished by preparative v.p.c. on column H (205 °C), m.p. 95.5—96.5 °C: i.r. 2 960m, 2 875m, 2 245w, 1 767s, 1 472w, 1 462m, 1 415m, 1 310m, 1 177m, and 1 140m  $cm^{-1}$ ; n.m.r. (220 MHz)  $\delta$  2.74br (s, 1 H), 2.47—2.38 (m, 3 H), 2.18 (d,  $J = 17$  Hz, 1 H), and 1.93—1.60br (m, 6 H) (Found: C, 74.45; H, 7.05; N, 8.5. Calc. for  $C_{10}H_{11}NO$ : C, 74.51; H, 6.88; N, 8.69%).

9,9-Dimethyl-8-oxotricyclo[4.3.0.0<sup>3,7</sup>]nonane-1-carbonitrile (48c).—A solution of lithium di-isopropylamide (1 mmol) was prepared by adding *n*-butyl-lithium (1 mmol) to di-isopropylamine (101 mg, 1 mmol) in tetrahydrofuran (2.5 ml), magnetically stirred and cooled to 0 °C under a nitrogen atmosphere. The mixture was cooled to -78 °C and hexamethylphosphoramide (350  $\mu$ l, 2 mmol) was added to it. After 0.5 h, the cyano-ketone (48a) (100 mg, 0.62 mmol) was added in tetrahydrofuran (2 ml). The mixture was stirred for 0.75 h and after which iodomethane (100  $\mu$ l) was added. The mixture was maintained at -78 °C for ca. 4 h and was allowed to warm to 25 °C overnight. The mixture was poured into saturated aqueous  $NH_4Cl$ , the organic layer was

separated, and the aqueous phase was extracted with ether. The organic phases were combined, washed with dilute aqueous HCl, H<sub>2</sub>O, saturated aqueous NaHCO<sub>3</sub>, and brine, and then dried. After removal of solvent and bulb-to-bulb distillation (to 175 °C, 0.5 mmHg) 102 mg of an oil was obtained. V.p.c. analysis on column B (200 °C) indicated essentially one product and less than 5% of (48b).

Repetition of this procedure gave 96 mg (82%) of the dimethylcyano-ketone, (48c). Further purification was achieved on column H (200 °C): m.p. 81.5–82.5 °C; i.r. 2 990w, 2 960m, 2 870m, 2 237w, 1 755s, 1 445w, 1 387w, 1 370w, 1 145w, and 1 105m cm<sup>-1</sup>; n.m.r. (60 MHz) δ 2.99br (s, 1 H), 2.35br (s, 2 H), 2.29–1.37br (m, 6 H), 1.20 (s, 3 H), and 1.12 (s, 3 H) (Found: C, 76.3; H, 8.0; N, 7.45. Calc. for C<sub>12</sub>H<sub>15</sub>NO: C, 76.15; H, 7.99; N, 7.40%).

*Wolff-Kishner Reduction of (48c).*—The dimethylcyano-ketone (48c) (100 mg, 0.53 mmol) was treated with anhydrous hydrazine, KOH, and diethylene glycol following the procedure of Murray.<sup>27</sup> The period of heating at 180 °C was extended to 5.5 h, and the reaction mixture was then diluted with H<sub>2</sub>O and extracted with ether. V.p.c. analysis on column G (200 °C) indicated the formation of two compounds which were more conveniently separated on 6 g of activity IV Woelm neutral Al<sub>2</sub>O<sub>3</sub>. Pentane eluted 9,9-dimethyltricyclo[4.3.0.0<sup>3,7</sup>]nonane-1-carbonitrile, (49), (24.3 mg, 26%): i.r. 2 990w, 2 955s, 2 870m, 2 235w, 1 468w, 1 385w, and 1 367w cm<sup>-1</sup>; n.m.r. (220 MHz) δ 2.65br (s, 1 H), 2.10–1.87 (m, 3 H), 1.73–1.07br (m with s at 1.16 and 1.12, 13 H) (Found: C, 82.15; H, 9.95; N, 7.75. Calc. for C<sub>12</sub>H<sub>17</sub>N: C, 82.23; H, 9.78; N, 7.99%).

9,9-Dimethyltricyclo[4.3.0.0<sup>3,7</sup>]nonane-1-carboxamide,

(50), (51.2 mg, 50%) was eluted with ether–pentane (1:1): m.p. 145.5–147 °C: i.r. 3 495m, 3 405w, 3 145br, 2 945s, 2 860m, 1 672s, 1 605m, 1 577w, 1 470w, 1 385m, 1 367m, and 1 307w cm<sup>-1</sup>. Found: C, 74.25; H, 10.0; N, 7.1. Calc. for C<sub>12</sub>H<sub>19</sub>NO: C, 74.57; H, 9.91; N, 7.25%.

*Reaction of Methylmagnesium Iodide with (50).*—The tricyclic amide (51 mg) was added to an excess of methylmagnesium iodide (10 mmol) in ether, and the mixture was heated at reflux for 8 h following the method of Whitmore.<sup>28</sup> V.p.c. analysis on column G (200 °C) after the usual work-up indicated the presence of only the amide (50) and the nitrile (49); these were identified by their retention times and i.r. spectra.

*9,9-Dimethyltricyclo[4.3.0.0<sup>3,7</sup>]non-1-yl Methyl Ketone (51).*—The nitrile (49) (ca. 20 mg) was added to a solution of methyl-lithium (1.38 mmol). The mixture was stirred at 25 °C for 45 h and then heated at reflux for 8 h. Hydrolysis and work-up followed the procedure of House.<sup>28</sup> V.p.c. analysis on column G (170 °C) indicated the presence of some starting material and a single product (51). This product was collected and had i.r. and n.m.r. spectra, as well as v.p.c. retention time, identical to those of photochemically derived (13).

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