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1. *Photochemical Transformations. Part VI.* Photochemical Cleavage of Cyclohexadienones.*

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On irradiation with ultraviolet light in the presence of a suitable nucleophile all *ortho*-type cyclohexadienones undergo smooth fission to acids (or derivatives) in high yield. Depending on the substituents the products are either $\beta\gamma : \delta\varepsilon$-conjugated or $\alpha\beta : \delta\varepsilon$-conjugated. The structural factors influencing the nature of the product and the choice of nucleophile have been elucidated. In the case of the 6-acetoxycyclohexadienone from mesitol irradiation causes aromatisation rather than fission unless a strong nucleophile (cyclohexylamine) is added. Reaction schemes for these photochemical rearrangements have been advanced and shown to correlate the facts so far established. Irradiation of (−)-usnic acid affords the racemic isomer.

CYCLOHEXADIENONES of the *ortho*-type (as I; R^1 and R^2 = blocking groups) are readily available from the acetoxylation [1] or alkylation [2] of *ortho*-substituted phenols. We have found that such cyclohexadienones are converted on irradiation with ultraviolet light in the presence of an appropriate nucleophilic reagent into acids or acid derivatives in high yield. The reaction sequence represents a new procedure for the fission of the phenolic nucleus and, because of the high yields obtainable, may have synthetic applications.

Our first experiments were conducted with water as the nucleophilic reagent. Irradiation of 6-acetoxy-6-methylcyclohexa-2,4-dienone [1] (I; $R^1 = OAc$, $R^2 = Me$, $R^3 = R^4 = H$) gave in 79% yield (94% by ultraviolet determination on the total product) 6-acetoxyhepta-3,5-dienoic acid (II; $X = OH$, $R^1 = OAc$, $R^2 = Me$, $R^3 = R^4 = H$), m. p. 86—87°. The constitution of this compound is based on the following evidence. The ultraviolet absorption spectrum showed $\lambda_{max.}$ 235 mμ (ε 23,800) indicative of a diene system. In the infrared spectrum (see p. 5) the appropriate bands are present including, specifically, those for an enol-acetate grouping. Hydrogenation (two mols. uptake) afforded 6-acetoxyheptanoic acid (III) (characterised as the *p*-bromophenacyl ester), which on hydrolysis and oxidation by chromic acid gave 6-oxoheptanoic acid (IV; R = H) (identified as the methyl ester 2,4-dinitrophenylhydrazone). Treatment of the acetoxydiene acid (II; $X = OH$, $R^1 = OAc$, $R^2 = Me$, $R^3 = R^4 = H$) with methanolic 2,4-dinitrophenylhydrazine gave slowly the 2,4-dinitrophenylhydrazone of methyl 6-oxohept-4-enoate, the ultraviolet absorption of which indicated the presence of the conjugated ethylenic linkage.

Irradiation of 6,6-dimethylcyclohexa-2,4-dienone [3] (I; $R^1 = R^2 = Me$, $R^3 = R^4 = H$) in the same way gave 64% (86·5% by ultraviolet determination on the total product) of 6-methylhepta-3,5-dienoic acid (II; $X = OH$, $R^1 = R^2 = Me$, $R^3 = R^4 = H$), m. p.

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* Part V, *J.*, 1958, 3314. For a preliminary communication see Barton and Quinkert, *Proc. Chem. Soc.*, 1958, 197.

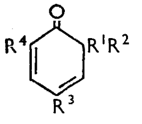
[1] Wessely and Sinwel, *Monatsh.*, 1950, **81**, 1055.

[2] Curtin, Crawford, and Wilhelm, *J. Amer. Chem. Soc.*, 1958, **80**, 1391.

[3] Alder, Flock, and Lessenich, *Chem. Ber.*, 1957, **90**, 1709.

48—50°. This showed $\lambda_{max.}$ at 238 mμ (ε 23,500) and the appropriate infrared bands (see p. 6). It was characterised as the *p*-bromophenacyl ester and gave acetone on ozonolysis.

6,6-Diacetoxy-4-methylcyclohexa-2,4-dienone [1] (I; $R^1 = R^2 =$ OAc, $R^3 =$ Me, $R^4 =$ H), on irradiation, similarly gave 6,6-diacetoxy-4-methylhexa-3,5-dienoic acid (II; X = OH, $R^1 = R^2 =$ OAc, $R^3 =$ Me, $R^4 =$ H), m. p. 70—71°, showing the correct infrared bands (see p. 6) and having ultraviolet absorption at 237 mμ (ε 12,200). To our knowledge, this is the first keten diacetate to be prepared.[4] As would be expected, such a compound was sensitive to temperature, especially in polar solvents.

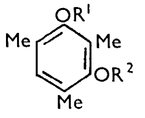

(I)

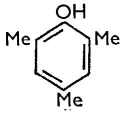
(II) $R^1R^2C{=}CH{\cdot}CR^3{=}CH{\cdot}CHR^4{\cdot}COX$

(III) $Me{\cdot}CH(OAc){\cdot}[CH_2]_4{\cdot}CO_2H$

(IV) $Me{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2R$

(V) $R^1R^2C{=}CH{\cdot}CHR^3{\cdot}CH{=}CR^4{\cdot}COX$


(VI)


(VII)

Irradiating 6-acetoxy-2,6-dimethylcyclohexa-2,4-dienone (I; $R^1 =$ OAc, $R^2 = R^4 =$ Me, $R^3 =$ H) gave an oily acid which contained, from its ultraviolet absorption spectrum, only about 50% of the expected conjugated diene (II; X = OH, $R^1 =$ OAc, $R^2 = R^4 =$ Me, $R^3 =$ H). 6-Acetoxy-4,6-dimethylcyclohexa-2,4-dienone [1] (I; $R^1 =$ OAc, $R^2 = R^3 =$ Me, $R^4 =$ H) gave an oily acid whose spectroscopic properties indicated that it had structure (V; X = OH, $R^1 =$ OAc, $R^2 = R^4 =$ Me, $R^3 =$ H) (see below).

The addition of more powerful nucleophiles than water gave interesting results. Irradiation of the acetoxy-compound (I; $R^1 =$ OAc, $R^2 =$ Me, $R^3 = R^4 =$ H) in the presence of aniline or cyclohexylamine afforded the corresponding crystalline amides (II; X = NHPh or $NH{\cdot}C_6H_{11}$, $R^1 =$ OAc, $R^2 =$ Me, $R^3 = R^4 =$ H) in high yield. Both showed the expected spectroscopic properties (see p. 6). The acetoxy-dimethyl analogue (I; $R^1 =$ OAc, $R^2 = R^4 =$ Me, $R^3 =$ H) in the presence of cyclohexylamine gave in 82% yield the cyclohexylamide (II; X = $NH{\cdot}C_6H_{11}$, $R^1 =$ OAc, $R^2 = R^4 =$ Me, $R^3 =$ H), which showed $\lambda_{max.}$ 238 mμ (ε 23,100) and had the expected infrared bands (see p. 6). However, the isomeric acetoxy-dimethyl-dienone (I; $R^1 =$ OAc, $R^2 = R^3 =$ Me, $R^4 =$ H) furnished in 81% yield the αβ-unsaturated cyclohexylamide (V; X = $NH{\cdot}C_6H_{11}$, $R^1 =$ OAc, $R^2 = R^3 =$ Me, $R^4 =$ H); this showed ultraviolet absorption indicative of an αβ-unsaturated amide and the correct infrared bands, specifically those for an enol-acetate grouping (see p. 7). The most simple explanation of the formation of compounds of this class (see below) is that the excess of cyclohexylamine used is sufficiently basic to isomerise the initially conjugated diene (II) into the isomer (V).

Irradiation of 6-acetoxy-2,4,6-trimethylcyclohexa-2,4-dienone [1] (I; $R^1 =$ OAc, $R^2 = R^3 = R^4 =$ Me) gave results which justified more prolonged investigation. In the presence of cyclohexylamine ring fission occurred smoothly in the usual way to furnish in 84% yield the cyclohexylamide (V; X = $NH{\cdot}C_6H_{11}$, $R^1 =$ OAc, $R^2 = R^3 = R^4 =$ Me), which showed ultraviolet and infrared absorption in agreement with this constitution, consumed two mols. of hydrogen on catalytic hydrogenation, and gave a nuclear magnetic resonance spectrum indicating the presence of six allylic protons in two methyl groups (line at 8·17 c/sec.).* In contrast, the βγ-unsaturated amides (II; X = $NH{\cdot}C_6H_{11}$, $R^1 =$ OAc, $R^2 =$ Me, $R^3 =$ H, $R^4 =$ H or Me) showed only three allylic protons in a methyl group (lines at 8·01 and 8·03 c/sec. respectively).

In dry ether, or in the presence of water or aniline, the trimethyl ketone (I; $R^1 =$ OAc, $R^2 = R^3 = R^4 =$ Me) did not undergo ring fission on irradiation. Instead, there was a

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* We are grateful to Dr. L. M. Jackman of this Department for the determination and interpretation of the nuclear magnetic resonance spectra mentioned in this paper.

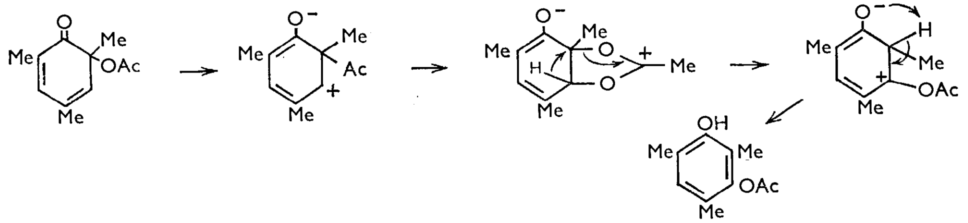
[4] Cf. Wasserman and Wharton, *Tetrahedron*, 1958, **3**, 321.

relatively slow formation of aromatic substances. The main product was 3-acetoxymesitol (VI; $R^1 = H, R^2 = Ac$), identified by hydrolysis to the known diol (VI; $R^1 = R^2 = H$) and acetylation to the known diacetate (VI; $R^1 = R^2 = Ac$). By paper chromatography the presence of mesitol itself (VII) was detected.

The mechanism of this aromatisation is of interest. It is conceivable that the dienone (I; $R^1 = OAc, R^2 = R^3 = R^4 = Me$) could be cleaved into acetoxyl and mesitoyl radicals which, after many fruitless *ortho-* and *para*-combinations might eventually combine at the *meta*-position to give the observed product. However, acetoxyl radicals are generally conceded [5] to decompose rapidly to methyl and carbon dioxide. It was shown that about 25% of the theoretical amount of carbon dioxide was evolved in the irradiation both in the presence and in the absence of 10 molecular proportions of *p*-cresol, a compound known to be an efficient trap for acetoxyl radicals.[6] The amount of carbon dioxide evolved corresponds to the amount of mesitol indicated by paper chromatography. We conclude that the radical mechanism of rearrangement can be excluded.

The rearrangement also proceeds in a polystyrene film as well as in thoroughly dry ether. If we accept that the excited state of the dienone would show charge separation and that the above results do indeed exclude the participation of water (or of other solvent molecules), then the reaction can be represented as in Scheme A. This assigns to the acetate residue its well-known capacity to bear a positive charge during neighbouring-group participation and thus explains the failure of the analogous compound (I; $R^1 =$ allyl, $R^2 = R^3 = R^4 = Me$) to undergo any rearrangement (see below).

Scheme A:



The irradiation of the 6-acetoxy-6-methyl-dienone (I; $R^1 = OAc, R^2 = Me, R^3 = R^4 = H$) in anhydrous ether (no nucleophile) also caused aromatisation, but here the main product was *o*-cresol, and acyl migration was not observed. We consider the loss of the acetoxyl to involve homolysis, the solvent ether probably acting as the source of hydrogen for the *o*-tolyloxy-radical.

Irradiation of 6-allyl-2,6-dimethylcyclohexa-2,4-dienone (I; $R^1 =$ allyl, $R^2 = R^4 = Me, R^3 = H$) in the presence of cyclohexylamine gave the βγ-unsaturated amide (II; $X = NH{\cdot}C_6H_{11}$, $R^1 =$ allyl, $R^2 = R^4 = Me, R^3 = H$), characterised by the appropriate spectroscopic measurements.

Prolonged irradiation of the allyltrimethyl ketone [2] (I; $R^1 =$ allyl, $R^2 = R^3 = R^4 = Me$) in the presence of water led to recovery unchanged. In contrast, irradiation in the presence of cyclohexylamine caused the usual smooth fission to furnish the αβ-unsaturated amide (V; $X = NH{\cdot}C_6H_{11}$, $R^1 =$ allyl, $R^2 = R^3 = R^4 = Me$) in 84% yield. The constitution assigned was fully supported by spectroscopic data.

The results described in this paper can be most simply rationalised in terms of Scheme B. In this we have not attempted to depict the various excited states that must be assumed, but have concentrated on definite chemical species. The initial product of ring fission is the *cis*-keten (VIII). This rearranges to the *trans*-keten (IX), which, on reaction with

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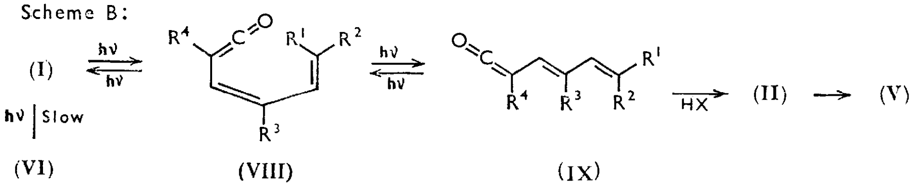
[5] Rembaum and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 3486; Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, 1957, pp. 491—493.

[6] Walling and Hodgdon, *J. Amer. Chem. Soc.*, 1958, **80**, 228.

the appropriate nucleophile, affords (II), and then (V), in the normal way. The *trans*-configuration of the diene system in (II) and thus in (IX) is established by the high intensity of ultraviolet absorption (ε ~25,000) in all compounds where R^3 = H.[7] When R^3 = Me as in compounds (II; R^1 = R^2 = OAc, R^3 = Me, R^4 = H) the value of ε is only about half this value.[8] One has to explain the special behaviour of the mesitol derivative (I; R^1 = OAc, R^2 = R^3 = R^4 = Me). For this compound the desired *trans*-keten (IX; R^1 = OAc, R^2 = R^3 = R^4 = Me) † has unfavourable 1,3-interactions between the three methyl groups R^2, R^3, and R^4. These must destabilise the *trans*-form (IX) relatively to the *cis*-keten (VIII) and thus increase the rate of the back-reaction to give the cyclohexadienone (I). Eventually the cyclic ketone (I) undergoes the much slower photochemical rearrangement to the acetoxymesitol (VI; R^1 = H, R^2 = Ac), or when R^1 = allyl instead of acetyl merely remains unchanged.

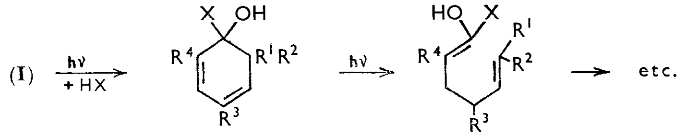
Scheme B:



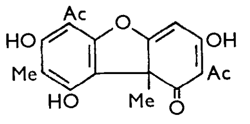
HX = nucleophile.

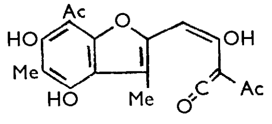
For 6-acetoxy-compounds where the *trans*-keten has only one unfavourable 1,3-interaction fission is faster than aromatisation. Thus the dienone (I; R^1 = OAc, R^2 = R^3 = Me, R^4 = H) gave, or irradiation in the presence of water, about 90% of fission and 10% of rearrangement. All other dienones studied which lacked the 4-methyl substituent (*i.e.*, where R^3 = H) gave no indication of aromatisation.

Scheme C:



We have also considered a further reaction scheme C. Apart from the improbability of nucleophile addition at the carbonyl-carbon atom, especially in the mesitol derivatives, such a scheme would not explain the paramount importance of the R^3 substituent and would not rationalise the marked difference between the behaviour of the trimethyl ketone (I; R^1 = OAc, R^2 = R^3 = R^4 = Me) and the dimethyl analogue (I; R^1 = OAc, R^2 = R^4 = Me, R^3 = H). Also it is possible to choose a filter such that ergosterol, containing a cyclohexadiene system, is unaffected by irradiation under conditions which transform the ketone (I; R^1 = OAc, R^2 = R^4 = Me, R^3 = H) in the presence of cyclohexylamine smoothly into the amide (II; X = $NH{\cdot}C_6H_{11}$, R^1 = OAc, R^2 = R^4 = Me, R^3 = H) obtained earlier.


(X)


(XI)

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† The orientations (R^1 = OAc, R^2 = Me) and (R^1 = Me, R^2 = OAc) are not differentiated in any of the compounds discussed in this paper, although they must, of course, have one or other of the two possible configurations.

[7] See Braude and Waight in " Progress in Stereochemistry," Vol. I, Ed. by W. Klyne, Butterworths, London, 1954.

[8] Braude and Coles, *J.*, 1952, 1425; Braude and Evans, *J.*, 1954, 607.

The thermal racemisation of usnic acid (X) has also been postulated[9] as proceeding through a keten intermediate (XI). We have now shown that usnic acid, in agreement with Stork's mechanism, is smoothly racemised by ultraviolet light in dioxan solution.*

EXPERIMENTAL

Ultraviolet absorption spectra were obtained for ethanol solutions on the Unicam S.P. 500 spectrophotometer. Unless stated to the contrary, the light petroleum used was of b. p. 40—60°. M. p.s were determined on the Kofler block. Unless otherwise stated, B.D.H. silica gel and alumina standardised according to Brockmann and Schodder[11] were used for chromatography. Ethereal solutions were dried over $MgSO_4$ before evaporation.

The paper chromatography of phenols was carried out over Whatman No. 1 paper impregnated with dimethyl sulphoxide.[12] The chromatograms were developed by spraying consecutively with 10% potassium ferricyanide solution and 10% ferric chloride solution. Starting materials and non-phenolic irradiation products gave no colour under these conditions. Phenolic compounds gave a strong Prussian blue colour.

Nuclear magnetic resonance spectra were obtained with a Varian Associates spectrometer using a 40 mc. oscillator. The spectra were calibrated with tetramethylsilane as an internal reference.[13] Solutions (10%) in deuterated chloroform were used; results are expressed as τ.

General Procedure for Photochemical Cleavage.—Except where stated otherwise, the irradiations were carried out under oxygen-free nitrogen in a Pyrex flask by a mercury-lamp (250 w) at the b. p. of the solvent. The flask was placed at 10 cm. from the light source. The solutions contained 0·1—1% of cyclohexadienone. Aliquot parts were removed at 30 min. (or shorter if more convenient) intervals for ultraviolet-absorption measurement. When there was no further change the reaction mixture was irradiated for a further 30 min. and then worked up. In every case a control experiment was carried out without irradiation. It was shown by ultraviolet-absorption measurements as well as by the appropriate isolation of starting material that in no case was there any chemical reaction from purely thermal causes. In each case the heat from the mercury lamp caused the ethereal solvent to reflux.

Irradiation of 6-*Acetoxy*-6-*methylcyclohexa*-2,4-*dienone in the Presence of Water.*—The cyclohexadienone[1] (1·24 g.) in ether (1240 ml.), previously saturated with water, was irradiated for 3 hr. The dried ($MgSO_4$) ethereal solution, which showed $\lambda_{max.}$ 234·5 mμ (ε 23,400) (93·5%), was evaporated and the residue crystallised twice from cyclohexane to give 6-*acetoxyhepta*-3,5-*dienoic acid* (1·09 g.), m. p. 86—87°, $\lambda_{max.}$ 235 mμ (ε 23,800), $\nu_{max.}$ (in $CHCl_3$) 3480 (unassociated OH), 2500—3440 (associated OH), 1748 (enol-acetate), 1726 (CO_2H), 1677 and 1622 (conjugated C=C), $\nu_{max.}$ (in CCl_4) 3500 (unassociated OH), 2500—3420 (associated OH), 1755 and 1208 (enol-acetate), 1715 (CO_2H), and 1655 (C=C) cm.$^{-1}$ (Found: C, 58·95; H, 6·75. $C_9H_{12}O_4$ requires C, 58·7; H, 6·55%). The acetoxy-acid (200 mg.) in methanol (3 ml.) was warmed with 2,4-dinitrophenylhydrazine (238 mg.) in methanol (12 ml.) and aqueous 3N-hydrochloric acid (1 ml.) and left for some hours. The precipitate was recrystallised from methanol to give *methyl* 6-(2,4-*dinitrophenylhydrazono*)*hept*-4-*enoate* (133 mg.), m. p. 118—119°, $\lambda_{max.}$ 374 mμ (ε 26.800), $\nu_{max.}$ (in $CHCl_3$) 1735 (saturated ester), 1645 (unsaturated $>$C=N–), 1617 (C=C), and 967 (*trans*–CH=CH–) cm.$^{-1}$ (Found: C, 50·2; H, 4·85; N, 17·15. $C_{14}H_{16}O_6N_4$ requires C, 50·0; H, 4·8; N, 16·65%). The compound was insoluble in aqueous sodium hydrogen carbonate solution.

Hydrogenation of 6-*Acetoxyhepta*-3,5-*dienoic Acid.*—The acetoxy-acid (910 mg.) in ethanol (30 ml.) was hydrogenated over 5% palladised charcoal (300 mg.) until saturated. The oily product was characterised by conversion in the usual way into p-*bromophenacyl* 6-*acetoxyheptanoate*, m. p. 59—60° (from 95% ethanol) (Found: C, 53·55; H, 5·9; Br, 20·65. $C_{17}H_{21}O_5Br$ requires C, 53·3; H, 5·5; Br, 20·75%). The major portion (700 mg.) of the hydrogenation product was refluxed for 40 min. with potassium hydroxide (6 g.) in methanol (100 ml.). The resulting acid did not crystallise. It was, therefore, oxidised in acetone (3 ml.) at 0° with

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* Earlier work[10] did not distinguish between racemisation and general destruction of optically active material.

[9] Stork, *Chem. and Ind.*, 1955, 915.
[10] Mackenzie, *J. Amer. Chem. Soc.*, 1955, **77**, 2214.
[11] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.
[12] Wachtmeister and Wickberg, *Acta Chem. Scand.*, 1958, **12**, 1335.
[13] van Dyke Tiers, *J. Pnys. Chem.*, 1958, **62**, 115.

sulphuric–chromic acid (0·8 ml.) according to the procedure of Bowden, Heilbron, Jones, and Weedon.[14] The acidic product (437 mg.) crystallised at 0° but was molten at room temperature. Treatment with excess of redistilled ethereal diazomethane and then with methanolic 2,4-dinitrophenylhydrazine gave *methyl* 6-(2,4-*dinitrophenylhydrazono)heptanoate* (862 mg.), m. p. 123—124°. Recrystallised from ethanol, this had $\lambda_{max.}$ 360 mμ (ε 21,800) (Found: C, 49·8; H, 5·35; N, 16·7. $C_{14}H_{18}O_6N_4$ requires C, 49·7; H, 5·35; N, 16·55%). It was undepressed in m. p. on admixture with a specimen prepared from 6-oxoheptanoic acid.[15]

Irradiation of 6-*Acetoxy*-6-*methylcyclohexa*-2,4-*dienone in the Presence of Organic Bases.*—(a) *Aniline.* The dienone (543 mg.) and redistilled aniline (614 mg.) in dry ether (540 ml.) were irradiated for 100 min. Removal of the excess of aniline by shaking with 4N-hydrochloric acid and working up in the usual way gave the anilide of 6-acetoxyhepta-3,5-dienoate. Purified by filtration in benzene solution over silica gel (5 g.) and crystallisation from aqueous ethanol this (670 mg.) had m. p. 105—106°, $\lambda_{max.}$ 245 mμ (ε 33,400), $\nu_{max.}$ (in $CHCl_3$) 3384 (secondary amide), 1755 (enol-acetate) and 1682 (anilide C=O) cm.$^{-1}$ (Found: C, 69·7; H, 6·7; N, 5·25. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·6; N, 5·4%).

(b) *Cyclohexylamine.* The dienone (1·22 g.) and cyclohexylamine (1·51 g.) in dry ether (800 ml.) were irradiated for 2 hr. The excess of cyclohexylamine was removed as above and the product isolated in the usual way. Recrystallisation from ether gave the *cyclohexylamide* of 6-acetoxyhept-3,5-dienoic acid as needles (1·55 g.), m. p. 86·5—88°, $\lambda_{max.}$ 237 mμ (ε 23,900), $\nu_{max.}$ (in CCl_4) 3389 (secondary amide), 1759 (enol-acetate), and 1670 (cyclohexylamide C=O) cm.$^{-1}$ (Found: C, 67·85; H, 8·6; N, 5·3. $C_{15}H_{23}O_3N$ requires C, 67·9; H, 8·75; N, 5·3%).

Irradiation of 6-*Acetoxy*-6-*methylcyclohexa*-2,4-*dienone in Anhydrous Ether.*—The dienone (1·65 g.) in anhydrous ether (750 ml.) was irradiated for 16 hr. The solvent was removed *in vacuo* to furnish a reddish oil (1·5 g.) smelling of *o*-cresol. The product was filtered through alumina (250 g.; Grade III) in light petroleum–benzene (1 : 1) and then treated in methanol (10 ml.) under nitrogen with 10% aqueous sodium hydrogen carbonate (20 ml.) at room temperature for 48 hr. Acidification and extraction into ether gave an oil (350 mg.) which afforded, on 3,5-dinitrobenzoylation (method of Brewster and Ciotti [16]), filtration in methylene dichloride through alumina (5 g.; Grade III), and crystallisation from methanol, *o*-tolyl 3,5-dinitrobenzoate (m. p., mixed m. p., and infrared spectrum) as well as traces of a second 3,5-dinitrobenzoate, m. p. 182—184°.

Irradiation of 6,6-*Dimethylcyclohexa*-2,4-*dienone.*—The dienone [3] (330 mg.) in ether (330 ml.) saturated with water was irradiated for 3 hr. The product (86·5% by ultraviolet absorption), crystallised from light petroleum (b. p. 60—80°), gave 6-methylhepta-3,5-dienoic acid (244 mg.), m. p. 48—50°, $\lambda_{max.}$ 238 mμ (ε 23,500), $\nu_{max.}$ (in CCl_4) 3542 (unassociated OH), 2500—3400 (associated OH), 1733 (saturated C=O), and 1677 and 1632 (conjugated C=C) cm.$^{-1}$ (Found: C, 68·3; H, 8·7. $C_8H_{12}O_2$ requires C, 68·5; H, 8·6%). The derived *p-bromophenacyl ester*, crystallised from ethanol, had m. p. 108—108·5° (Found: C, 57·3; H, 5·5; Br, 23·9. $C_{16}H_{17}O_3Br$ requires C, 57·0; H, 5·1; Br, 23·7%).

6-Methylhepta-3,5-dienoic acid (152 mg.) in " AnalaR " acetic acid (18 ml.) was treated with excess of ozone at 20°. The final excess of ozone was removed with nitrogen, and water (20 ml.) and 4N-aqueous sodium hydroxide (48 ml.) were added. After 15 minutes' refluxing and then cooling to room temperature, N-aqueous potassium permanganate (20 ml.) was added and the mixture was heated for a further 10 min. on the steam-bath. Steam-distillation into an ethanolic 2,4-dinitrophenylhydrazine reagent gave, after crystallisation from methanol, acetone 2,4-dinitrophenylhydrazone (112 mg.), identified by m. p., mixed m. p., and crystal form.

Irradiation of 6,6-*Diacetoxy*-4-*methylcyclohexa*-2,4-*dienone.*—The dienone [1] (510 mg.) in ether (510 ml.) saturated with water was irradiated for 2·5 hr. The residue had ultraviolet absorption corresponding to 93% of the cleavage product. Crystallisation from light petroleum gave 6,6-*diacetoxy*-4-*methylhepta*-3,5-*dienoic acid* (319 mg.), m. p. 70—71°, $\lambda_{max.}$ 237 mμ (ε 12,200), $\nu_{max.}$ (in $CHCl_3$) 3473 (unassociated OH), 2500—3400 (associated OH), 1775 (enol-acetates), 1730 (saturated C=O), and 1685 and 1628 (conjugated C=O) cm.$^{-1}$ (Found: C, 54·9; H, 6·0. $C_{11}H_{14}O_6$ requires C, 54·55; H, 5·85%). The compound is sensitive to temperature, especially when dissolved in polar solvents and should be crystallised with care.

Irradiation of 6-*Acetoxy*-4,6-*dimethylcyclohexa*-2,4-*dienone.*—(a) *In the presence of water.*

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[14] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

[15] Schaeffer and Snoddy, *Org. Synth.*, 1951, **31**, 3.

[16] Brewster and Ciotti, *J. Amer. Chem. Soc.*, 1955, **77**, 6214.

The dienone [1] (476 mg.) in ether (350 ml.) saturated with water was irradiated for 100 min. The oily product did not crystallise and had (ε 6700) at 211—221 mμ, infrared bands (in CCl_4) at 3520 (unassociated OH), 2600—3400 (associated OH), 1748 (enol-acetate), and 1702 (αβ-unsaturated C=O) cm.$^{-1}$. Paper chromatography indicated the presence of a small quantity of a phenol. This was confirmed by the presence of a band at 274 mμ of intensity equivalent to at the most 10% of phenolic material.

(b) *In the presence of cyclohexylamine.* The dienone (750 mg.) in anhydrous ether (750 ml.) containing cyclohexylamine (836 mg.) was irradiated for 4 hr. After removal of the cyclohexylamine with 3N-hydrochloric acid, the product was filtered in light petroleum through silica gel (15 g.) and then crystallised from light petroleum to give the 6-*acetoxy*-N-*cyclohexyl*-4-*methylhepta*-2,5-*dienamide* (1·09 g., 81%), m. p. 52—54°, end absorption at 210 mμ (ε 4500), $\nu_{max.}$ (in CCl_4) 3379 (secondary amide), 1749 (enol-acetate), 1678 (amide (C=O), and 1225 (enol-acetate) cm.$^{-1}$ (Found: C, 68·8; H, 8·9; N, 5·05. $C_{16}H_{25}O_3N$ requires C, 68·8; H 9·0; N, 5·0%).

Irradiation of 6-*Acetoxy*-2,6-*dimethylcyclohexa*-2,4-*dienone*.—(a) *In the presence of water.* The dienone [17] (475 mg.) in ether (350 ml.) saturated with water was irradiated for 100 min. The oily product (486 mg.) had $\lambda_{max.}$ 243 mμ (ε 12,600), $\nu_{max.}$ (in CCl_4) at 3535 (unassociated OH), 2400—3400 (associated OH), 1756 (enol-acetate), 1735 (saturated CO_2H), 1690 (αβ-unsaturated CO_2H), and 1635 (conjugated C=C) cm.$^{-1}$. The intensity of the ultraviolet absorption and the infrared bands indicate the presence of approximately 50% of a conjugated diene. Phenols could not be detected by paper chromatography.

(b) *In the presence of cyclohexylamine.* The dienone (635 mg.) in dry ether (635 ml.) containing cyclohexylamine (819 mg.) was irradiated for 2 hr. The excess of cyclohexylamine was removed as before and the product (in benzene) was filtered through silica gel (5 g.) to give 6-*acetoxy*-N-*cyclohexylhepta*-3,5-*diene*-2-*carboxyamide* (906 mg., 82%). Recrystallised from light petroleum (b. p. 60—80°), this had m. p. 134—135°, $\lambda_{max.}$ 238 mμ (ε 23,100), $\nu_{max.}$ (in CCl_4) 3360 (secondary amide), 1755 (enol-acetate) and 1672 (amide C=O) cm.$^{-1}$ (Found: C, 68·5; H, 9·2. $C_{16}H_{25}O_3N$ requires C, 68·8; H, 9·0%).

(c) *With a filter.* For these experiments a 2·5 cm. layer of 0·5% aqueous potassium hydrogen phthalate solution was employed. This was replaced at least every 24 hr. The filtered solution was placed in a Pyrex Petri dish, and the reaction solution in a quartz flask immediately above the filter solution. Irradiation of ergosterol (761 mg.) in dry ether (760 ml.) for 30·5 hr. caused no chemical change (recovery of ergosterol, 757 mg.; identified by m. p., mixed m. p., rotation, and ultraviolet absorption). Irradiation of the dienone (823 mg.) in dry ether (825 ml.) containing cyclohexylamine (5 ml.) for 5·25 hr. and processing as above gave the cyclohexylamide (1024 mg., 72%) of 6-acetoxyhepta-3,5-diene-2-carboxylic acid, identified by m. p., mixed m. p., and ultraviolet absorption.

Irradiation of 6-*Allyl*-2,6-*dimethylcyclohexa*-2,4-*dienone*.—The crude dienone [18] (530 mg.) in dry ether (550 ml.) containing cyclohexylamine (3 ml.) was irradiated for 3 hr. Removal of excess of cyclohexylamine and chromatography over alumina (Grade III; 350 g.) gave, on elution with light petroleum–ether (8 : 2), a main fraction having $\lambda_{max.}$ 245 mμ (ε 18,000). Rechromatography then furnished the *cyclohexylamide* (216 mg.) of 6-methylnona-3,5,8-triene-2-carboxylic acid. Recrystallised from light petroleum this had m. p. 79—81°, $\lambda_{max.}$ 245 mμ (ε 25,200), $\nu_{max.}$ (in CCl_4) 3390 (secondary amide), 1670 (amide C=O) and 910 and 990 (vinyl group) cm.$^{-1}$ (Found: C, 78·05; H, 10·2; N, 5·4. $C_{17}H_{27}ON$ requires C, 78·1; H, 10·4; N, 5·35%).

Irradiation of 6-*Allyl*-2,4,6-*trimethylcyclohexa*-2,4-*dienone*.—(a) *In the presence of water.* The dienone [2] (7·5 g.) in ether (1 l.) saturated with water was irradiated for 93 hr. without change in the ultraviolet absorption spectrum. After drying and removal of the solvent the dienone (6·8 g.) was recovered.

(b) *In the presence of cyclohexylamine.* The dienone (2·84 g.) in anhydrous ether (500 ml.) containing cyclohexylamine (3 ml.) was irradiated for 13·5 hr. The excess of cyclohexylamine was removed as before to give an oil (2·88 g.). A portion (840 mg.) of this product was chromatographed in light petroleum over acid silica gel.[19] Elution with 5 : 1 light petroleum–ether gave the *cyclohexylamide* (615 mg., 83·5%) of 4,6-dimethylnona-2,5,7-triene-2-carboxylic

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[17] Cavill, Cole, Gilham, and McHugh, *J.*, 1954, 2785.

[18] Curtin and Crawford, *J. Amer. Chem. Soc.*, 1957, **79**, 3156.

[19] Brockmann and Muxfeldt, *Chem. Ber.*, 1956, **89**, 1393.

acid which crystallised. Recrystallised in the cold from light petroleum this had m. p. 50—53°, end absorption of ε 12,300 at 210 mμ, and $\nu_{max.}$ (in CCl_4) at 3358 (secondary amide), 1673 (amide C=O), and 916 and 982 (vinyl) cm.$^{-1}$ (Found: C, 78·65; H, 10·3. $C_{18}H_{28}ON$ requires C, 78·8; H, 10·3%).

Irradiation of 6-*Acetoxy*-2,4,6-*trimethylcyclohexa*-2,4-*dien*-1-*one*.—(a) *In the presence of water*. The dienone [1] (787 mg.) in ether (790 ml.) saturated with water was irradiated for 23·5 hr. The product, on crystallisation from light petroleum (b. p. 60—80°), gave *3-acetoxymesitol* (324 mg,, 41%) as needles, m. p. 90—90·5°, $\lambda_{max.}$ 279 mμ (ε 2350), $\nu_{max.}$ (in CCl_4) 3592 (unassociated OH), 3468 (associated OH), and 1760 (phenolic OAc) cm.$^{-1}$ (Found: C, 68·05; H, 7·45. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·25%).

The total irradiation product was also investigated by paper chromatography. In three systems [light petroleum; light petroleum–benzene (4 : 1); and light petroleum–di-isopropyl ether (4 : 1)] the presence of 3-acetoxymesitol (most intense spot) and mesitol (second most intense spot) was detected. Two other, less intense spots represented compounds which were not investigated.

3-Acetoxymesitol (1·73 g.) in ethanol (110 ml.) containing concentrated hydrochloric acid (10 ml.) was heated under reflux for 5 hr. The ethanol was removed *in vacuo* and the residue extracted into ether. Removal of the ether gave a residue (1·3 g.) which crystallised from light petroleum (b. p. 60—80°) to furnish mesitylene-2,4-diol [20] (988 mg.), identified by m. p., mixed m. p., and ultraviolet and infrared absorption (Found: C, 71·25; H, 7·95. Calc. for $C_9H_{12}O_2$: C, 71·0; H, 7·9%).

3-Acetoxymesitol (410 mg.) in acetic anhydride (25 ml.) was heated under reflux for 6 hr. The excess of anhydride was removed *in vacuo* and the residue crystallised from 95% ethanol to give 2,4-diacetoxymesitylene [20] (392 mg.), identified by m. p., mixed m. p., and ultraviolet and infrared absorption (Found: C, 66·45; H, 6·75. Calc. for $C_{13}H_{16}O_4$: C, 66·1; H, 6·85%).

(b) *In dry ether*. Irradiation was as above except that a slow stream of dry nitrogen was passed through the irradiated solution and then through a series of three wash-bottles containing 1·67N-barium hydroxide. The dienone (715 mg.) in anhydrous ether (750 ml.) was irradiated for 19·5 hr. The evolution of carbon dioxide was 42 mg. (26%), duplicated, within a few percent, in two further experiments. To the irradiated solution *p*-cresol (8·0 g.) was added and the product worked up by removal of the solvent *in vacuo*. The oily product was distilled at 0·2 mm. and the fractions showing the 1760 cm.$^{-1}$ phenol ester band in the infrared spectra were collected and treated with 15% aqueous ammonia (40 ml.) at room temperature until all had dissolved (53 hr.). Acidification with 6N-hydrochloric acid and extraction into ether gave an oil (412 mg.) which crystallised from light petroleum (b. p. 60—80°) to furnish mesitylene-2,4-diol (269 mg., 48%).

In a further experiment the dienone (809 mg.) in anhydrous ether (810 ml.) containing *p*-cresol (9 g.) was irradiated for 20 hr. as above. The evolution of carbon dioxide was 53 mg. (29%) and the product afforded mesitylene-2,4-diol (284 mg., 45%) when worked up in the same way.

(c) *In the presence of aniline*. The dienone (950 mg.) in anhydrous ether (850 ml.) containing redistilled aniline (1·02 ml.) was irradiated for 26·5 hr. The aniline was removed by washing with 3N-hydrochloric acid (150 ml.), and the product chromatographed over alumina (280 g.; Grade III). Elution with light petroleum (b. p. 60—80°)–benzene (1 : 1) gave 3-acetoxymesitol (485 mg.).

(d) *In the presence of cyclohexylamine*. The dienone (1·19 g.) in anhydrous ether (550 ml.) containing cyclohexylamine (1·19 g.) was irradiated for 2 hr. The solvent and excess of cyclohexylamine were removed *in vacuo* and the product filtered in light petroleum through silica gel (150 g.) to give the *cyclohexylamide* (1·51 g., 84%) of 6-acetoxy-4-methylhepta-2,5-diene-2-carboxylic acid. Recrystallised from light petroleum (998 mg.), this had m. p. 76—79°, λ(shoulder) 219—225 mμ (ε 3000), $\nu_{max.}$ (in CCl_4) 3363 (secondary amide), 1745 (enol-acetate), 1678 (amide C=O), and 1230 (enol-acetate) cm.$^{-1}$ (Found: C, 69·4; H, 9·1; N, 4·8. $C_{17}H_{27}O_3N$ requires C, 69·6; H, 9·4; N, 4·75%), This amide took up rapidly 1·9 mols. of hydrogen on microhydrogenation over platinum in ethyl acetate.

(e) *In a polystyrene film*. A film cast from polystyrene (15%) and the dienone (15%) in benzene showed the expected infrared bands characteristic of the dienone. The film was

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[20] Knecht, *Annalen*, 1882, **215**, 83.

irradiated for 14 hr. (cooling with a fan to $\not>40°$), and the infrared spectrum was again determined. The dienone spectrum had been replaced by that of mesitylene-2,4-diol.

Racemisation of (—)-*Usnic Acid.*—(—)-Usnic acid (723 mg.) in anhydrous dioxan (720 ml.) was irradiated for 124 hr. at $\not>55°$ (cooling fan). The solution was stirred by passage of a stream of dry oxygen-free nitrogen. Removal of the solvent *in vacuo* gave, after crystallisation from methanol, (±)-usnic acid (628 mg., 87%), identified by m. p., mixed m. p., and rotation. A solution of (—)-usnic acid, $[\alpha]_D$ $-495°$ in $CHCl_3$, kept at 56·5° for the same time showed no racemisation ($[\alpha]_D$ $-491°$ in $CHCl_3$).

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