QUARTERLY REVIEWS

PHOTOCHEMICAL REARRANGEMENTS AND RELATED TRANSFORMATIONS

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1. Scope

Within the last few years a number of Reviews on various aspects of photochemistry, both mechanistic[1] and preparative,[2,3] have appeared. The present Review is concerned with photochemically induced rearrangements and related transformations which occur in condensed phases. Although incidental addition of solvent may occur in these processes, this Review does not in general include intermolecular reactions such as dimerisation[4] or the addition of large molecules,[2,3,5] or of oxygen[6] or other small molecules.[7] Photo-oxidative processes are excluded,[6] as are also rearrangements of free radicals or carbenes[2,3] which may efficiently be produced by non-photochemical methods. The Süs rearrangement of diazo-ketones has been adequately covered elsewhere.[2,3] All the substances considered contain chromophores having absorption bands in the ultraviolet region, and hence the rearrangements are induced by light of these wavelengths.

2. Simple Aldehydes and Ketones

Aldehydes and ketones absorb weakly in the 290 mμ region of the ultraviolet with an extinction of 10—30;[8] stronger absorption also occurs below 200 mμ, that at shortest wavelength being analogous to that occurring in the spectra of the related olefins.[9] The weak band in the carbonyl spectrum is attributed to an $n \rightarrow \pi^*$ transition of a non-bonding electron on the oxygen atom to an anti-bonding π-orbital in the multiple

[1] *Inter al.*, Simons, *Quart. Rev.*, 1959, **13**, 3; C. Reid, *ibid.*, 1958, **12**, 205; Wyman *Chem. Rev.*, 1955, **55**, 625.

[2] Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958.

[3] Mayo, "Advances in Organic Chemistry", Interscience Publ. Inc., New York, 1960, Vol. II, p. 367.

[4] Mustafa, *Chem. Rev.*, 1952, **51**, 1.

[5] Schönberg and Mustafa, *Chem. Rev.*, 1947, **40**, 181.

[6] Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367; Bateman, *Quart. Rev.*, 1954, **8**, 147; Schenck, *Angew. Chem.* 1957, **69**, 579; Nickon and Bagli, *J. Amer. Chem. Soc.*, 1961, **83**, 1498.

[7] Schenck and Schmidt-Thomée, *Annalen*, 1953, **584**, 199.

[8] Bielecki and Henri, *Ber.*, 1913, **46**, 3627.

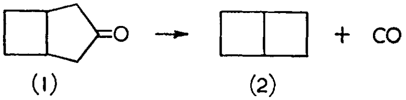
[9] Wheland, "Resonance in Organic Chemistry", Wiley, New York, 1955, p. 278.

bond to give a singlet.[10] It is this absorption and consequent formation of an energised state which appears to be responsible for most of the photochemical transformations of saturated aldehydes and ketones in condensed phases. After absorption, the energy may be disposed of by re-emission, by photo-chemical reactions such as dissociation, rearrangement, and reaction with the medium, by intersystem crossing, and by internal conversion.[11]

In the photochemical transformations to be described, there is, as yet, little evidence to indicate the nature of the initial reacting species, and studies successfully directed to this end for condensed-phase reactions have been comparatively few.[12,13] In the following discussion, therefore, no distinction will, in general, be made.

(a) The Cleavage of Cyclic Ketones.—Irradiation of acyclic ketones in the vapour phase leads to bond cleavage between the α-carbon atom and the carbonyl group, followed by intermolecular reactions of the derived free radicals in ways dependent on the temperature.[14] Cyclic ketones behave similarly, but the diradicals so formed may subsequently undergo a number of intramolecular reactions.

One such reaction, apparently only observed in the gas phase, is the extrusion of carbon monoxide and recyclisation to the hydrocarbon containing one carbon atom less.[15] A recent example is the conversion of the ketone (1) into the hydrocarbon (2).[16] In solution the intermediate diradical formed by the initial cleavage may recyclise without extrusion of carbon monoxide and such a process is probably involved in the epimerisation of androsterone (3) to lumiandrosterone (4),[17] and of other related transformations.[18] Such a process may also take place in the gas phase, but no suitably substituted carbonyl compound appears to have been irradiated under these conditions.



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[10] Mulliken, *J. Chem. Phys.*, 1935, **3**, 564; McMurray, *ibid.*, 1941, **9**, 231; see also Sidman, *Chem. Rev.*, 1958, **58**, 689.

[11] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

[12] *Inter al.*, Hammond and Moore, *J. Amer. Chem. Soc.*, 1959, **81**, 6334; Hammond, Leermalkers, and Turro, *ibid.*, 1961, **83**, 2395, 2396; Cundall and Milne, *ibid.*, 1961, **83**, 3902.

[13] See the discussion of photo-reactions of anthracene by Hochstrasser and Porter, *Quart. Rev.*, 1960, **14**, 146.

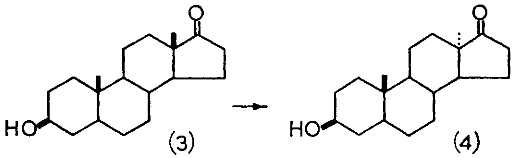
[14] Davis, *Chem. Rev.*, 1947, **40**, 201.

[15] Benson and Kistiakowsky, *J. Amer. Chem. Soc.*, 1942, **64**, 80; Blacet and Miller, *ibid.*, 1957, **79**, 4327.

[16] Cremer and Srinivasan, *Tetrahedron Letters*, 1960, No. 21, 24.

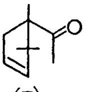
[17] Butenandt and Poschmann, *Ber.*, 1944, **77**, 394.

[18] *Inter al.*, Butenandt *et al.*, *Ber.*, 1941, **74**, 1308; 1942, **75**, 1931; 1944, **77**, 392; Barton, Campos-Neves, and Scott, *J.*, 1957, 2698; Bots, *Rec. Trav. chim.*, 1958, **77**, 1010.

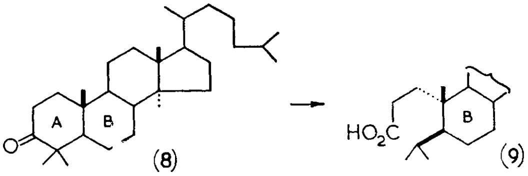

(3) (4)

A second mode of reaction of the carbonyl-alkyl diradical is exemplified by the conversion of cyclohexanone into hex-5-enal.[19,20,21] It has also been observed in the irradiation of camphor (5) which gives, as the main product, campholenaldehyde (6).[22,23] It has been suggested that the ketone (7) is another of the products but decisive evidence for this structure is lacking.[23] The mechanism of this transformation also has not been rigidly established although it has been reasonably proposed that direct transfer of a hydrogen atom from a β-carbon atom to the carbonyl group takes place, possibly before dissociation.[24]


(5) (6)


(7)

A third mode of reaction of the same diradical has been observed. Irradiation of cyclic ketones in reactive solvents (water, alcohol, aqueous acetic acid) results in solvolysis of the ring. This reaction, first reported by Ciamician and Silber,[19,25] has recently found application in terpenoid chemistry. It is exemplified by the conversion of lanostanone (8) into the acid (9),[26] and the partial synthesis of dihydronyctanthic acid,[26] and has been applied in the elucidation of the structures of dammarenolic acid[26] and valeranone.[27] In all cases the cleavage takes place to give the expected more stable alkyl radical. Recent investigation of the mechanism of this



(8) (9)

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[19] Ciamician and Silber, *Ber.*, 1908, **41**, 1071; 1909, **42**, 1510; 1913, **46**, 3077.
[20] Kharasch, Kuderna, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 1225.
[21] Srinivasan, *J. Amer. Chem. Soc.*, 1959, **81**, 5541.
[22] Ciamician and Silber, *Ber.*, 1910, **43**, 1340.
[23] Srinivasan, *J. Amer. Chem. Soc.*, 1959, **81**, 2604.
[24] Srinivasan, *J. Amer. Chem. Soc.*, 1959, **81**, 1546.
[25] Ciamician and Silber, *Ber.*, 1907, **40**, 2415.
[26] Arigoni, Barton, Bernasconi, Djerassi, Mills, and Wolff, *J.*, 1960, 1900.
[27] Krepinsky, Romanuk, Herout, and Sorm, *Tetrahedron Letters*, 1960, No. 7, 9.

reaction has indicated that the diradical formed initially undergoes an intramolecular hydrogen transfer to give the corresponding keten, which then reacts with the solvent to give the final product.[28] The transformations just described, therefore, all represent alternate modes of decomposition of the same diradical, and such a scheme is illustrated, for the case of cyclohexanone, in Fig. 1.

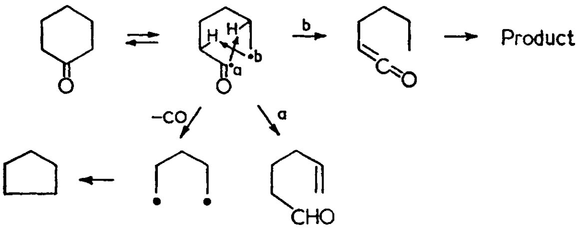
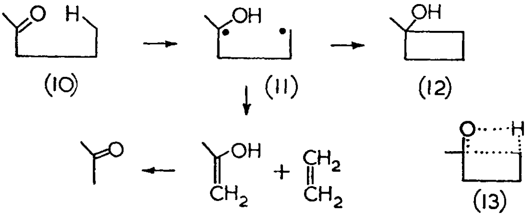


Fig. 1.

(b) Reactions involving γ-Hydrogen Atoms.—Irradiation of carbonyl compounds in the presence of substances capable of giving stable radicals by hydrogen abstraction (*e.g.*, diphenylmethane,[29] cyclohexene,[30] acenaphthene[31]) is known to lead to the formation of alcohols. These are formed by addition of the hydrocarbon radical to the carbonyl compound (or a partially reduced intermediate derived from it).[30] Aliphatic ketones undergo the same reaction intramolecularly if a hydrogen atom is available on the γ-carbon atom: pentan-2-one (10), for example, gives the cyclobutanol (12), presumably through the diradical (11).[32] Disposition of the electrons in an alternative sense results in decomposition of the intermediate (11) to acetone and ethylene.[33] In the irradiation of ketones, these two reactions in general accompany each other, but the corresponding cyclisation of aldehydes has not been reported. The formation of the



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[28] Quinkert, personal communication.

[29] Paternò and Chieffi, *Gazzetta*, 1909, **39**, 415.

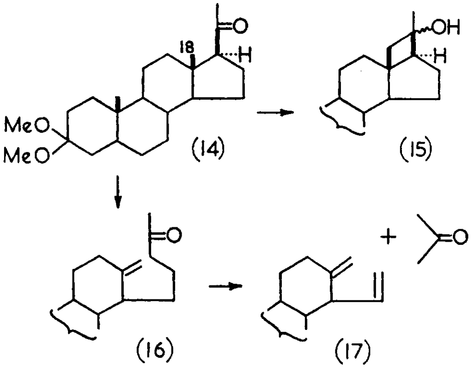
[30] Mayo, Stothers, and Templeton, *Canad. J. Chem.*, 1961, **39**, 488.

[31] Mayo and Stoessl, unpublished work.

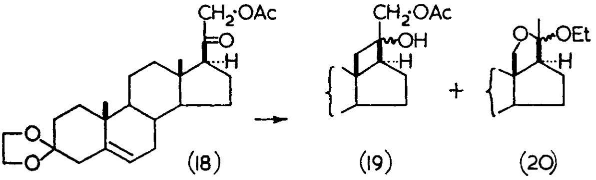
[32] Yang and Yang, *J. Amer. Chem. Soc.*, 1958, **80**, 2913.

[33] Davis and Noyes, *J. Amer. Chem. Soc.*, 1947, **69**, 2153; Manning, *ibid.*, 1957, **79**, 5151; Brunet and Noyes, *Bull. Soc. chim. France*, 1958, 121; Srinivasan, *J. Amer. Chem. Soc.*, 1959, **81**, 5061; see, however, Pitts, *J. Chem. Educ.*, 1957, **34**, 112.

alcohols has been depicted as a four-centre rearrangement,[34] as in (13), but later work[35] has shown that the reaction is not stereospecific as was originally supposed,[34] and that, for instance, 3,3-dimethoxypregnan-20-one (14) gives two isomers of the alcohol (15). Several steroids have been found to undergo this reaction together with the concomitant decomposition leading, in this case to the products (16) and (17) and acetone. The



expected cyclobutanol (19) is formed on irradiation in ethanol of a steroid 20-ketone containing a 21-acetoxyl group (as in 18). In addition, however, the acetal (20) is obtained.[36]



Other proximity reactions involving intramolecular hydrogen abstraction by a radical formed by photolysis have been used in synthesis. Irradiation of the nitrite group[37] results in cleavage followed by an intermolecular addition of the NO radical to form an oxime.[38,39] In this way, a three-step synthesis of aldosterone 21-acetate (22) from corticosterone acetate (21) has been achieved.[39] However, the reaction takes a different course in the case of 17β-nitrites and leads to hydroxamic acids,[40] presumably by

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[34] Buchschacher, Cereghetti, Wehrli, Schaffner, and Jeger, *Helv. Chim. Acta*, 1959, **42**, 2122.

[35] Yang and Yang, *Tetrahedron Letters*, 1960, No. 4, 10.

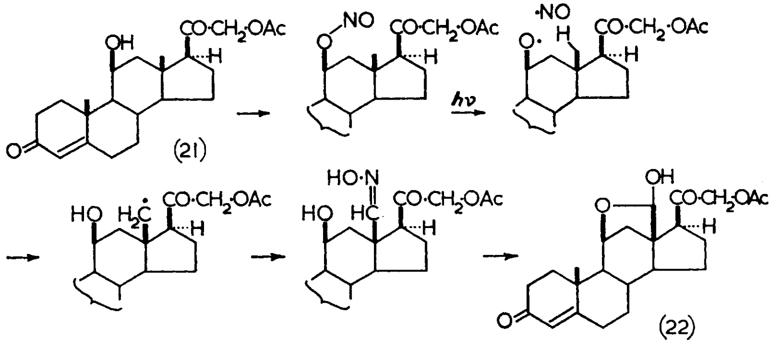
[36] Wehrli, Cereghetti, Schaffner, and Jeger, *Helv. Chim. Acta*, 1960, **43**, 367.

[37] The photolysis of t-butyl nitrite to give acetone and nitrosomethane has been reported; Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516.

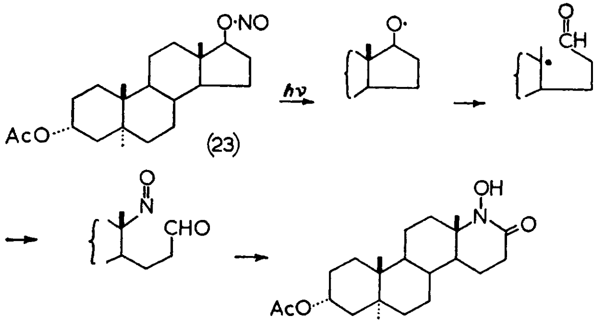
[38] *Inter al.*, Naylor and Anderson, *J. Org. Chem.*, 1953, **18**, 115.

[39] Barton, Beaton, Celler, and Pechet, *J. Amer. Chem. Soc.*, 1960, **82**, 2640; Nussbaum, Carlon, Oliveto, Townley, Kabasakalian, and Barton, *ibid.*, 1960, **82**, 2973; Barton and Beaton, *ibid.*, 1961, **83**, 750; Barton and Beaton, *ibid.*, 1960, **82**, 2641.

[40] Robinson, Gnoj, Mitchell, Wayne, Townley, Kabasakalian, Oliveto, and Barton, *J. Amer. Chem. Soc.*, 1961, **83**, 1771.

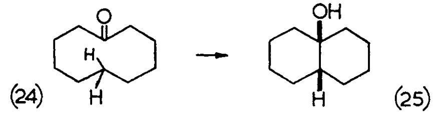


carbon–carbon bond cleavage of the radical formed by photolysis of the nitrite. This is illustrated below for the 17β-nitrite of 3α-acetoxy-5α-androstan-17β-ol (23). The existence of a C_{13}-radical as intermediate is supported by the fact that 13-α-*iso*-compounds are also formed. Related



transformations have been achieved with hypohalites.[41] Azides such as n-butyl and n-octyl azide undergo photochemical transformation into pyrrolidines, and this has been used in a synthesis of conessine.[42a] The Hofmann–Löffler–Freytag reaction as applied, for instance, to the synthesis of the pyrrolidine ring in dihydroconessine[42b] can also be carried out photochemically.

A proximity effect of a different kind has been observed in the conversion of cyclodecanone (24) into *cis*-9-decalol (25).[43] Hex-5-en-2-one (26),



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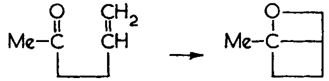
[41] Akhtar and Barton, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; Walling, "Free Radicals in Solution," Wiley, New York, 1957, p. 386.

[42] (*a*) Barton and Morgan, *Proc. Chem. Soc.*, 1961, 206; (*b*) Corey and Hertler, *J. Amer. Chem. Soc.*, 1959, **81**, 5209.

[43] Barnard and Yang, *Proc. Chem. Soc.*, 1958, 302.

however, is converted into the bicyclic ether (27) by photochemical addition,[44a] the intermolecular equivalent of which has been known for some time.[44b]

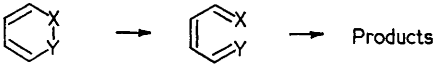


(26) (27)

3. Conjugated Monocyclic Systems

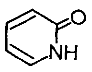
A number of photochemical transformations take place, at least formally, by electron redistribution within the centres constituting an unsaturated ring system. These reactions may be divided, somewhat arbitrarily, on the basis of the size of the ring and the nature of the π-electron system involved. For the most part only systems containing extended conjugation have been investigated. The small, but important, group of cross-conjugated transformations will therefore be considered separately (p. 410).

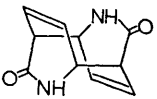
(a) **Even-numbered Rings.**—(i) *Six-membered rings.* This group consists of substances containing the system indicated in (28). On irradiation these are converted, in general, and as pointed out by Barton,[45] into extended systems such as (29) or substances derived from (29) by chemical reaction with the medium. Exceptions to this behaviour appear to be of two kinds. The first is dimerisation, and so does not come within the scope of this Review. It occurs generally when one of the ethylenic linkages forms part of a fused aromatic ring,[4] but has recently been reported to occur with α-pyridone (30). The product does not have the cyclobutane structure originally assigned,[46] and recent work in these laboratories and in those of the University of Alberta has established structure (31) as correct.



(28) (29)

(30)





(31)

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[44] (*a*) Srinivasan, *J. Amer. Chem. Soc.*, 1960, **82**, 775; (*b*) Paternò and Chieffi, *Gazzetta*, 1909, **39**, 341.

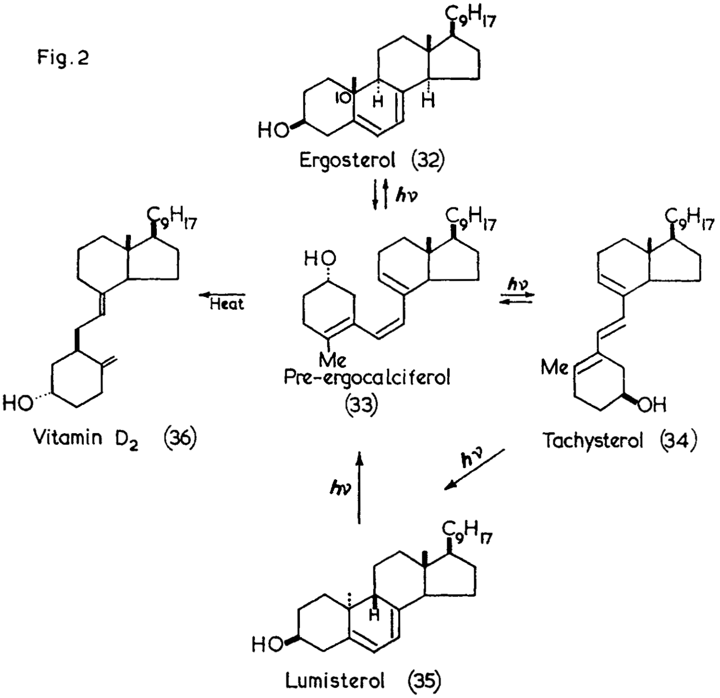
[45] Barton, *Helv. Chim. Acta*, 1959, **42**, 2604.

[46] Taylor and Paudler, *Tetrahedron Letters*, 1960, No. 25, 1.

although the available evidence does not exclude one formed by 1,2:1,4- or 1,4:1,4-addition. It is very probable that, at least in monocyclic systems, the predominance of cleavage or of dimerisation depends on the concentration of the irradiated solution. The second reaction which may intervene is carbon bridging (p. 414).

The conversion of carbocyclic systems containing the grouping (28) into (29) has been observed with simple hydrocarbons such as cyclohexadiene[45,47] and α-phellandrene,[47] but undoubtedly the most studied reaction of this type is that occurring in the irradiation of ergosterol (32) to give the vitamin D precursor, pre-ergocalciferol (33). The latter is further transformed under the influence of light and of heat, the scheme presented in Fig. 2 being that of Havinga and his group.[48] The subject has been reviewed elsewhere.[48,49] The conversion of lumisterol (35) into pre-ergocalciferol (33) is a parallel transformation, and equivalent transformations have been carried out in other steroid systems including those lacking the 10-methyl group.[50] An analogous transformation of the triterpenoid

Fig. 2



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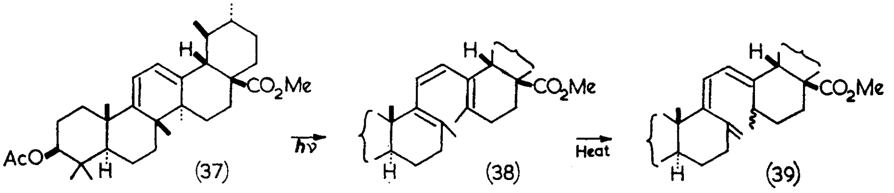
[47] deKock, Minnaard, and Havinga, *Rec. Trav. chim.*, 1960, **79**, 922.

[48] Havinga, deKock, and Rappoldt, *Tetrahedron*, 1960, **11**, 276.

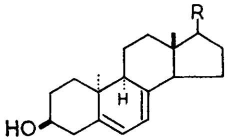
[49] Fieser and Fieser, "The Steroids," Reinhold Publ. Corp., New York, 1959, p. 146; Inhoffen and Irmscher, *Fortschr. Chem. Org. Naturstoffe*, 1959, **17**, 70; Lythgoe, *Proc. Chem. Soc.*, 1959, 141.

[50] Velluz and Amiard, *Bull. Soc. chim. France*, 1955, 205; Velluz, Goffinet, and Amiard, *Tetrahedron*, 1958, **4**, 241.

methyl dehydroursolate (37) to compounds (38) and (39) has been reported.[51]



Investigation of the mechanism of cleavage has, at present, revealed no evidence for a triplet state (phosphorescence) on the irradiation of ergosterol in isopentane–ethanol at 80°K. Fluorescence was observed however, suggesting that collapse to the triene may take place from a singlet state.[48] The ergosterol (and dehydrocholesterol) system appears to be the only reported example of the cyclisation of a triene.* In the case of the ergosterol series the same stationary state is reached by prolonged irradiation of each of the isomers involved, but it is not clear why (33) gives (32) whereas (34) is believed to give (35). A further stereochemical specificity which is not mechanistically clear is revealed in the irradiation of pyrocalciferol (40) and isopyrocalciferol (41). These substances differ from ergosterol only in the stereochemistry of the ring fusions, but irradiation in these cases leads (as is general in seven-membered rings where no cleavage reaction is available) to bond formation, as in (42).[52] This has been interpreted on the assumption that collapse to the cyclic valency tautomer from the initial excited singlet is preferred. The *anti*-isomers (32) and (35) take, in this argument, the abnormal course because of the increased energy of the ring fusions, whilst (40) and (41) are not so inhibited.[52] This, however, does not explain why a simple substance such as cyclohexadiene does not form the bridged tautomer. The explanation may well be a subtle one since the cleavage reaction is a photoequilibrium whilst the formation of the bicyclohexane system is not, since no absorbing chromophore remains. The observed photochemical epimerisation of isodehydrocholesterol (43) to coprosta-6,8-dienol (44)[53] provides further evidence for the existence of



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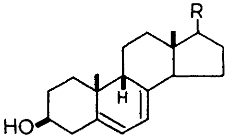

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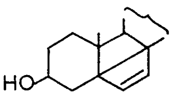

(42)

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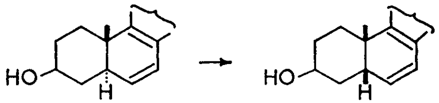
* The formation of cyclohexadiene by the irradiation of *cis, trans*-1,3,5-hexatriene has now been reported (Srinivasan, *J. Amer. Chem. Soc.*, 1961, **83**, 2806).

[51] Autrey, Barton, and Reusch, *Proc. Chem. Soc.*, 1959, 55.

[52] Dauben and Fonken, *J. Amer. Chem. Soc.*, 1959, **81**, 4060.

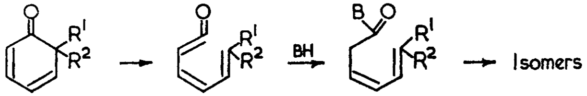
[53] Windaus, Linsert, and Eckhardt, *Annalen*, 1938, **534**, 22; Windaus and Zühlsdorff, *ibid.*, 1938, **536**, 204.



(43) (44)

such an equilibrium as it can easily be envisaged as proceeding *via* the cyclodecatriene. In systems such as that in (44) in which the equilibrium is displaced towards the diene (presumably because of medium-ring formation), it would be of interest to seek for carbon-bridging by prolonged irradiation.

Replacement of X or Y in structure (28) by a trigonal atom does not affect the general course of the reaction. 6-Substituted cyclohexa-3,4-dienones (45) are converted in the first place into ketens (46) which then react with a base which may be water, an amine, etc.[54] The product (47) obtained may be further transformed by *cis–trans*-isomerism (or such isomerism may take place in the keten itself), and in addition, the amides and acids obtained may be $\alpha\beta$- or $\beta\gamma$-unsaturated. This may be because of initial protonation at either the α- or the γ-position in different substances, because of isomerisation under the influence of the stronger bases used, or because of shift of the double bond under the influence of light, as recently reported.[55] The presence of substituents in the remaining position next to the carbonyl group inhibits the cleavage, so that compound (48) does not undergo ring fission even in the presence of aniline. This has been attributed to steric hindrance to the formation of the intermediate *trans*-keten (51). Instead, a slow aromatisation takes place to give a phenol (50), and



(45) (46) (47)

the scheme shown has been proposed.[54] In contrast the irradiation of 6-acetoxy-6-methyl-2,4-dienone (45; R^1 = AcO, R^2 = Me) in anhydrous ether gives, slowly, *o*-cresol, with acetoxyl elimination.[54] A modified rationalisation of these aromatisations would be that the intermediate (49) is formed directly from the *cis*-keten (as in 52). This avoids the necessity of invoking a photochemically produced intermediate with charge separation, and in addition rationalises the different behaviour of the ketone (45; R^1 = AcO, R^2 = Me) since the keten derived from the latter will exist predominantly in the *trans*-form to which the process indicated in (52) cannot apply. Aromaticity, in this case, is then achieved by the alternative homolysis of the acetoxyl group.

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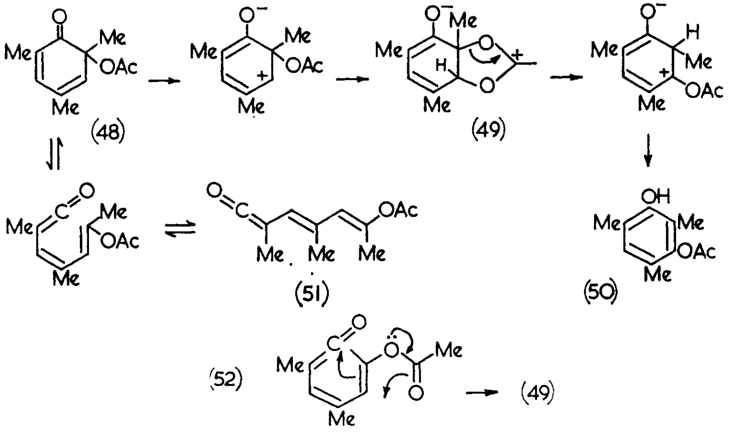
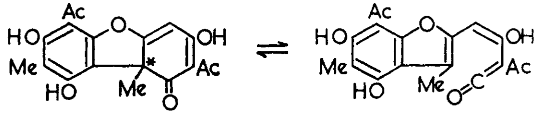
[54] Barton and Quinkert, *J.*, 1960, 1.

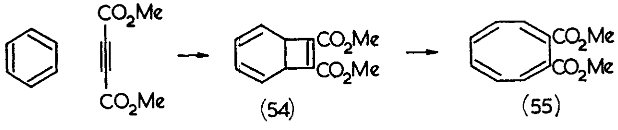
[55] Levina, Kostin, and Gembitskii, *J. Gen. Chem.* (*U.S.S.R.*), 1959, **29**, 2421.



An example in which one of the ethylenic linkages in the cyclohexadienone (45) is present in an enol has been recorded in the racemisation of

(53)


usnic acid (53).[54] A final example of interest is the preparation of the cyclooctatetraene derivative (55) by addition of dimethyl acetylenedicarboxylate to benzene. It is presumably formed through the adduct (54) which then rearranges. [56]



Substances of type (28) where X is a hetero-atom behave similarly. The pyran–ionone equilibrium (56),[57] the methanolysis of the α-pyrone (57),[58] and the rearrangement of certain spiropyrans (*e.g.*, 58) to give coloured open-chain substances (59)[59] are representative examples. Both X and Y may be hetero-atoms in (28). Unsaturated sultones, on irradiation in methanol or ether–benzylamine, give the expected sulphonic acid derivatives: this is exemplified by the conversion of (60) into (62).[60] By analogy

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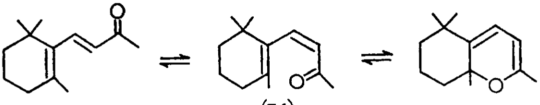
[56] Grovenstein and Rao, *Tetrahedron Letters*, 1961, No. 4, 148.
[57] Büchi and Yang, *J. Amer. Chem. Soc.*, 1957, 79, 2318.
[58] Esterle, Girling, Mayo, and Wiley, unpublished observations.
[59] Heiligman-Rim, Hirshberg, and Fischer, *J.*, 1961, 156.
[60] Henmo, Mayo, Sattar, and Stoessl, *Proc. Chem. Soc.*, 1961, 238.



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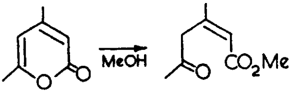
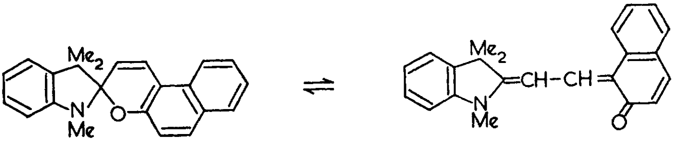


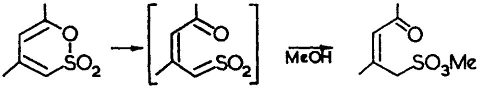
(57)

(*cis* or *trans*)



(58) (*cis* or *trans*) (59)

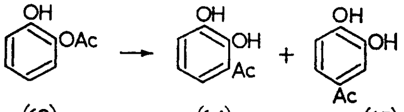
with the work just described this presupposes the intermediacy of a "sulphen" (61). Although certain of these diene systems are further



(60) (61) (62)

extended by conjugation with a carbonyl group, it seems probable that a similar photochemical process is involved—one in which the non-bonded electrons on the carbonyl-oxygen atom are not concerned.

The partial conversion of benzene into fulvene, and the analogous transformations of toluene, isopropylbenzene, and anisole,[61] are the only examples known of photochemically induced bond cleavage in a 6-membered aromatic ring. A photochemically induced Fries rearrangement of catechol monoacetate (63) to (64) and (65) has been claimed[62] to be intramolecular.

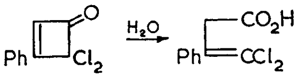


(63) (64) (65)

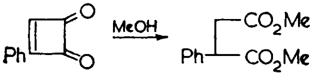
(ii) *Other even-membered rings.* Although cyclobutene is the four-centre analogue of the six-centre systems discussed in the previous section, it does not absorb light above 220 mμ. However, if an absorbing system is introduced similar behaviour is observed. Again no satisfactory evidence is available as to whether the keten (or its equivalent) is formed directly from a singlet or through other, intermediate, species. As example may be quoted the conversion of the cyclobutenone (66) into an acid (67)[45]

[61] Angus, Blair, and Bryce-Smith, *J.*, 1960, 2003.
[62] Anderson and Reese, *Proc. Chem. Soc.*, 1960, 217.

and of the butenedione (68) into the ester (69).[63] The six-centre equivalent to the latter transformation does not appear to have been reported yet, such *o*-quinones readily undergoing addition with unsaturated system[5] or alternatively reduction to the quinol.[64]

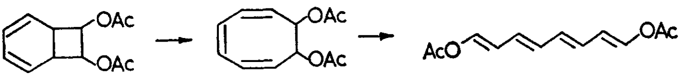


(66) (67)



(68) (69)

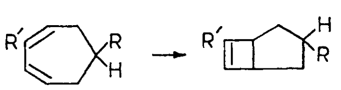
Only one example appears to have been recorded of an eight-centre rearrangement. This is the transformation of a bicyclic compound (70) in a six-centre rearrangement to the cyclo-octatriene (71), which is further transformed into the open-chain tetraene (72)[45] that was, however, only characterised spectroscopically.



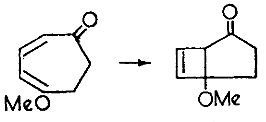
(70) (71) (72)

(b) Seven-membered Rings.—No rearrangement product from an unsaturated five-membered ring has been reported.[45] The rearrangement of seven-membered rings has, in contrast, been observed in many instances both with two and with three units of unsaturation.

(i) *Rings containing two endocyclic double bonds.* Cyclohepta-1,3-diene itself (73; R = R′ = H), certain of its derivatives (73; R = OH, R′ = H or OMe), and the ketone (75), are converted on irradiation into substituted bicyclo[3,2,0]heptanes (74) and (76).[65,66] Eucarvone (77), on irradiation in alcohol or acetic acid gives a similar bicyclo-compound (78),[67,68] and this



(73) (74)



(75) (76)

is further transformed by irradiation in alcohol, in a photoequilibrium, into an isomer (80).[67] This further transformation presumably proceeds by cleavage between the α-carbon atom and the carbonyl group (p. 394), followed by bond formation at the alternative position in the allylic

[63] Mallory and Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 393 (footnote 6).

[64] Ciamician and Silber, *Ber.*, 1901, **34**, 1530.

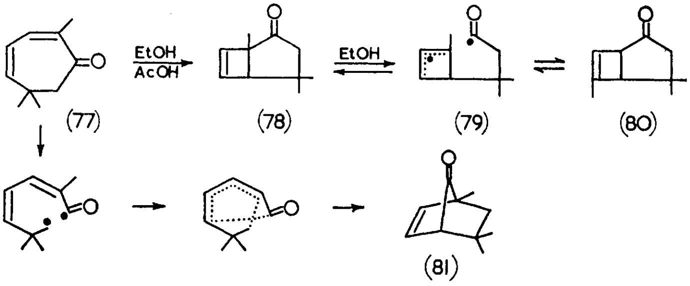
[65] Chapman and Pasto, *Chem. and Ind.*, 1961, 53; Rigaudy and Courtot, *Tetrahedron Letters*, 1961, No. 3, 95.

[66] Dauben and Cargill, *Tetrahedron*, 1961, **12**, 186.

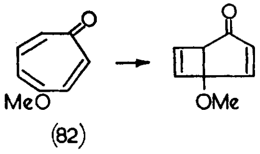
[67] Büchi and Burgess, *J. Amer. Chem. Soc.*, 1960, **82**, 4333.

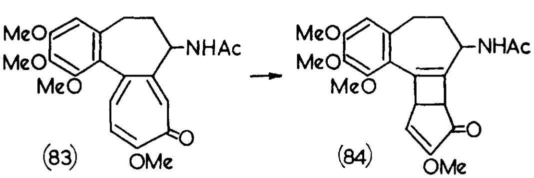
[68] Hurst and Whitham, *Proc. Chem. Soc.*, 1961, 116.

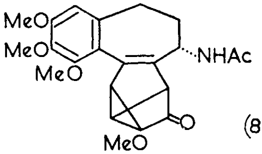
radical (79). Irradiation in acetic acid gives, as a second product, a bicyclo[2,2,1]heptanone (81), which is the result of a more complex rearrangement,[68] perhaps through the route indicated, although the specific function, if any, of the solvent is not clear.



(ii) *Rings containing three endocyclic double bonds.* Cycloheptatriene[66] and certain of its oxygenated derivatives[65] behave analogously to seven-membered dienes. Amongst these derivatives are γ-tropolone methyl ether (82)[69] and colchicine (83).[70] The latter gives three products, two of which, α- and β-lumicolchicine, are stereoisomers (84). Such evidence as was recently presented for (85) as the structure of α-lumicolchicine is not yet compelling,[71] but it appears that interconversions between the isomers are possible.*







(85)

The irradiation of α-tropolone (86; $R = R' = R'' = H$) itself has been more closely studied[72] and the situation found more intricate than had

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* Recent work by Chapman and Smith (*J. Amer. Chem. Soc.*, 1961, **83**, 3914) has established that α-lumicolchicine is a dimer of β-lumicolchicine.

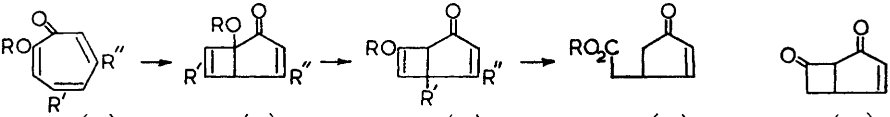
[69] Chapman and Pasto, *J. Amer. Chem. Soc.*, 1958, **80**, 6685.

[70] Forbes, *J.*, 1955, 3864; Gardner, Brandon, and Haynes, *J. Amer. Chem. Soc.*, 1957, **79**, 6334.

[71] Schenck, Kuhn, and Neumüller, *Tetrahedron Letters*, 1961, No. 1, 12.

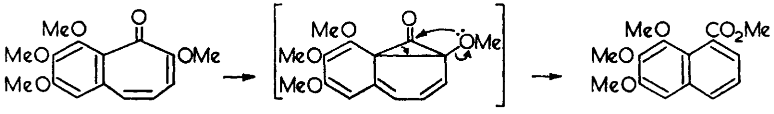
[72] Dauben, Koch, and Thiessen, *J. Amer. Chem. Soc.*, 1960, **82**, 6087; Dauben, Koch, Chapman, and Smith, *ibid.*, 1961, 83, 1768.

at first been thought. Irradiation of the tropolone in methanol gave the ester (89; R = Me) and irradiation of the methyl ether in water gave the same substance. However, irradiation of the methyl ether in methanol gave in the first place a bicyclo[3,2,0]heptadienone (87; R = Me, R′ = R″ = H) which on further irradiation disappeared with the concomitant formation of an isomer (88; R = OMe, R′ = R″ = H). On addition of water the latter was then transformed into the monocyclic ester (89; R = Me). The final stages appear mechanistically reasonable, particularly in the case of the tropolone itself. Here the intermediate corresponding to (88; R = R′ = R″ = H) would be the ketone (90) and this might be expected to afford the keten (p. 396) which would then react with the solvent. The detailed mode of conversion of (87) into (88) is as yet unclear, but insight has been gained by the fact that the tropolones (86; R = Me, R′ = Me, R″ = H) and (86; R = Me, R′ = H, R″ = Me) give first (87) and then (88) (R's as before).



(86) (87) (88) (89) (90)

A six-centre rearrangement, with formation of the norcaradiene system has apparently not been observed among cycloheptatrienes,[73,74] perhaps because of its ready reversibility. Such a rearrangement may be involved in the conversion of the benzotropolone methyl ether (91) into the naphthoic ester (92).[75]



(91) (92)

4. A Heteroannular Olefinic System

The only heteroannular diene whose irradiation has been reported so far is that contained in the cholestane derivative (93). In ethanol, this gave the 3,5-cyclo-ether (94),[76] and the stereochemistry of the cyclopropane ring is the reverse of that formed in solvolysis of cholesterol derivatives. It may be envisaged as formed, formally, from a species* such as (95).

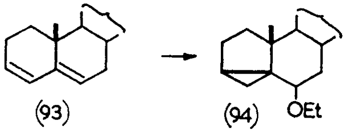
* No implication is intended as to the parity of the electrons designated.

[73] Forbes and Ripley, *Chem. and Ind.*, 1960, 589.

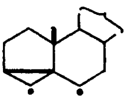
[74] For a discussion of the norcaradiene problem see Doering and Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

[75] Forbes and Ripley, *J.*, 1959, 2770.

[76] Dauben and Ross, *J. Amer. Chem. Soc.*, 1959, **81**, 6521.

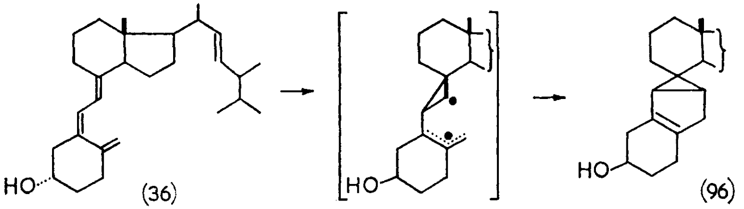


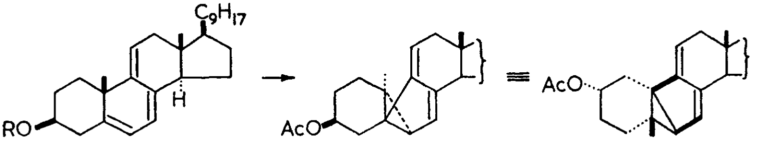
(93) (94)



(95)

Suprasterol-II, for which the structure (96) has been proposed,[77] is obtained by overirradiation of calciferol (36); its genesis may involve a vinylogously equivalent process. Dehydroergosterol (97; R = H) contains the same chromophore as does calciferol with the modification that the *cisoid* portion now forms part of a six-membered ring. The product (98) of irradiation of the acetate (97; R = Ac) is derived by cleavage of the 9,10-bond and bond redistribution.[78] However, cleavage of the bond to give a diradical is inadmissable as an initiating step, since the reaction has been shown to be stereospecific. Dehydrolumiergosterol acetate (97; α-Me at $C_{(10)}$, R = Ac), on irradiation, gives a product differing from (98) in the configuration of the methyl group; and in both photochemical transformations, the configuration is inverted. Bond migration and bond cleavage must therefore be concurrent,[79] but the nature of the intermediate species, if any, is conjectural.





(97) (98)

5. Intramolecular Addition Reactions

Whilst there is a very large number of examples of substances which contain ethylenic linkages which, by forming part of an absorbing conjugated system, can be induced either to dimerise[4,80] or to add to a suitable

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[77] Dauben, Bell, Hutton, Laws, Rheiner, and Urscheler, *J. Amer. Chem. Soc.*, 1958, **80**, 4116.

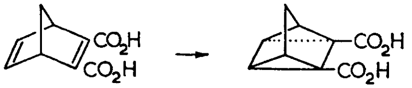
[78] Barton and Kende, *J.*, 1958, 688.

[79] Barton, Bernasconi, and Klein, *J.*, 1960, 511.

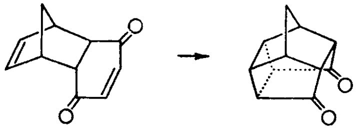
[80] Cookson and Hudec, *Proc. Chem. Soc.*, 1959, 11.

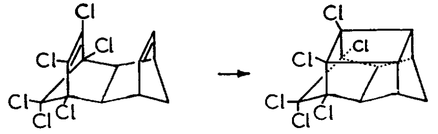
unsaturated substrate[56,81] on irradiation, similar intramolecular reactions are far more restricted in scope. The requirements are, of course, that at least one of the π-electron systems should be activated by the light used, and that the two systems should be able to come close together. Conformational rigidity is not required.

Irradiation of bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid (99) in ether gives a good yield of the quadricycloheptane isomer (100).[82]

(99)  (100)

The double bonds are sufficiently close for homoallylic interaction to be unexceptional: the interaction is reflected in the abnormal ultraviolet spectrum of the acid (99) ($\lambda_{\text{max.}}$ 243 mμ) in comparison with that of maleic acid ($\lambda_{\text{max.}}$ 210 mμ).[83] The adduct (101) of cyclopentadiene and *p*-benzoquinone undergoes similar internal addition to give a "near cage" molecule (102).[84] A single ethylenic linkage, when substituted by chlorine has sufficient absorbance (ϵ_{198} 9000) for activation, and the insecticide "isodrin" (103) is also converted into a cage isomer (104).[85] On the other hand, carvone has considerable conformational flexibility, the most suitable conformation for internal addition being that represented in (105). However, since even in this arrangement bonding distance appears too great, it may be that the particular excited species involved has greater flexibility, for on irradiation, carvone camphor (106) is obtained[86]—probably the earliest example of this type of reaction. Verbenone (107), having a chromophore similar to that of carvone but lacking the isolated

(101)  (102)

(103)  (104)

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[81] *Inter al.*, Ayer and Büchi, U.S.P. 2,805,242; Angus and Bryce-Smith, *J.*, 1960, 4791; Bryce-Smith and Vickery, *Chem. and Ind.*, 1961, 429.

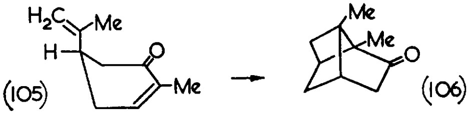
[82] Cristol and Snell, *J. Amer. Chem. Soc.*, 1958, **80**, 1950.

[83] Ley and Wingchen, *Ber.*, 1934, **67**, 501.

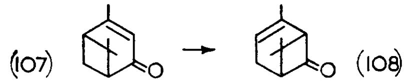
[84] Cookson, Crundwell, and Hudec, *Chem. and Ind.*, 1958, 1003; see also Yates and Eaton, *Tetrahedron*, 1961, **12**, 13.

[85] Cookson and Crundel, *Chem. and Ind.*, 1958, 1004.

[86] Ciamician and Silber, *Ber.*, 1908, **41**, 1928; Sernagiotto, *Gazzetta*, 1917, **47**, 153; 1918, **48**, 52; Büchi and Goldman, *J. Amer. Chem. Soc.*, 1957, **79**, 4741.



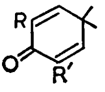
ethylene linkage, rearranges on irradiation to chrysanthenone (108).[87] This transformation is reminiscent of the racemisation of α-pinene under



thermal conditions,[88] a process which presumably proceeds through a monocyclic diradical. A similar discrete species may be involved in the conversion (107)→(108).

6. Cross-conjugated Dienones

Of all the cross-conjugated systems available, only that expressed in the cipher (109; R = R′ = H or Me) has so far been examined. The system



(109)

has maximal absorption (above 200 mμ) at about 240 mμ, so it seems that, since many of the transformations to be discussed occur in Pyrex vessels, absorption in the low-intensity band at about 320 mμ ($n \rightarrow \pi^*$) is responsible for the transformation.

These investigations were conducted with the terpenoid santonin (110),[89] and the transformations found were amongst the earliest photochemical rearrangements discovered: more recent work has extended the study to steroid derivatives.

The irradiation of santonin (110) in aqueous acetic acid gives isophotosantonic lactone (111)[90] and photosantonic acid (113).[91,92] Irradiation in ethanol or dioxan or in water containing one equivalent of alkali gives a substance, lumisantonin, unknown to the original workers.[89] This has been

[87] Hurst and Whitham, *J.*, 1960, 2864.

[88] Fuguitt and Hawkins, *J. Amer. Chem. Soc.*, 1947, **69**, 319.

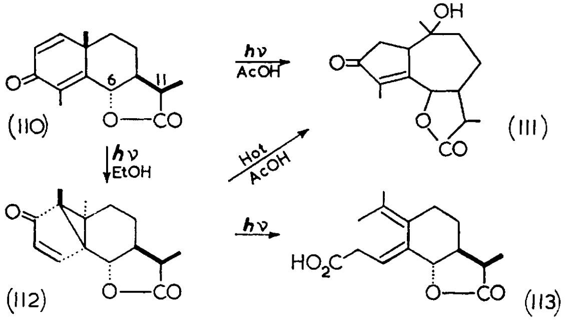
[89] Simonsen and Barton, "The Terpenes," Cambridge Univ. Press, 1952, Vol. III, p. 292.

[90] Barton, Mayo, and Shafiq, *J.*, 1957, 929.

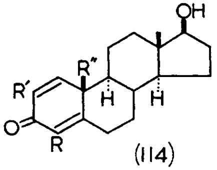
[91] van Tamelen, Levin, Brenner, Wolinsky, and Aldrich, *J. Amer. Chem. Soc.*, 1958, **80**, 501.

[92] Barton, Mayo, and Shafiq, *J.*, 1958, 3314.

shown to have the structure[93] and stereochemistry[94] shown in (112). Lumisantonin is converted into isophotosantonic lactone (111) by the action of hot aqueous acetic acid (in the absence of light) or into an acid (113) by irradiation in cold acetic acid. There must presumably be, therefore, a direct and an indirect route to (111) from (110). Transformations precisely analogous to the formation of lumisantonin have been achieved by the



irradiation of 1,2-dehydro-4-methyltestosterone (114; R = R″ = Me, R′ = H) and 1,2-dehydro-2,4-dimethyltestosterone[95] (114; R = R′ = R″ = Me) in dioxan. A transformation analogous to the formation of isophotosantonic lactone has been carried out on prednisone acetate (115).[96] A number of further observations have been made. The



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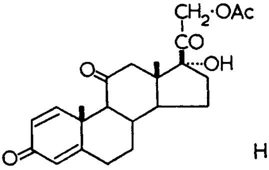

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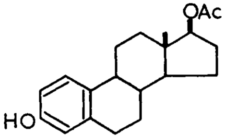

(116)

transformation of santonin (110) into the lactone (111) occurs independently of the configurations at position 6 and 11.[97] Further, whereas the isophotosantonic lactone type of rearrangement (in acetic acid) is not apparently affected to any major degree by substitution at position 4, the conversion of the lumisantonin type is: irradiation of the compound (114; R = R′ = H, R″ = Me) in dioxan gave at least eight products. Replacement of the 10-methyl group (R″) by acetoxyl led to loss of the acetyl group and formation of the phenol (116).[98]

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[93] Barton, Mayo, and Shafiq, *J.*, 1958, 140; Arigoni, Bosshard, Bruderer, Büchi, Jeger, and Krebaum, *Helv. Chim. Acta*, 1957, **40**, 1732; see also Cocker, Crowley, Edward, McMurry, and Stuart, *J.*, 1957, 3416.

[94] Barton and Gilham, *J.*, 1960, 4596.

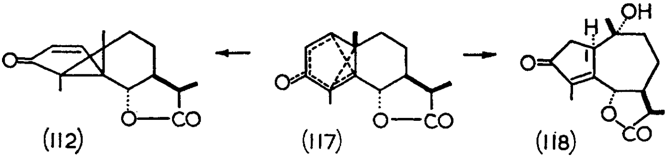
[95] Weinberg, Utzinger, Arigoni, and Jeger, *Helv. Chim. Acta*, 1960, **43**, 236.

[96] Barton and Taylor, *J.*, 1958, 2500.

[97] Barton, *Proc. Chem. Soc.*, 1958, 61.

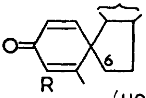
[98] Warszawski, Schaffner, and Jeger, *Helv. Chem. Acta*, 1960, **43**, 501.

A simple general rationalisation for these changes would be that irradiation of santonin produces an excited species which can collapse to lumisantonin or to isophotosantonic lactone depending on the conditions. In both reactions a bond between $C_{(1)}$ and $C_{(5)}$ is formed, but to form luminsantonin (112), the electrons constituting the 1,10-bond move to form a bond between $C_{(4)}$ and $C_{(10)}$ whilst to form the lactone (111) the 5,10-bond must be cleaved. Such a species may be formally represented as (117) though there is as yet no evidence as to nature or number of the intermediate species involved. In keeping with this, the transformation to lumisantonin (112) is stereospecific and involves inversion of the angular methyl group.[94] A similar species may be involved in the rearrangement of dehydroergosterol (97; R = H).[79] Collapse of the intermediate (117) under the influence of acetic acid may then give isophotosantonic lactone (111). Approach of water to $C_{(10)}$ from the α-side with cleavage of the 5,10-bond leads to the stereochemistry implied by (118). This differs from the stereochemistry[45,99] previously suggested only at $C_{(1)}$,[99] and places this hydrogen and the hydroxyl group *cis* and α. On other grounds it has been suggested that these should be *cis*.[100] but with the interpretation that the hydroxyl group should be inverted.



(112) (117) (118)

In the absence of the 4-methyl group, irradiation in dioxan is more complex. From 1,2-dehydrotestosterone acetate (114; R = R′ = H, R″ = Me), as mentioned, eight substances have been isolated and structures (119; R = H, and 120—124) have been attributed to six of these.[101,102] One (121) is of the lumisantonin type. Whilst it is not yet clear what the



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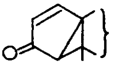

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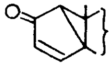

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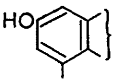
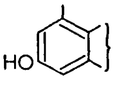
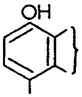


(122)



(123)



(124)

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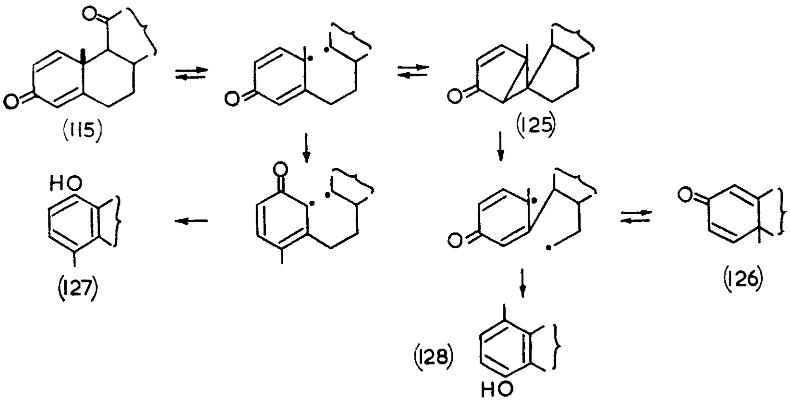
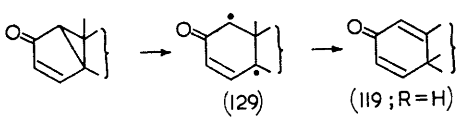
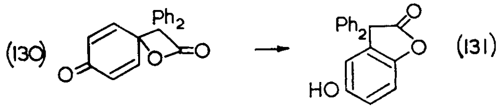
[99] Djerassi, Osiecki, and Herz, *J. Org. Chem.*, 1957, **22**, 1361.
[100] Huffman, *Experientia*, 1960, **16**, 120.
[101] Dutler, Bosshard, and Jeger, *Helv. Chim. Acta*, 1957, **40**, 494.
[102] Utzinger, Dutler, Weinberg, Arigoni, and Jeger, *Angew. Chem.*, 1959, **71**, 80.

nature of the intermediates is, fission of the 9,10-bond seems necessary. The situation is rendered clearer by consideration of the products of the irradiation of prednisone acetate (115) in ethanol. In this substance, the 9,10-bond is further weakened by the presence of the 11-keto-group. The formation of the main product, lumiprednisone acetate (125), was rationalised as indicated below.[96] In addition, neoprednisone acetate (126) was formed under prolonged irradiation, presumably by alternate cleavage of (125) to the less stable radical. Irradiation in dioxan gives a phenol (127) equivalent to (124) (or its inverted isomer 128). If it be assumed that a substance equivalent to (126) is formed in the irradiation of the dehydro-



androsterone derivative (114; R = R′ = H, R″ = Me) then the ketone (120) may be formed from it by a "lumisantonin" rearrangement. The genesis of compounds (121) and (124) then needs no further comment. The spiran (119; R = H) may be formed from (120) or (121) as indicated in (129),* and the conversion of (119) to (122) and (123) finds analogy in the conversion (130) → (131) reported by Staudinger.[104] No methyl migrations are involved in any of these transformations, and 1,2-shifts may be conceived as occurring by dissociation and addition.[105]





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* Umbellulone containing the same chromophore as (112) is quantitatively converted into thymol on irradiation,[103] whereas (112) is not aromatised easily presumably because of the blocking groups.

[103] Wheeler and Eastman, *J. Amer. Chem. Soc.*, 1959, **81**, 236.

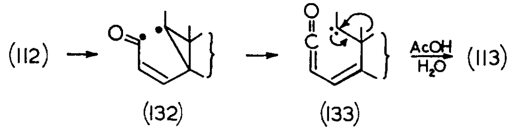
[104] Staudinger and St. Bereza, *Annalen*, 1911, **380**, 243.

[105] Berson, Olsen, and Walia, *J. Amer. Chem. Soc.*, 1960, **82**, 5000.

The differing behaviour in the absence and presence of the 4-methyl group may be the result of quite small energy differences leading to significant changes in the photochemical equilibria. Possibly the eclipsed methyl interaction (similar to that in *cis*-butene[106]) in the spiran (119; R = Me) together with the influence of the 6-hydrogen atom may suffice to suppress formation of this compound and hence of the compounds (122) and (123) derived from it.

A "lumisantonin" rearrangement has been reported recently to occur on irradiation of 3β-acetoxylanosta-5,8-dien-7-one.[107]

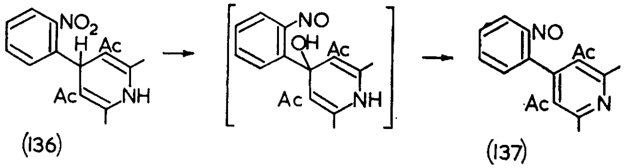
The final rearrangement in this group to be discussed is the conversion of lumisantonin (112) into photosantonic acid (113). Ketonic cleavage of the former, as in the case of lanostanone (8), would give a diradical (132) which could be converted by electron redistribution into a keten-carbene (133); rearrangement of this and reaction with the solvent (ethanol or aqueous acetic acid) would then give the lactone (113).[91]



7. Oxygen-transfer Rearrangements

A number of rearrangements are known in which a transfer of an oxygen atom, originally attached to nitrogen, takes place.

(a) *o*-Nitrobenzaldehyde rearrangement.—This group of reactions is the largest of this class and the most studied. The earliest example was the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid observed by Ciamician and Silber in 1901.[108] The reaction appears general for *ortho*-substituted nitrobenzene derivatives having an α-hydrogen atom, and typical examples are the conversions (134) → (135), and (the mechanism being assumed by analogy) (136) → (137).[109]



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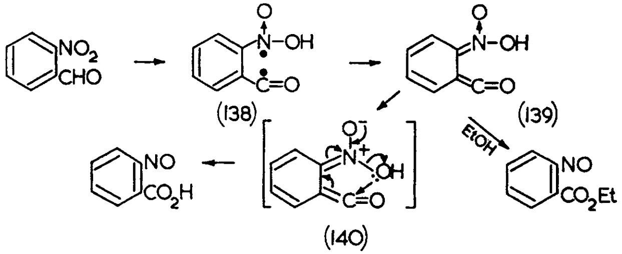
[106] Turner, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths Scientific Publn., London, 1959, p. 75.

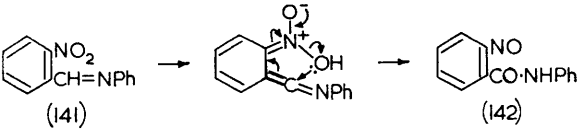
[107] Barton, McGhie, and Rosenberger, *J.*, 1961, 1215.

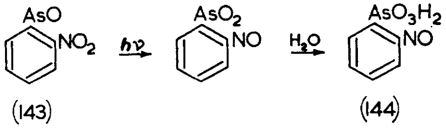
[108] Ciamician and Silber, *Ber.*, 1901, **34**, 2040.

[109] Tanasescu, *Bull. Soc. chim. France*, 1926, 1718; Berson and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 447.

Since, at least in the case of *o*-nitrobenzaldehyde itself, the transformation will take place in the crystal, this rearrangement should be intramolecular. In a number of studies,[110] however, not much has been found to clarify the problem. It seems, nevertheless, very probable that the first step is the abstraction of the benzyl hydrogen, by the photoactivated nitro-group, to give a species which may be represented as (138). Electron redistribution then leads to the keten (139) from which *o*-nitrosobenzoic acid is obtainable as indicated in (140). Support for this view is available in that *ortho*-substituted benzophenones have been shown[111] to be enolised under similar conditions, presumably by an equivalent process.* The latter represents a particular case of the general phenomenon of carbonyl γ-hydrogen abstraction already referred to. In the presence of alcohol (as solvent), the corresponding ester is obtained by intermolecular reaction with the keten, and a similar process can be written for the other related transformations. In particular the conversion (141) → (142)[112] would be envisaged as proceeding through the keten imine, whilst the discrete intermediate indicated in the conversion of (136) into (137) becomes unnecessary. It is interesting that an apparently similar transformation has been reported for the arsenic-containing compound (143) which is converted into the arsonic acid (144).[113]







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* The cyclopropane by-product obtained in the irradiation of β-ionone[57] has been shown in these laboratories to be, in fact, the alternative conjugated diene formed by similar hydrogen transfer.

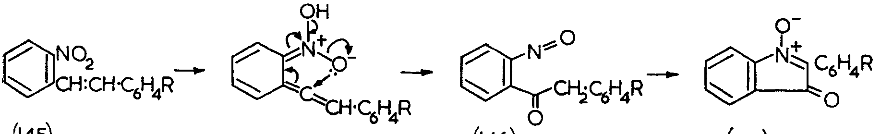
[110] Tanasescu, *Bull. Soc. chim. France*, 1926, 1443; Leighton and Lucy, *J. Chem. Phys.*, 1934, **2**, 756, 760.

[111] Yang and Rivas, *J. Amer. Chem. Soc.*,, 1961, **83**, 2213.

[112] Sachs and Kempf, *Ber.*, 1902, **35**, 2704.

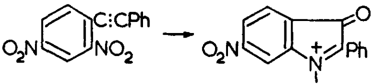
[113] Karrer, *Ber.*, 1914, **47**, 1783.

Irradiation of *o*-nitrostilbenes (145; R = NMe_2, OH, or OMe), if following the course indicated for other *o*-nitrobenzene derivatives, might be expected to give the ketones (146) through intermediate allenes. The products isolated, the isatogens (147),[114] may be derived from such ketones



(145) (146) (147)

by cyclisation and oxidation. No such oxidation is required in the photochemical conversion (148) → (149),[115] and this seems to require a modified mechanism.



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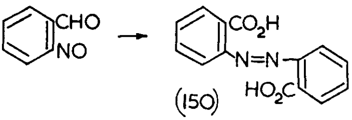
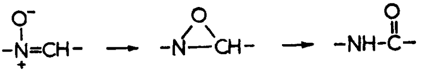


(150)

The conversion of *o*-nitrosobenzaldehyde into the azo-compound (150) is an example of this transformation at a lower oxidation level.[116]

(b) Nitrone rearrangement.—Irradiation of nitrones (151) gives, by internal addition, oxazirans (152) which, being unstable, frequently rearrange spontaneously to amides.[117] With certain *N*-phenylnitrones, irradiation in benzene gives the oxaziran whereas irradiation in ethanol gives the amide.[114,118] The oxaziran in benzene solution is converted back



(151) (152)

into the nitrone in the dark within 24 hours. The oxazirans obtained are, where they have been compared, identical with those prepared by oxidation of the Schiff's bases with peracetic acid.[119] The fused oxaziran (154) prepared by the action of light on 5,5-dimethyl-1-pyrroline 1-oxide (153) appears to be remarkably stable,[120] although it is thermally rearranged to 5,5-dimethylpyrrolid-2-one on prolonged heating. Other examples of this

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[114] Splitter and Calvin, *J. Org. Chem.*, 1955, **20**, 1086.

[115] Pfeiffer and Kramer, *Ber.*, 1913, **46**, 3655; see also Pfeiffer, *Ber.*, 1912, **45**, 1819; Tanasescu, *Bull. Soc. chim. France*, 1927, 1074; Kröhnke, Kröhnke, and Vogt, *Chem. Ber.*, 1953, **86**, 1500.

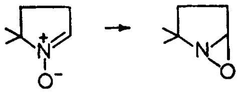
[116] Ried and Wilk, *Annalen*, 1954, **590**, 91.

[117] Kamlet and Kaplan, *J. Org. Chem.*, 1957, **22**, 476; Kröhnke, *Annalen*, 1957, **604**, 203.

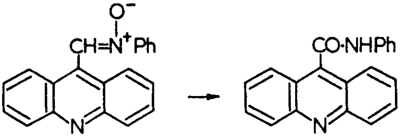
[118] Splitter and Calvin, *J. Org. Chem.*, 1958, **23**, 651.

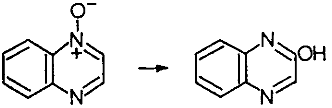
[119] Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.

[120] Bonnett, Clark, and Todd, *J.*, 1959, 2102.

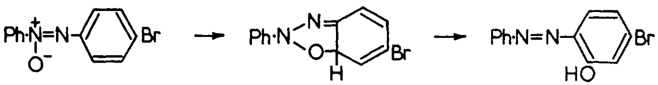
(153)  (154)

transformation include the conversion of 9-acridyl-*N*-phenylnitrone (155) into the anilide (156),[121] and of the quinoxaline derivative (157) into the hydroxyquinoxaline (158),[122] whilst the conversion of azoxybenzenes into phenolic azo-compounds[123] may be a vinylogous extension of this reaction.

(155)  (156)

(157)  (158)

If so, the transformation of the bromoazoxy-compound (159) into the phenol (160) may be as represented here.



(159)

(160)

We are indebted to Professor R. B. Woodward (Harvard) for stimulating discussions.

[121] Chardonnens and Heinrich, *Helv. Chim. Acta*, 1949, **32**, 656; Mikhaĭlov and Ter-Sarkisyan, *Bull. Acad. Sci. U.S.S.R.*, 1954, 559.

[122] Landquist, *J.*, 1953, 2830.

[123] Badger and Buttery, *J.*, 1954, 2243.