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DEMONSTRATION OF LACK OF INVERSION OF THE MIGRATING ALLYL GROUP IN PHOTOCHEMICAL REARRANGEMENT OF A HEXA-1,5-DIENE DERIVATIVE

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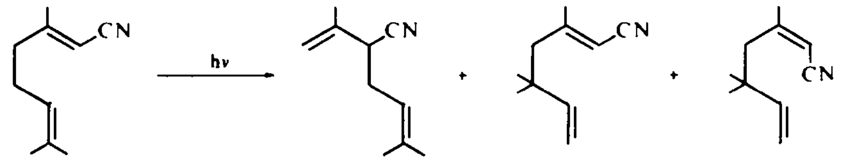
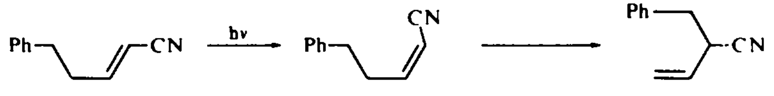
Abstract—UV irradiation of *trans*-2-(3'-deuterioallyl)cyclohexylidenemalononitrile (XIa) induces rearrangement to allyl-1-cyclohexenylmalononitrile, in which the deuterium is still entirely at the 3-position of the allyl group but has lost its geometrical configuration (XIIa and b). Thermal Cope rearrangement of the mixture (XIIa and b) or of pure synthetic *cis*-isomer (XIIa) forms 2-(1'-deuterioallyl)cyclohexylidenemalononitrile (XIb). Since XIa recovered from incomplete irradiation is quite unchanged and the *cis*-isomer (XIIa) is stable to irradiation even in the presence of cyclohexylidenemalononitrile, the *cis-trans* equilibration must occur during the migration of the allyl group.

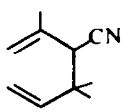
Photochemical allylic shifts have recently been observed in derivatives of hexa-1,5-diene. Thus UV irradiation of geranonitrile (*cis* or *trans* I) gives a mixture of the rearranged nitriles II, III and IV, and 5-phenylpentenonitrile (V) gives VII, *via* the *cis*-isomer[1,2] (VI). It is notable that in each case only one allyl group undergoes inversion, hinting that the rearrangement may involve a concerted 1,3-shift in an



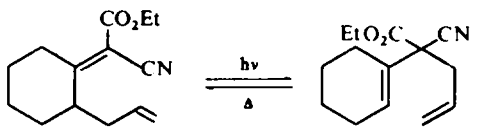
I II III IV



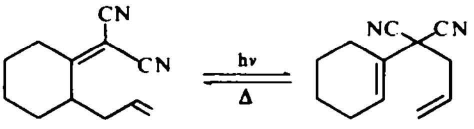
V VI VII



VIII



IX X

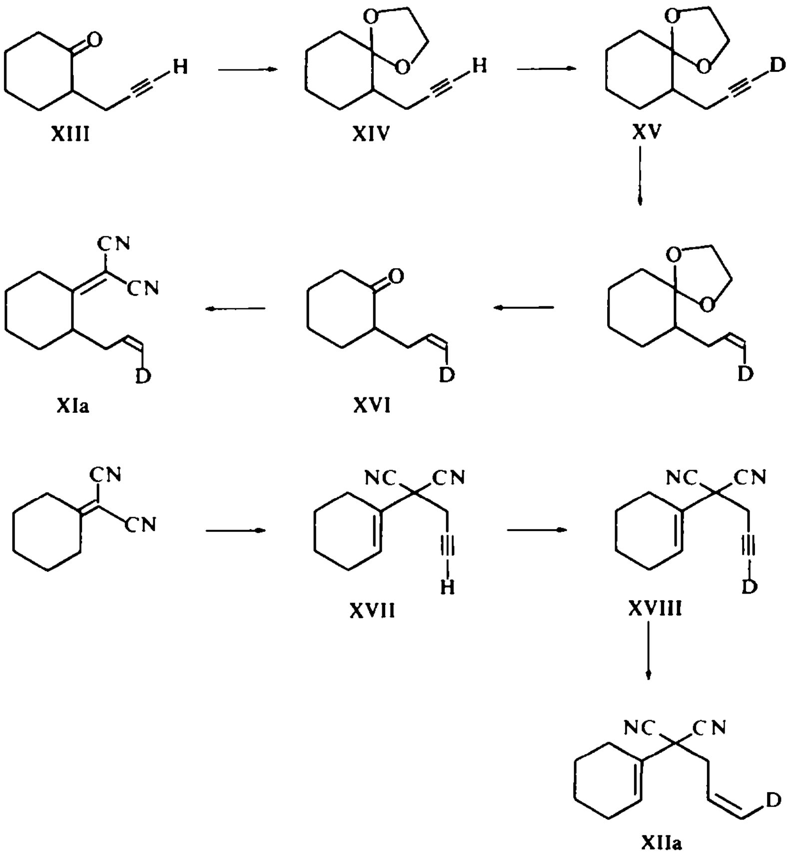


XI XII

excited state, rather than dissociation into two allyl radicals that recombine. However, the absence of the fourth possible isomer (VIII) in the first case might have been due to steric repulsion, and the absence of *o*-phenyl substituted products in the second could have been ascribed to resistance to disruption of the benzene ring. A labelled allyl derivative free of such complications was therefore selected to find whether or not inversion occurs when either course is equally possible.

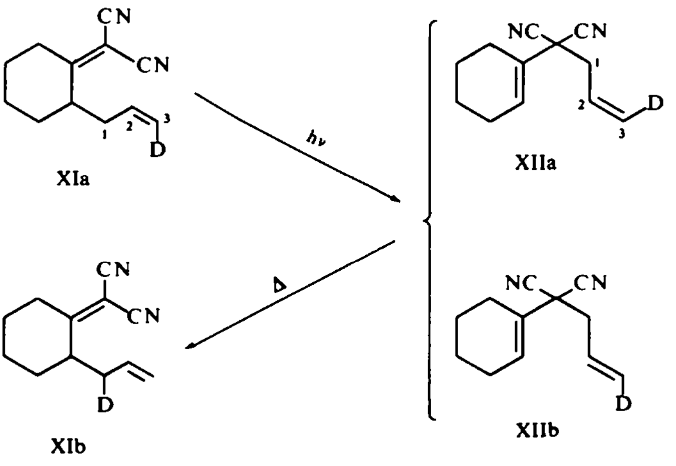
One of the classical examples of the thermal Cope rearrangement[4] is the conversion of the unconjugated cyano-ester (X) into the conjugated isomer (IX). The reversal of this rearrangement on irradiation[1,3] (IX → X) seemed to be a suitable system for detailed scrutiny but for the unnecessary complication of *cis-trans* isomerization in the conjugated isomer (IX). The dinitrile (XI), which underwent the same rearrangement (to XII), does not suffer from this disadvantage.

The compound with the *trans*-3 hydrogen atom specifically replaced by deuterium (XIa) was made as shown in the formulae, the key step being the catalytic hydrogenation of the deuteriopropargyl derivative (XV). The merit of this pattern of labelling is that not only can the two ends of the allyl group be identified but *cis-trans* isomerization can also be observed. The labelled isomer (XIIa) was made similarly by hydrogenation of the deuteriopropargyl compound (XVIII). The structure and stereochemistry of the conjugated isomer (XIa) were confirmed by its spectra. The PMR spectrum was



identical with that of the undeuteriated form (XI), except in the vinyl region, where the absorption from one of the methylene protons was missing: the ratio of olefinic to saturated protons was 0·181 (calc. 0·182) and of —CH= to =CHD 1·01 (a small peak at τ 5·10 suggested the presence of a trace of =CH_2). The 3-proton of the allyl group appeared as a simple doublet at τ 4·9, the coupling constant of 10·2 c/s confirming its *trans* configuration to the 2-proton. In the IR spectrum the bands from the vinyl group at 935 and 1005 cm^{-1}, present in XI, had vanished, to be replaced by a strong broad band at 815 cm^{-1} from deformation of =CHD out of the plane (o.o.p. def.) and a weaker one at 990 cm^{-1}. The C=C stretching vibration of the allyl group had shifted from about 1640 cm^{-1} in XI to 1620 in XIa. The =C—D stretching vibration that appears at 2257 cm^{-1} in the spectrum of *cis*-1-deuteriopropene* and at about the same frequency in that of the ketone (XVI), was obscured in the spectrum of the dinitrile (XIa) by the strong C≡N stretch at 2240 cm^{-1} (the shoulder on the high-frequency side of this band may represent the expected =C—D stretch). Analysis by mass spectrum was unsatisfactory because both ions $[M]^{\cdot +}$ and $[M\text{-}1]^{\cdot +}$ are formed: some undeuteriated compound and small amounts of both the propargyl and propyl derivatives seemed to be present, suggesting that the material consisted of XIa to the extent of about 90%. The chemical purity would have depended on the purity of the ketone (XVI), which after purification through the semicarbazone gave (for what that is worth) a single peak on gas chromatography on polypropylene glycol.

There were analogous differences in the spectra of the unconjugated compounds XII and XIIa. The spectra were identical in the region of the saturated protons and the cyclohexenyl proton (multiplet at τ 3·78) but one of the methylene protons from the vinyl group was missing, leaving the other as a doublet at τ 4·6 (J = 10 c/s). Again the C=C stretching frequency of the allyl group fell from about 1640 to 1620 cm^{-1} on deuteriation. The deuteriocompound (XIIa) had a very strong broad band at 830 cm^{-1} from the o.o.p.def. of the *cis*-olefinic hydrogen atoms.



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* cf. IR spectrum of *cis*-1-deuteriopropene, compared with those of the *trans*-isomer and of normal propene.[5]

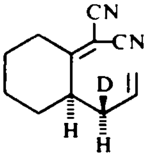
Thermal Cope rearrangement of XIIa gave XIb, the infrared spectrum of which was indistinguishable from that of the undeuteriated compound (XI), the C—D stretching frequency, that appears at 2210 cm^{-1} in the spectrum of 3-deuteriopropene,[6] again being obscured by the strong CN band at 2240 cm^{-1}. The PMR spectrum was also identical with that of XI but for a change in the pattern of the vinyl proton —CH=, and reduction in the intensity of the "triplet" at about τ 7·57 (J = 7 c/s, presumably from approximately equal coupling of the saturated CH_2 group of the allyl to the tertiary and olefinic protons on either side). If the Cope rearrangement proceeds mainly through the transition-state resembling a chair rather than a boat,[7] the diastereoisomer XIX should predominate over XX.

Irradiation of XIa in ethanol with light from a mercury arc emitting mainly at 254 nm until none remained induced rearrangement to a deuteriated form of the unconjugated isomer (XII) in about 50% yield. The PMR spectrum made it clear that the deuterium was still present entirely at the 3-position of the allyl group. Thus the absorption from the cyclohexenic proton at τ 3·80 to that from the vinyl protons at higher field to that from the saturated methylene protons of the allyl group to that from the eight other methylene protons was in the ratio of 1·0:1·96:1·97:7·8. However, comparison with the spectra of the undeuteriated compound (XII) and of the pure *cis*-deuterioisomer (XIIa) showed that *cis* and *trans* isomers were present (XIIa and XIIb) in equal amounts. Because of the small geminal coupling between the vinyl methylene protons the pattern from the three vinyl protons was almost the same as in the spectrum from the undeuteriated sample (XII), except that the signals from the methylene protons were only half as intense. Both *cis* (10 c/s) and *trans* (17 c/s) couplings were evident. Similarly the IR spectrum showed peaks for the allyl double bond at both 1620 and 1640 cm^{-1} and also the o.o.p.def. frequencies of the vinyl group characteristic of both *cis* and *trans*-deuterio-allyl. (Thermal Cope rearrangement of this 50:50 mixture of XIIa and XIIb gave a sample of XIb spectroscopically indistinguishable from XIb produced by Cope rearrangement of pure XIIb, even though a different proportion of the two diastereoisomers would have been expected. In the PMR this is probably just because the two saturated allylic methylene protons have the same chemical shift even though they are not geometrically equivalent.)

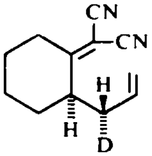
The loss of configuration about the double bond might have occurred before, during or after the 1,3 shift. An experiment was made in which irradiation was stopped before completion of the rearrangement: isolation gave two parts of recovered XIa to one of the product (XIIab). The recovered XIa and the product had identical spectra to those of the previous samples. In particular, no sign of any *trans* isomer of XIa could be detected in the recovered material. Since the *cis* and *trans* isomers of XI would photo-rearrange at almost exactly the same speeds, the loss of configuration cannot occur before migration. The lack of any measurable excess of *cis* (XIIa) over *trans* product (XIIb) shows that if configuration is lost after migration it must occur faster than migration. The *cis*-isomer (XIIa), being almost transparent, was stable to irradiation. The only remaining alternative explanation to *cis-trans* equilibration *during* migration was that the unchanged XIa acted as a photosensitizer for *cis-trans* isomerization of initially formed XIIa. This possibility, which seemed most unlikely because of the failure of XIa itself to undergo *cis-trans* isomerization, was disposed of by an experiment in which XIIa was irradiated in the presence of cyclohexylidenemalononitrile, expected to be at least as efficient a photosensitizer.

XIIa was recovered free of any detectable amount of XIIb. Thus both *cis*-reactant (XIa) and *cis*-product (XIIa) are configurationally stable, and we conclude therefore that the *cis-trans* isomerization is an integral part of the rearrangement.

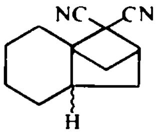
The first question to settle in considering the mechanism of the reaction is whether triplet or only singlet states are involved. Before the results with deuterium were known a possible reaction path seemed to be conversion of the excited singlet to the triplet, cleavage into a pair of allylic radicals, and recombination within an unusually efficient solvent cage. However, the complete lack of inversion of the migrating deuterio-allyl group renders this mechanism unlikely. When the lowest triplet state is actually produced, by energy transfer from triplet acetone, the product is completely diverted from that of allylic shift (XII) to cyclobutane formation (XXI).[8] Since reaction through any but the lowest triplet state is unlikely, the unsensitized rearrangement must go through an excited singlet state. Whether it is the $n\pi^*$ or $\pi\pi^*$ state is uncertain,[9] but a 1,3-shift in the lowest $\pi\pi^*$ excited state is allowed by symmetry.[10] Presumably the rearrangement of XI proceeds through the conformation with the allyl group axial, and the *cis-trans* isomerization in XIa suggests that at the half-way point the *p*-orbitals of C-3 and C-2 of the migrating allyl group are orthogonal. Alternatively the *cis*-product (XIIa) may be formed with enough vibrational energy to cause *cis-trans* isomerization. Experiments in progress to find out the stereochemical fate of the other centres in the photochemical rearrangement of diallylic compounds should clarify the mechanism.



XIX



XX



XXI

EXPERIMENTAL

General methods

Thin layer chromatography. The dinitrile mixtures could be analysed by TLC on silica gel with 60/80° petrol:ether (85:15 v/v). R_f values were rather variable because of the volatility of the solvent, but in general the following separations could be effected: methylenemalononitrile (R_f 0·2), XI (0·3) and XII (0·6). Spots were developed with iodine vapour (strong reaction with conjugated compounds, weak with unconjugated).

Column chromatography. On a column of silica gel (100–200 mesh) the unconjugated photo-product (XII) could be separated from conjugated starting material (XI) by elution with 60/80° petrol containing 2–5% of ether, and analysis of each fraction by TLC.

Distillation of photo-product. The photo-product (XII) undergoes Cope reaction very easily (half life at 120° ~70 min). In the original work it was distilled at 60°/1 × 10^5 mm to avoid this. In the present work chromatographic fractions, pure by TLC, were short-path distilled at ~120° (bath)/0·2–0·3 mm without change (TLC, IR); the time of distillation for a ~200 mg sample was ~3 min.

Spectra. IR spectra of liquid films were measured on a Unicam SP200. Although markers at 2851 and 1603 cm^{-1} were used frequencies between 3500 and 2000 were accurate to ±10 cm^{-1} and below 2000 to ±5 cm^{-1}. All bands were strong or medium unless designated w (weak).

NMR spectra of solns in CCl_4 containing TMS were run on a Varian A-60. Integrals were the average of 5 runs.

2-*Propargylcyclohexanone ethylene ketal and its deuteriation at* C-3′

2-Propargylcyclohexanone[11] (23·2 g) was heated with benzene (180 ml), ethylene glycol (15 ml), and toluene-*p*-sulphonic acid (35 mg) under a Dean and Stark water trap for 4 hr, and the product was then distilled to give the above *ketal* as an oil (26·8 g, 87%), b.p. 67–69°/0·7 mm. (Found: C, 73·0; H, 8·95. $C_{11}H_{16}O_2$ requires: C, 73·3; H, 8·95%); IR spectrum: 3310 (≡CH str), 2130 w (C≡C str); NMR spectrum: τ 6·16 s (ethylene ketal), τ 8·22 ~s (acetylenic H), τ 8·28 ~s (1′-methylene).

The above ketal (26·4 g) was heated under N_2 with EtOD (40 ml) containing EtONa (from 50 mg Na) for 1·5 hr. Most of the EtOD was then distilled, and the residue further treated 3 times with 25 ml portions of EtOD. After each addition the soln was heated under reflux for 1 hr before removal of the exchanged EtOD by distillation. Finally MeCOOD (0·5 ml) was added, and the deuterated ketal was isolated by addition of water and extraction with ether. Distillation gave the 3′-deuteriated ketal (24·9 g), b.p. 65°/0·4 mm. IR spectrum: No ≡CH band near 3300 cm^{-1}; C—D str at 2600 cm^{-1}. The C≡C str band was not clearly visible; there was a very weak band near 2000 cm^{-1}. NMR spectrum: τ 6·16 s (ethylene ketal), τ 8·28 s (1′-methylene).

2-(*Allyl*-cis-3′-D) *cyclohexanone*

The 3′-deuteriated propargylcyclohexanone ketal (20·0 g) was partially hydrogenated by the method of Cram and Allinger[12] over 5% $Pd/BaSO_4$ (0·5 g) in MeOH (100 ml) containing quinoline (0·5 ml). Absorption of 1 mol H_2 was complete in 3 hr, and hydrogenation was then stopped because slow absorption of H_2 was continuing. Filtration and evaporation of the soln gave an oil which was dissolved in methoxyethanol (150 ml) and heated on the steam bath with boric acid (90 g) for 2 hr to hydrolyse the ketal group (method of Hartmann[13]). The soln was poured into water (1·5 l.) and the ketone was extracted with ether (4 × 50 ml). The ether extract was washed with 2N H_2SO_4 to remove quinoline, and then with water and $NaHCO_3$aq. Evaporation of the dried soln and distillation of the residue gave the crude ketone (12·6 g), b.p. 82–84°/15 mm, which was shown by VPC to contain impurities (2-propargyl- and propylcyclohexanones?) having retention times very close to that of the major component. The crude ketone was converted to the semicarbazone, which after two recrystallizations from 90% EtOH had m.p. 171–172°, not depressed by admixture with authentic 2-allylcyclohexanone semicarbazone.[14] (Found: C, 61·4; H + D, 8·1; N, 21·4. $C_{10}H_{14}DON_3$ requires: C, 61·8; H + D, 8·3; N, 21·6%). The whole of this semicarbazone was steam distilled with oxalic acid (30 g) in water (150 ml). The oil which distilled was extracted with light petroleum and re-distilled (short-path/water pump) to give the *deuteriated ketone* (9·3 g, 60%). VPC of this sample (polypropylene glycol DE208, 125°) showed a single sharp symmetrical peak, but mass spectrometry of compounds derived from it showed that small amounts of impurities were still present. IR spectrum: 3050 sh, w (=C—H str), 2270 w (=C—D str), 1705 (C=O), 1640 vw (small amount of either R—CH=CH_2 or *trans*- R—CH=CHD), 1618 w (*cis* R—CH=CHD) and 825 sh, 810 cm^{-1} (*cis* R—CH=CHD o.o.p. def.) NMR spectrum: The spectrum was very similar to that of 2-allylcyclohexanone, except in the vinyl region. This was well separated into two multiplets at τ ~5 (terminal methylene) and τ ~4·3 (R—CH=). The ratio of the integrals of these two signals in the spectrum of the deuteriated sample was 1·1 (3′ monodeuteriation requires 1·0) in agreement with the conclusion from inspection of the IR spectrum that about 10% of undeuteriated compound was present.

2-*Allylcyclohexylidenemalononitrile and* cis-3′-D *derivative*

(a) 2-Allylcyclohexanone[15] (28·6 g) was condensed with malononitrile (17·0 g, excess) by the method of Prout,[16] using an AcOH/β-alanine catalyst, to give 2-allylcyclohexylidenemalononitrile[4] (24·3 g, 61%), b.p. 95°/0·1 mm. (Found: C, 77·5; H, 7·4; N, 15·2. Calc. for $C_{12}H_{14}N_2$: C, 77·4; H, 7·6; N, 15·0%), λ_{max} (EtOH) 240 mμ (ε 16,600). IR spectrum: =3070 (=C—H str), 2240 (C≡N conj.), 1640 (allyl C=C str), 1590 (C=C conj.), and 1005, 995 sh, 935 cm^{-1} (allyl o.o.p.def.). NMR spectrum: ratio olefinic/saturated proton integrals 0·25 (calc. 3/11 = 0·27).

(b) *cis*-3′ Deuteriated allylcyclohexanone (6·0 g) was similarly condensed with malononitrile (6·0 g) to give *2-allylcyclohexylidene-malononitrile* cis-3′-D (5·73 g, 72%), b.p. 100–102°/0·2 mm. IR spectrum: 3050 (=C—H str), 2240 (strong C≡N obscuring weak =C—D str), 1640 sh, w (residual R—CH=CH$_2$ str), 1620 (*cis*- R—CH=CH—D str), 1590 (C=C conj), 990 m and 815 s (*cis*- R—CH=CH—D o.o.p. def.). NMR spectrum: The spectrum was identical with that from (a) except in the vinyl region. The ratio of olefinic/saturated proton signal integrals was 0·18 (calc. for 1 × D at 3′, 0·18). Mass spectrum: Mass spectral analysis of isotopic composition was complicated by the occurrence of both M$^{+\cdot}$ and M-1$^+$ peaks in the spectrum of the undeuteriated compound, and by the presence of deuteriated and undeuteriated impurities (propargyl and propyl compounds) in the deuteriated sample. The approximate composition suggested by measurement of ion currents in the range *m/e* 184–188 was $C_{12}H_{14}N_2$, 10%; $C_{12}H_{13}DN_2$, 85–90%; impurities, ≤4%.

Propargyl-1-cyclohexenyl-malononitrile and its deuteriation

Attempted alkylation of cyclohexylidene-malononitrile[16] with propargyl bromide in EtOH and EtONa by the general method of Cope *et al.*[4] gave as the major product the mono-imino-ether [IR spectrum: 3320 (NH), 1650 (C=N), 1100 (=C—O—Et); 2260 w (C≡N unconj)]. The same compound was also isolated from preliminary experiments on the deuteriation of propargyl-1-cyclohexenyl-malononitrile with EtOD/NaOD. This addition was avoided by working in t-butanol.

(a) Cyclohexylidene-malononitrile (10·0 g) was added under nitrogen to a soln of K (2·7 g) in anhyd t-BuOH (120 ml). Propargyl bromide (9·0 g) was added dropwise during 15 min, and the soln was then warmed gently for 30 min. The t-BuOH was evaporated (rotary evaporator), and the oily residue, dissolved in ether, was repeatedly shaken with 20% NaHSO$_3$aq[4] until a sample no longer showed the intense absorption at 1690 cm^{-1} due to the conjugated starting material. Short-path distillation of the residual oil from a small Hickman still gave *propargyl-1-cyclohexenyl-malononitrile* as a colourless oil (9·6 g, 76%), b.p. ca. 90°/0·2 mm. This still showed a very weak band at 1590 cm^{-1}, but chromatography of a sample (500 mg) on silica gel (15 g), and short-path distillation of the material eluted with 150 ml of light petroleum containing 8% of ether, gave the pure nitrile named above. (Found: C, 78·2; H, 6·6; N, 15·3. $C_{12}H_{12}N_2$ requires: C, 78·2; H, 6·6; N, 15·2%). IR spectrum: 3300 (≡C—H str), 2260 w (C≡N), 2150 w (C≡C), 810 m ($>C{=}\overset{|}{C}\text{—H}$ o.o.p. def.) cm^{-1}. NMR spectrum: τ 3·70, mult., 1H (H-2), τ 7·06, doublet, *J* = 3 c/s, 2H (1′-CH$_2$), τ 7·68, partly obscured triplet, *J* = 3 c/s (H-3′). Partial hydrogenation of this propargyl compound (250 mg) over Pd/BaSO$_4$ ½% quinoline in MeOH gave allyl-1-cyclohexenyl-malononitrile, identified by its IR spectrum and by TLC.

(b) The propargyl compound was deuteriated at C-3′ by heating it (1·55 g) under N$_2$ with EtOD (recovered sample, ca. 90% D, 20 ml) and Et$_3$N (20 ml) for 2 hr. These solvents were distilled off, and the residue was then exchanged with fresh EtOD (5 ml) and Et$_3$N (5 ml). Finally the soln was evaporated and residual solvents were removed at 1 mm. CH$_3$COOD (0·2 ml) was added, and the residue, dissolved in ether (5 ml) and light petroleum (15 ml) was filtered through a short column of silica gel (5 g). The column was washed with a further 60 ml of this mixed solvent, and the eluates evaporated to give the crude 3′-deuteriated propargyl compound as a pale yellow oil (1·5 g). The IR spectrum of this material showed no acetylenic CH near 3300 cm^{-1}; bands at 2600 and 2000 cm^{-1} could be assigned to ≡C—D and C≡C stretching modes respectively.

Allyl-(cis-3′-D)*-1-cyclohexenyl-malononitrile*

The crude 3′-deuteriated propargyl compound above (1·5 g) was partially hydrogenated over 5% Pd/BaSO$_4$ (150 mg) in MeOH (20 ml) containing quinoline (5 drops). Hydrogenation was stopped after absorption of 1 mol of H$_2$, and the crude allyl compound (1·43 g) isolated essentially as described for the ethylene ketal case. TLC of this crude material showed that the allyl compound was the major component, but that some propargyl compound remained. The crude material was chromatographed on silica gel (75 g) and eluted with light petroleum containing (i) 3% ether (250 ml) and (ii) 5% ether (200 ml). The fractions eluted by solvent (ii) (1·2 g) were combined and distilled at 100° (bath)/0·1 mm to give the *cis*-3′-deuteriated allyl-1-cyclohexenyl-malononitrile. IR spectrum: 3050 sh (=CH), 2260 w (C≡N and =C—D), 1620 (*cis*- R—CH=CHD), 830 (*cis*- R—CH=CHD o.o.p. def.), 815 sh (cyclohexene o.o.p. def.) cm^{-1}. Two other bands of medium intensity at 990 and 935 cm^{-1} may also be deformation bands of the cis- R—CH=CHD system. NMR spectrum: The spectrum was identical with that of the undeuteriated compound, except in the olefinic region. This was changed in a manner consistent with complete and specifically *cis* 3'-deuteriation. The ratio of the integrals olefinic $\mathrm{H/1'CH_2}$, was $1{\cdot}4_6$ (calc. 1·50). Highfield (3') proton showed J_{cis} = 10 c/s.

Irradiation of 2-allylcyclohexylidene-malononitrile

The nitrile (1·0 g) was dissolved in EtOH (75 ml) in a silica test tube of volume ca. 125 ml. The soln was roughly degassed by repeated evacuation (water pump), and the sealed test tube was irradiated in an air-cooled Rayonet photochemical reactor (8 × 8 watts, 254 nm) for 19 hr. Examination of the yellow soln by TLC suggested that the required photoisomerization was not going to completion because the formation of much dark polymer was preventing the useful absorption of light. The ethanol was evaporated, the residue was extracted with hot light petroleum, and the petroleum extract was passed through a short column of silica gel to remove polymer. The light petroleum was evaporated and the oily residue was re-dissolved in EtOH (75 ml) and irradiated for a further 21 hr. The light petroleum–soluble product of this second irradiation was chromatographed on silica gel (6 × 1·5 cm) and eluted with light petroleum containing 5% ether. Short-path distillation of the residue from the main fraction gave an oil (401 mg) which was substantially the required photoproduct (IR spectrum), but which contained several minor impurities (TLC). This oil (330 mg) was further purified by chromatography on silica gel (8 g) and elution with light petroleum containing 3% ether. Finally the major fraction was distilled at 120° (bath)/0·3 mm to give allyl-1-cyclohexenyl-malononitrile. (Found: C, 77·45; H, 7·4; N, 15·2. Calc. for $\mathrm{C_{12}H_{14}N_2}$: C, 77·4; H, 7·6; N, 15·0%), which showed end absorption below 220 nm, and only broad, weak absorption ($\lambda_{\max}$ (EtOH) 225 nm, $\varepsilon_{\max}$ 60) at longer wavelengths. IR spectrum: 3070 ($\mathrm{{=}C}$ str), 2260 w ($\mathrm{C{\equiv}N}$), 1640 ($\mathrm{R{-}CH{=}CH_2}$ str), 1000 and 945 ($\mathrm{R{-}CH{=}CH_2}$ o.o.p. def.). NMR spectrum: τ 3·80 mult. (2-CH of cyclohexene) and vinyl pattern integrated for 4H with respect to the following ten saturated protons: τ 7·28 d, *J* = 6 c/s (1'-$\mathrm{CH_2}$), τ 7·85 mult. and τ 8·2–8·3 mult. (ring $\mathrm{CH_2}$'s).

The petroleum-insoluble material (ca. 0·4 g) was insoluble in ether, but readily soluble in $\mathrm{CHCl_3}$, $\mathrm{Me_2CO}$, or EtOH. The IR spectrum of a film cast from $\mathrm{CHCl_3}$ showed fairly strong absorption near 2250 $\mathrm{cm^{-1}}$ (conjugated ? $\mathrm{C{\equiv}N}$).

In a similar experiment the nitrile (0·5 g) in degassed EtOH (50 ml) was irradiated for 24 hr (4 × 8 watt lamps, 254 nm). After irradiation the head gas (volume ca. 75 ml) was expanded through a short column of self-indicating silica gel to remove most of the EtOH vapour into an evacuated 200 ml gas sampling bulb. VPC of this head gas on a 6 in column of di(2-ethylhexyl)sebacate (3% on silica gel; column DE108/K515') at 40° showed a single peak (retention time 12·5 min) identified as propene by comparison with the chromatogram of a calibration gas containing methane, ethane, propane (4·8 min), ethylene (3·7 min), and propene.

TLC of the EtOH soln showed that ca. 20–40% of photoisomerization had occurred.

Long irradiation of cis-*3'-deuteriated 2-allylcyclohexylidene-malononitrile*

The deuteriated dinitrile (1·5 g) in degassed EtOH (85 ml) was irradiated in a closed silica test tube (254 nm) for 39 hr. The product of this irradiation was separated from polymer (520 mg) by extraction with warm light petroleum, and re-irradiated in EtOH (80 ml) for 15 hr. Short-path distillation of the yellow oil thus formed gave a colourless oil (907 mg). This was chromatographed on silica gel (50 g; 25 × 2·5 cm) and eluted with light petroleum containing 2% ether. The photo-isomer (750 mg) was eluted first, followed by a more polar fraction (195 mg) which contained some starting material and also an unidentified nitrile. The latter was not obtained free of starting material (TLC) even after repeated column chromatography; its infrared spectrum showed bands at 2250 and 1595 $\mathrm{cm^{-1}}$ attributable to a conjugated nitrile and too intense to be due to starting material.

The main fraction was distilled at 120° (bath)/0·3 mm to give the deuteriated allyl-1-cyclohexenyl-malononitrile (640 mg). (Found: C, 77·2; H + D, 7·7; N, 14·8. $\mathrm{C_{12}H_{13}DN_2}$ requires: C, 77·0; H + D, 8·0; N, 15·0%), ε at 240 nm (EtOH), ~80. IR spectrum: 3050 sh ($\mathrm{{=}CH}$ str), 2260 w ($\mathrm{C{\equiv}N}$ and $\mathrm{{=}C{-}D}$), 1640 ($\mathrm{R{-}CH{=}CHD}$ *trans* and residual $\mathrm{R{-}CH{=}CH_2}$), 1620 (*cis* $\mathrm{R{-}CH{=}CHD}$), 990 and 935 (*trans* $\mathrm{R{-}CH{=}CHD}$ o.o.p. def.), and 830, 815 sh (*cis* $\mathrm{R{-}CH{=}CHD}$ and cyclohexene o.o.p. def.) NMR spectrum: The spectrum was substantially identical with that of the undeuteriated compound except in the olefinic region. This was changed in a manner consistent with deuteriation at the terminal C-3' only. The ratio of the integrals olefinic $\mathrm{H/1'CH_2}$ was 1·48. (Calc. for monodeuteriation at C-3', 1·50). The 3' proton showed splittings of 10 and 17 c/s (≃ *cis* and *trans* *J*'s). This deuteriated unconjugated dinitrile (120 mg) was heated in a sealed tube at 190° for 2 hr to effect thermal Cope isomerization to the conjugated allylcyclohexylidene-malonitrile structure. The crude product in light petroleum containing 8% ether was filtered through a short column of silica, and the filtrate was evaporated to a colourless oil, which contained only the conjugated isomer (TLC). The IR spectrum of this oil was indistinguishable from that of the undeuteriated material in all save one respect. This was that a sharp, weak band at 815 cm^{-1} in the spectrum of the undeuteriated compound, was rather broader ($\sim$820 cm^{-1}) and stronger in the spectrum of the deuteriated oil, consistent with the major deuteriated component being R—CHD—CH=CH_2, with 5–10% of R—CH_2—CH=CHD (strong band at 815 cm^{-1} in *cis*-isomer).

NMR spectrum: This was generally similar to the spectrum of the undeuteriated compound except near τ 7·6 (replacement of 1′—CH_2 by 1′—CHD). The ratio of olefinic/saturated proton integrals was 0·27. (Calc. for monodeuteriation at C-1′, 0·30; for undeuteriated compound, 0·27; for monodeuteriation at C-3′, 0·18).

Short irradiation of cis-*3′-deuteriated 2-allylcyclohexylidene-malononitrile*

The deuteriated dinitrile (1·0 g) in degassed EtOH (80 ml) was irradiated (low intensity) at 254 nm for 12 hr, when 20–30% conversion to the photo-isomer occurred (TLC, intensity of IR absorption at 1595 cm^{-1}). The light petroleum-soluble product (0·9 g) was chromatographed on silica gel (60 g) and eluted with light petroleum containing 2% ether. The first fractions eluted contained the crude photo-product (236 mg), an intermediate mixed fraction (121 mg) was rejected, and later fractions contained the conjugated starting material (390 mg).

After short-path distillation the recovered material (282 mg) was found to be indistinguishable from the starting material as shown by comparison of TL chromatograms, IR spectra, and NMR spectra (ratio of integrals of olefinic/saturated protons, 0·18). Thus no geometrical isomerization of the deuteriated allyl group occurred.

The photo-product fraction was re-chromatographed on silica gel (15 g), and the main fraction eluted with light petroleum containing 2% ether was short-path distilled to give deuteriated allyl-1-cyclohexenyl-malononitrile (149 mg).

IR spectrum: This was indistinguishable from that of the deuteriated photo-isomer obtained on long irradiation. NMR spectrum: This was indistinguishable from that of the product of long irradiation. Mass spectrum: Measurement of ion currents in the range 184–188 suggested the composition $C_{12}H_{14}N_2$, M 186 (9·3%); $C_{12}H_{13}DN_2$, M 187 (85%); M 188 (5·7%).

The deuteriated photo-isomer (110 mg) was rearranged to the conjugated isomer by heating for 2 hr at 190°. The purified product showed IR and NMR spectra indistinguishable from the corresponding product in the long irradiation series. In particular the same increased infrared absorption near 820 cm^{-1} was present.

Attempted cis/trans *isomerization of* cis-*3′-deuteriated allyl-1-cyclohexenyl-malononitrile*

The *cis*-3′-deuteriated nitrile (400 mg) and cyclohexylidene-malononitrile (42 mg) in EtOH (40 ml) were irradiated in silica at 254 nm for 20 hr. The EtOH was evaporated and the residual oil was chromatographed on silica gel (15 g). The unconjugated nitrile fraction was eluted with light petroleum containing 5% ether, and short-path distilled. The IR spectrum was indistinguishable from that of the starting material, so that no *cis/trans* isomerization occurred in this experiment.

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