acetyl derivative, 58462-95-6; **8a**, 29537-31-3; **8b**, 28277-70-5; ethyl β-(2-mercapto-6-methyl-4-oxo-5-pyrimidine)propionate, 58462-96-7; *S*-methylisothiourea sulfate, 867-44-7; diethyl α-acetylglutarate, 1501-06-0; benzoyl chloride, 98-88-4; (*S*)-alaninol, 2749-11-3; isosparsomycin, 58462-97-8.

References and Notes

(1) We wish to thank Dr. Marvin Grostic for his invaluable assistance with the mass spectra. This work was supported by Contracts PH 43-62-168 and PH 43-68-1023 with the Division of Cancer Treatment, National Institutes of Health, Department of Health, Education and Welfare.
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Sigmatropic Hydrogen Migration and Electrocyclization Processes in Compounds in the Vitamin A Series. Photochemistry of Polyenes. 10[1]

V. Ramamurthy and R. S. H. Liu*[2]

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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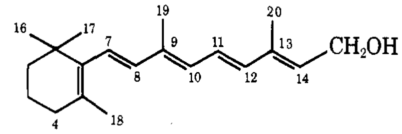
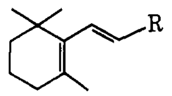
Reactions of dienes, trienes, and tetraenes in the vitamin A series brought about by direct irradiation were examined. In addition to the previously known sigmatropic 1,5-hydrogen migration from C-18 to C-8 and the hitherto unnoticed electrocyclization, geometric isomerization also appears to be an important reaction from S_1. Electrocyclization and geometric isomerization are reversible processes; hence in most cases the end products are retro-γ derivatives. Mechanistically it was shown that the hydrogen migration process can originate from either the 7-cis or 7-trans isomers of the conjugated systems. A case of 6e-electrocyclic ring opening process involving both the excited states of the product and the reactant is presented.

Compounds in the vitamin A (I) series are known to undergo a variety of photochemical reactions. In addition to the geometric isomerization reactions, which appear to be the exclusive reaction of the triplet states,[3] direct irradiation leads to hydrogen migration, cyclization, and intramolecular cycloaddition products. In this paper, the sigmatropic 1,5-hydrogen migration and 6e-electrocyclization processes are examined.

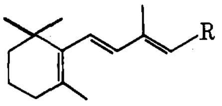


I



II

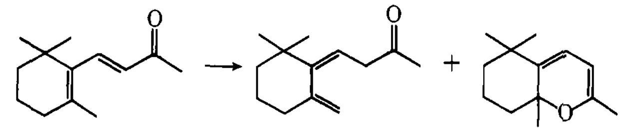
a, R = COCH$_3$
b, R = CHCH$_3$OH
c, R = CN



III

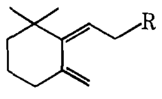
a, R = CN
b, R = CO$_2$Et
c, R = CO$_2$H
d, R = H
e, R = CHO
f, R = COCH$_3$

The earliest report on hydrogen migration in compounds in this series was on β-ionone (IIa) in 1957,[4] but its correct structure, a retro-γ derivative (IVa), was not recognized until 4 years later.[5] In this case, it is a minor product, the major being the α-pyran V which was later shown to be in equilibrium with *cis*-ionone.[6] In a series of papers in the early 1960's, Mousseron-Canet and co-workers[7] established the generality of the sigmatropic hydrogen migration reaction in trienes (β-ionylidene derivatives, III) as well as dienes in the vitamin A series. Furthermore, because of detection of 7-cis isomer(s) prior to significant accumulation of the retro-γ products, they suggested that the retro-γ products are formed by way of the 7-cis isomer(s) in two separate photochemical steps.



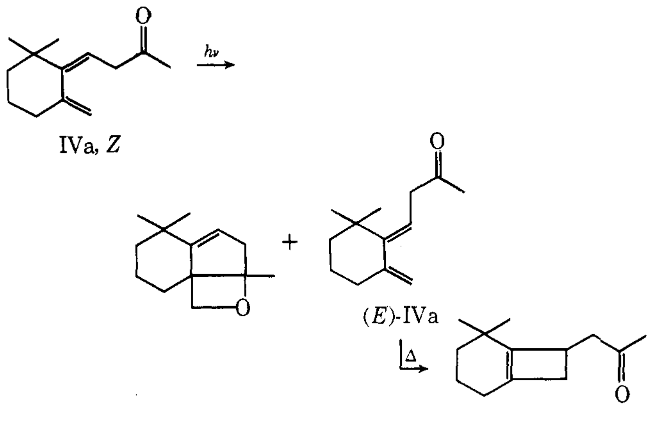
IIa IVa V

The initially formed retro-γ products are believed to have the *Z* configuration. This was deduced from their lack of reactivity toward maleic anhydride.[7a] More recently, it was found that (*Z*)-retro-γ-ionone undergoes secondary photochemical reactions of geometric isomerization and internal cycloaddition giving (*E*)-retro-γ-ionone and the tricyclic ether shown.[8] Upon heating, (*E*)-retro-γ-ionone [(*E*)-IVa] further rearranged to a cyclobutene[8]—one of few cases where a cyclobutene is more stable than the corresponding diene.[9]



(*Z*)-IV

a, R = COCH$_3$
b, R = CHCH$_3$OH
c, R = CN



IVa, *Z*

(*E*)-IVa

Table I. Characteristic NMR Data of (*Z*)-Retro-γ-ionyl (IV) and -ionylidene (V) Derivatives[a]

Registry no.	Compd	H-7	CH_2-8,8	H-10	Exo CH_2	CH_3-19
		γ-Ionyl				
	IVa[b]	5.33 (t)	3.16 (d)		4.96, 4.51	
35986-44-8	R = $COCH_3$	$J_{7,8}$ = 7.1 Hz				
	IVb	5.18 (t)	2.18 (d)		4.53, 4.91	
35986-46-0	R = $CHCH_3OH$	$J_{7,8}$ = 7.0				
	IVc	5.72 (t)	3.13 (d)		5.15, 5.58	
58503-66-5	R = CN	$J_{7,8}$ = 7.0				
		5.23 (t)	3.10 (d)		4.45, 4.85	
58503-67-6	R = CO_2H	$J_{7,8}$ = 7.0				
		5.20 (t)	3.28 (d)		4.50, 4.82	
58503-68-7	R = C_6H_5	$J_{7,8}$ = 7.0				
		5.18 (t)	2.20 (d)		4.40, 4.75	
58503-69-8	R = $(CH_3)_2COH$	$J_{7,8}$ = 6.5				
		γ-Ionylidene				
58503-70-1	R = CN, 9-trans	5.12 (t)	3.93 (d)	5.04	4.50, 5.00	1.96
58503-71-2	9-cis	5.12 (t)	3.20 (d)	5.04	4.56, 4.92	1.80
		$J_{7,8}$ = 7.5				
58503-72-3	R = CO_2Et, 9-trans	6.16 (t)	3.01 (d)	5.68	4.62, 5.00	2.19
58503-73-4	9-cis	6.23 (t)	3.60 (d)	5.68	4.26, 5.00	1.86
		$J_{7,8}$ = 7.5				
58503-74-5	R = CO_2H, 9-trans	5.19 (t)	3.08 (d)	5.72	4.62, 5.02	2.22
58503-75-6	9-cis	5.26 (t)	3.64 (d)	5.72	4.62, 5.08	1.92
		$J_{7,8}$ = 7.0				
58503-76-7	R = H	5.24 (t)	2.82 (d)	4.68	4.60, 4.94	1.70
		$J_{7,8}$ = 7.5				

[a] HA-100. In $CDCl_3$-Me_4Si. δ in parts per million, in J in hertz. [b] Data of P. de Mayo, J. B. Stothers, and R. W. Yip, *Can. J. Chem.*, **39**, 2135 (1961).

During the course of our investigation we found photochemical 6e-electrocyclization also to be an important reaction in compounds in the series. (The formation of the α-pyran from *cis*-ionone is probably a thermal process.) In selected systems other secondary internal cycloaddition reactions were also observed and have been reported elsewhere.[10]

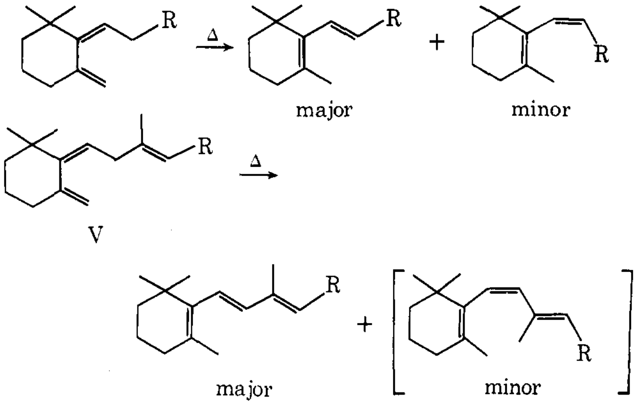
Results

β-Ionol (IIb) and Other Dienes. Direct irradiation (254 nm) of an ether solution of the cis isomer was found to give the same retro-γ-ionol as from trans-ionol. GLC was used to follow the reaction. The trans isomer was not found to be present during any stage of irradiation.

The uv absorption spectrum of *trans*-β-cyclocitrylideneacetonitrile (IIc) is sufficiently different from those of *cis*-IIc and the retro-γ product so that the use of Pyrex filters allows selective excitation of the trans. Under such conditions the product mixture was found to contain 35% *cis*-IIc[11] and 65% of IVc (NMR data listed in Table I). This ratio is independent of the solvent used ($CDCl_3$, CD_3OD, CD_3CN, C_6D_6, and *n*-butyl bromide). Upon removal of the Pyrex filter (in CD_3OH and CD_3CN) IVc became the only product. Similarly irradiation of *cis*-IIc in a quartz vessel gave initially *trans*-IIc as well as IVc; but the final product was again only the retro-γ product.

Our results on *trans*-β-ionone (IIa) are in agreement with those in the previous reports.[4-6] However, additionally we also found that starting from an equilibrium mixture of *cis*-ionone and the α-pyran, retro-γ-ionone (IVa) can also be obtained. The reaction was initially accompanied by formation of *trans*-IIa.

β-Ionylideneacetonitrile (IIIa) and Other Trienes. Direct irradiation of the trienes IIIa–d was examined. The end products were the corresponding retro-γ products. We confirmed the observation of efficient geometric isomerization of IIIb giving all four isomers during early stages of irradiation. Similar behavior exists in the other three compounds. However, sometimes the reaction is further complicated by the presence of another primary photoproduct. Since this product probably involves a hitherto unnoticed reaction in compounds in this series and the process appears to be most efficient in β-ionylideneacetonitrile (IIIa), we examined the latter system in some detail. The ^1H NMR data of isomers of β-ionylideneacetonitrile are in the literature.[11] The assignment of its retro-γ products (V) was based on analogy of its NMR spectrum (Table I) with those of other known retro-γ products (those from β-ionone, ethyl β-ionylideneacetate, and β-ionylideneethanol).[7c] For example, the original doublets of H-7 and H-8 are now replaced by three vinyl hydrogens, two in the high-field region (4.5–5.0 ppm) characteristic of terminal methylenes and the remaining one a triplet. The latter is coupled with a new methylene doublet around 3 ppm and the methyl-18 signal is no longer present. The geometry around C-7 is believed to be trans for the same lack of reactivity toward a dienophile as noted earlier[7a] and also for its behavior in thermal rearrangement. Upon heating an inert solution of the compound to ~130 °C a mixture of the geometric isomers of IIIa was formed. This reverse hydrogen migration is, in fact, characteristic of all retro-γ derivatives of compounds in this series (see below).



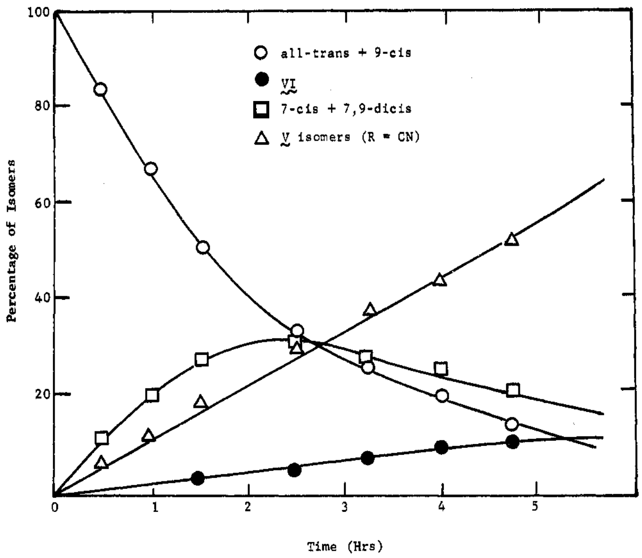


Figure 1. An action plot of direct irradiation of a mixture of the two 7-trans isomers of β-ionylideneacetonitrile (IIIa).

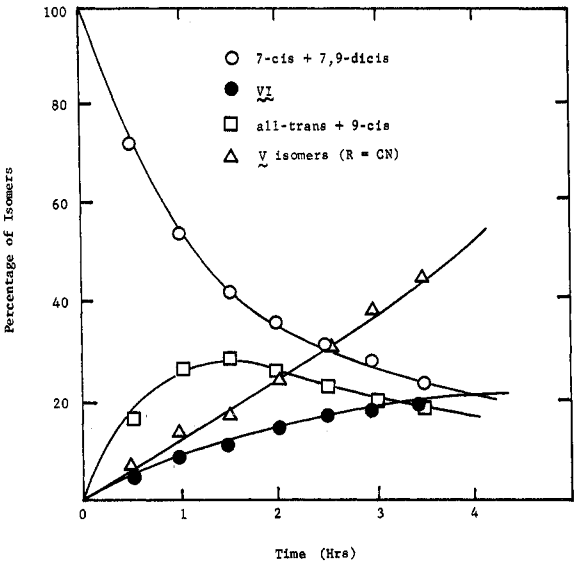


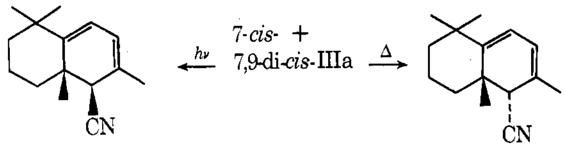
Figure 2. An action plot of direct irradiation of a mixture of the two 7-cis isomers of β-ionylideneacetonitrile (IIIa).

Since the E isomer of a retro-γ product is expected to undergo ring closure to a cyclobutene, we conclude that the initial photoproducts must also have the Z configuration.

Careful examination of the NMR of the E-retro-γ product revealed the presence of two isomers. The CH_3-19 signal appears as two unequal singlets. This is not surprising in view of the fact that two isomers (all trans and 9-cis) are present in the starting trienes. They are therefore geometric isomers around the same double bond. Configurational assignments were based on the chemical shift of CH_3-19. It shifts downfield when the group is cis to the substituent at C-10. An explanation based on change of electron density around the hydrogens in CH_3-19 (steric polarization) has been advanced to account for the change in chemical shift.[12] The key NMR data of the retro-γ products from IIIa and also other triene derivatives are listed in Table I along with those of dienes.

The course of reaction of IIIa was followed by NMR. Geometric isomerization was the major process at early stages of irradiation giving substantial amounts of the two 7-cis isomers. Then, formation of the retro-γ product was accompanied by a new product, VI. The latter apparently was photolabile. Its buildup reached a maximum amount of ~20% and then diminished with other triene nitriles. At the end only the retro-γ products remained. The slope of the lines in an action plot of this reaction (Figure 1), however, suggests that all three types of products are primary photoproducts. Similar results were obtained when starting with a mixture of the two 7-cis isomers (Figure 2).

Attempts to isolate the new product presented some difficulties. By repeated column chromatography, a fraction containing about equal amounts of VI and a mixture of the retro-γ isomers was obtained. After comparison of the NMR spectra of the mixture and the retro-γ isomers the following information about VI was obtained. The compound contains four different methyl groups, therefore the geminal dimethyl groups are no longer equivalent. The shift of CH_3-18 signal to δ 1.1 indicates that it is now attached to a saturated carbon. The CH_3-19 signal remains at 1.92. Two vinyl hydrogens are present, appearing as a singlet. The H-10 signal is now a singlet in the saturated region (3.22 ppm). These features are only in agreement with a cyclized cyclohexadiene structure. We have also observed that thermal rearrangement of a mixture of 7-*cis*- and 7,9-di-*cis*-β-ionylideneacetonitrile resulted in the formation of a single product. Its ^1H NMR spectrum closely resembles that of VI. Again, four different methyl groups are present with CH_3-18 now shifted to a higher field and CH_3-19 appearing ~0.1 ppm upfield from the corresponding signal in VI. The two vinyl hydrogens are nonequivalent but close in chemical shift and the coupling constant is that normally found for 2,3 hydrogens in cyclohexadienes. This thermal product coming from a different electronic state is probably an epimer of VI.[13] For reasons delineated in the Discussion section, the photoproduct (VI) is believed to have the stereochemistry shown and the thermal product, its epimer VIa.

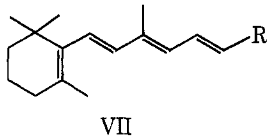


VI VIa

By direct irradiation of the thermal product, VIa, the cyclohexadiene products were shown to undergo reverse ring opening reactions.[14] The course of the reaction was followed by NMR. The results were shown in the action plot.[14]

Trienal IIIe and trienone IIIf were found not to undergo electrocyclization nor sigmatropic rearrangements under direct irradiation. Geometric isomerization appears to be the only important characterizable photochemical reaction.

β-Ionylidenecrotononitrile (VIIa) and Other Tetraenes. The tetraenenitrile under direct irradiation again resulted in efficient geometric isomerization and 6e-electrocyclization. The irreversible hydrogen migration in this case is relatively an inefficient process; therefore the product mixture passes through a stage containing substantial amounts of the cyclized product(s). They are partially isolable by column chromatography. In one attempt two useful fractions were collected. One contained essentially a single isomer, the NMR data of which are listed in Table II. The features informative of the structure are (1) the presence of four nonequivalent methyls, (2) the presence of a low-field methine doublet (δ 3.28) which was shown by decoupling experiments to be coupled with a vinyl hydrogen, (3) the same vinyl hydrogen is coupled to another vinyl hydrogen with J = 11 Hz,



a, R = CN
b, R = $COCH_3$

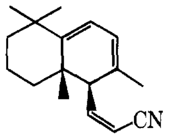
VII

Table II. Characteristic NMR Data of the Electrocyclized Products[a]

Registry no.	Compd	H_7	H_8	H_{10}	H_{11}	H_{12}	CH_3-19	CH_3-18	CH_3-16,17
43161-05-3	VI[b]	5.78	5.78	2.56			1.92	1.10	
43161-06-4	VIa	5.72	5.80	2.51			1.82	1.11	1.00
		$J_{7,8}$ = 5.5 Hz							1.04
58503-77-8	VIII	5.72	5.80	3.28	6.70	5.42	1.66	1.16	0.98
		$J_{7,8}$ = 5.5		$J_{10,11}$ = 11.0		$J_{11,12}$ = 11.2			1.14
58526-11-7	VIIIa[c]	5.72	5.80	3.32	6.74	5.32	1.68	1.18	0.98
		$J_{7,8}$ = 5.5		$J_{10,11}$ = 11		$J_{11,12}$ = 17			1.14

[a] HA-100. In $CDCl_3$-Me_4Si. [b] From a mixture of VI and retro-γ-ionylideneacetonitrile. [c] From a mixture of VIII and VIIIa.

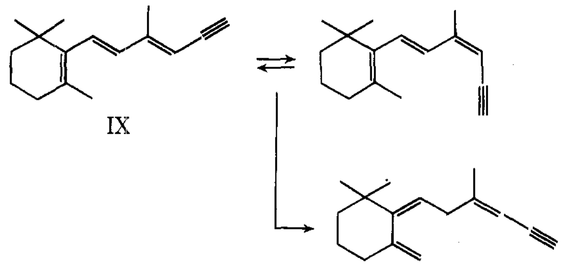
indicative of the cis geometry. These features are in agreement with the structure VIII shown. In analogy with the photoproduct from IIIa, the stereochemistry about the new bond is believed to be cis.


VIII

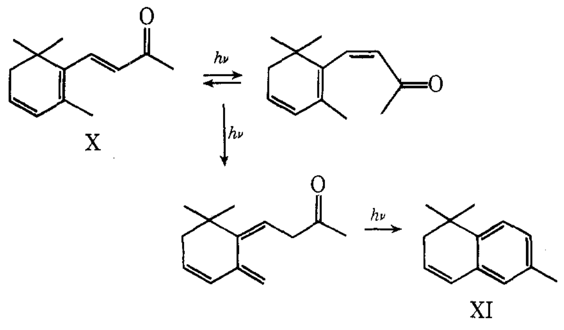
The second fraction contained a mixture of two compounds, VIII being one of them. From the difference of the spectra of the two fractions we gathered the spectral data for the second photoproduct, also listed in Table II. With the exception of the coupling constants between H-11 and H-12, it closely resembles that of VIII. It is probably a geometric isomer of VIII. The larger vinyl coupling constant ($J_{11,12}$ = 17 Hz) suggests that it is the trans isomer (VIIIa).

Prolonged irradiation again led to retro-γ products as indicated by the characteristic NMR features as discussed for the trienes. However, the mixtures were too complex and not separable for complete configurational assignments.

Irradiation (254 nm) of the all-trans isomer of the hydrocarbon IX led to isomerization around the 9,10 bond with a slower rate of formation of only the retro-γ products. The two isomers of the latter could not be separated, but the NMR spectrum of the mixture was sufficiently informative [H-7 (t) 5.2; CH_2-8,8′ (d) 3.2, 2.9; CH_3-19 1.74, 1.90; exo-CH_2 4.6, 5.2, and 4.98]. Irradiation (>300 nm) of the C_{18}-tetraene ketone, VIIb, on the other hand, only caused photoisomerization around the 9,10 and 11,12 double bonds.


IX

3,4-Dehydro-β-ionone (X). Its photochemistry was discussed in some detail in an earlier preliminary paper.[15] The initial geometric isomerization and hydrogen migration are followed by a secondary photoreaction giving the hydrocarbon XI. With properly filtered light (Pyrex) the reaction could be made to terminate at the retro-γ-dehydroionone stage.



X
XI

Discussion

The Retro-γ Products. In agreement with earlier studies by Mousseron-Canet and co-workers[7] we found sigmatropic hydrogen migration from methyl-18 to C-8 to be a general reaction in compounds in the vitamin A series. The only exceptions are the aldehydes and ketones where the only identifiable reaction is geometric isomerization. Based on the results described above some generalizations can be made.

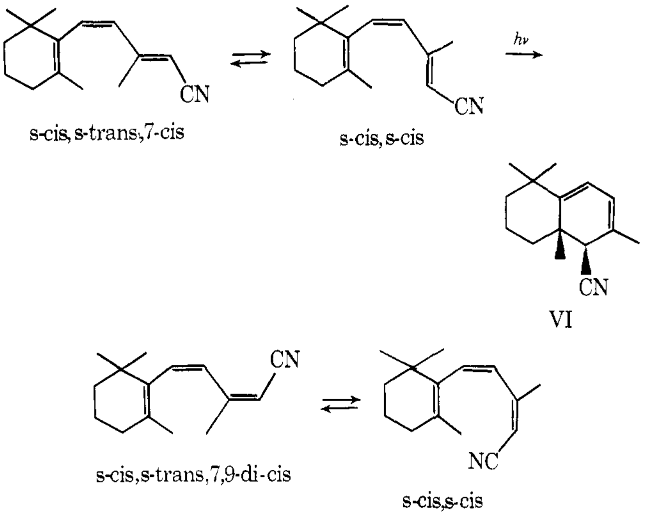
Although quantum yields have not been determined, the relative efficiencies of the reaction appear to be of the order of dienes, trienes, and then tetraenes. In no instances did we observe formation of retro-γ products from pentaenes in the series. Neither were there reports on such reactions in longer carotenoids.[7a] This trend of reactivity parallel with the energy content of the excited singlets is not a surprising one especially in view of the considerable activation involved in similar ground state reactions. However, other factors probably also affect the efficiency of the reaction. For example, of the two trienones, β-ionylideneacetone (IIIf) and dehydro-β-ionone (X), only the latter undergoes hydrogen migration. The small difference in ring chain conformation expected for the two systems may have an effect on the reactivities of the two compounds, but we suspect that a more important factor is the difference in electron density at C-8 in the excited states of the two molecules. In dehydro-β-ionone C-8 is a terminal carbon of the triene unit (or the third atom in the trienone) while in IIIf the same carbon is in the middle of the triene unit (same for the trienone); therefore the electron density at C-8 in X should be higher. Electron density probably also partly accounts for the high reactivity of β-ionyl derivatives and the higher reactivity of β-ionol than β-ionone.

We have no evidence to support the postulate that retro-γ products are only derived from the 7-cis isomers.[7] The observation of the 7-cis isomers prior to significant accumulation of the retro-γ products clearly is not a sufficient condition for the postulate. In fact, that the 7-cis isomers were not detected in other systems would force one to conclude that geometric isomerization was the rate-determining step in this postulated mechanism of two consecutive steps of photoreaction. This is quite contrary to known reactivity of polyenes, the quantum yield of geometric isomerization being generally higher than other concerted processes.[18] Symmetry rules do not impose any restriction to hydrogen migration from either isomer. Furthermore molecular models do not suggest reasons to suspect that the antarafacial process[13] should be more favored from the 7-cis isomer. Our results with β-citrylideneacetonitrile (IIc) in which the 7-trans isomer was selectively excited clearly showed that the retro-γ product can directly come from the 7-trans isomer. Furthermore, the observation of formation of retro-β-ionol from 7-*cis*-β-ionol without detectable amounts of 7-*trans*-β-ionol strongly suggests that retro product can also originate directly from the 7-cis isomer. We therefore believe that hydrogen migration can proceed from either isomer. It generally represents a leakage from the reversible geometric isomerization process. However, in some instances, where molecules are especially suitable for hydrogen migration (e.g., β-ionol with high energy content and high electron density at C-8) this leakage becomes the predominant process.

The thermal rearrangement of the retro-γ product back to the corresponding β-ionol and β-ionylidene derivatives should now involve *suprafacial* 1,5-hydrogen *migration*.[13] Same as the photochemical reaction, it shows little selectivity resulting in the formation of both the 7-cis and the 7-trans isomers. The 7-cis isomers of trienes understandably further rearranged immediately after formation to cyclohexadienes (see below).

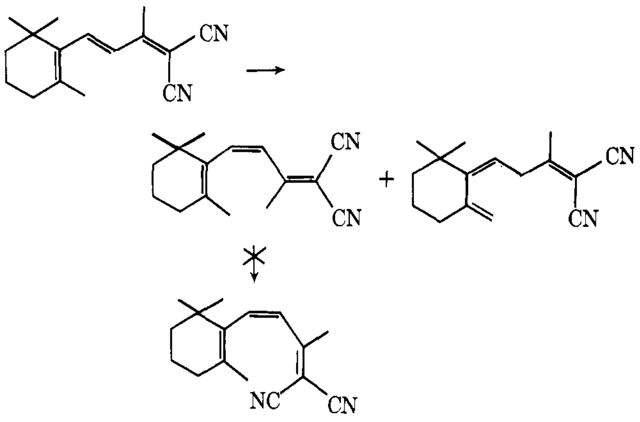
Electrocyclization Products. The reversible photochemical 6e-electrocyclization process is of course a well-known reaction in trienes and higher polyenes. In fact, examples of these were important in the formulation of the Woodward–Hoffmann rule on electrocyclization.[13] However, the case we described in β-ionylideneacetonitrile apparently represents the first example of such a reaction in compounds in the vitamin A series.

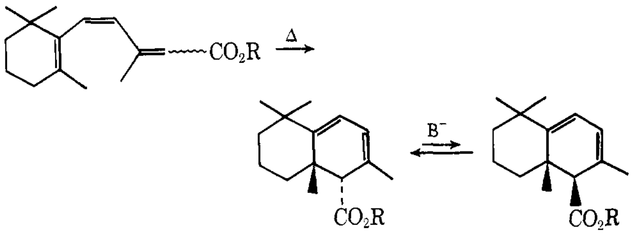
The action plots of photoreactions of the 7-trans and the 7-cis isomers of the trienenitrile are shown in Figures 1 and 2, respectively. The more rapid rise of the curve of the electrocyclized products in Figure 2 than the corresponding curve in Figure 1 appears to suggest that the photoelectrocyclization occurs only from the 7-cis isomers. Therefore, starting from the 7-trans isomers two separate photochemical steps are required.[17] Furthermore, that only one geometric isomer of the cyclized product is formed suggests that only one of the two 7-cis isomers is reactive. Consideration of probable ground state conformation of the two isomers and the necessary conformation for electrocyclization provides the answer. The 7-cis isomer may exist in conformations resembling either the s-cis,s-trans or the s-cis,s-cis conformer while the 7,9-di-cis isomer is likely to exist only in the less crowded s-cis-s-trans conformation. However, only the di-s-cis conformer can be excited to the now conformationally rigid di-cis singlets necessary for cyclization.[18] Therefore, only 7-cis cyclizes giving according to the rule the conrotatory product VI. For the same reason, thermal cyclization is expected to proceed only from 7-cis giving the disrotatory product VIa. However, that the thermal reaction did proceed to completion suggests that geometric isomerization from 7,9-di-cis to 7-cis takes place concurrently with electrocyclization at elevated temperatures.



VI

In agreement with the above explanations, we found that β-ionylidenemalononitrile where the s-cis,s-cis conformer of even the 7-cis isomer is not likely to exist does not undergo photochemical electrocyclization. In this case, the only primary photochemical processes are geometric isomerization and sigmatropic hydrogen migration. Also, in agreement with the above interpretation is the recent work of Frater where the same 6e-electrocyclization was observed in a related system of a mixture of 7-*cis*- and 7,9-di-*cis*-β-ionylideneacetate.[16] The thermal product, assigned with the same stereochemistry as VIa, was epimerized in the presence of a base to give a small amount of a product which spectroscopically is in agreement with the compound with the opposite stereochemistry thus equivalent to VI.

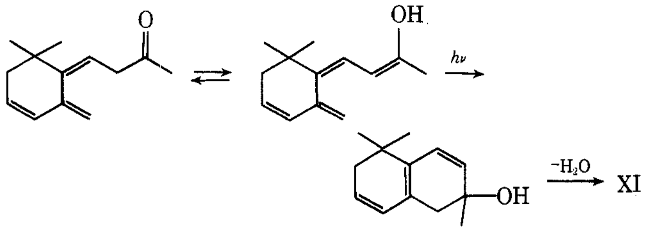




Figures 1 and 2 also show that the cyclization process is photochemically reversible. After prolonged irradiation, products from the less efficient but irreversible sigmatropic process predominate. This process is more clearly demonstrated by irradiation of the thermal product VIa. Triene products were followed by the appearance of the retro products.[14] The rule for 6e-electrocyclization predicts the formation of the 7,9-di-cis isomer of IIIa from conrotatory ring opening of VIa. However, it was shown earlier[14] that all four geometric isomers appear almost concurrently. This apparent violation of the rule was explained by assuming that the ring-opened product is formed in its excited singlet state which is capable of further reactions. From a cyclohexadiene to a hexatriene, energetically this is a downhill process thus not suffering from the same difficulty as in excited state conversion of butadiene to cyclobutene, pointed out by Dauben.[19]

Our study and also previous studies show that the photochemistry of dienes and trienes in this series is marked by the absence of other types of products commonly observed in the photochemistry of dienes and triene (e.g., cyclobutene, bicyclobutane, and bicyclo[3.1.0]hexane products). We believe that this is due to the ground state conformation of the unsaturated C_5–C_{10} unit in these compounds. From space filling molecular models and also shown by NMR studies,[20] it is believed that the 5,6 and 7,8 double bonds are far from coplanar (whether the cisoid or the transoid form) for concerted reactions to cyclobutenes or bicyclobutanes. On the other hand, there is little difficulty for electronic overlap between C_5 and C_{10} in a 7-cis isomer in a Möbius manner[21] giving the cyclohexadiene with the cis stereochemistry. Models also show that any conformation involving close proximity of C_5 and C_9 (i.e., the s-cis-s-trans conformation necessary for formation of bicyclo[3.1.0]hexenes)[22] only results in even closer proximity of C_9 and hydrogens on C_{18}. We believe that this accounts for the formation of the sigmatropic hydrogen migration products and not the internal cycloaddition products.

Lastly, the formation of dehydro-γ-ionone (XI) from dehydroretro-γ-ionone is clearly a photoprocess (the retro product is thermally stable). It probably involves photoelectrocyclization of the enol followed by dehydration catalyzed by trace acids.



Experimental Section

Procedures to prepare the compounds used in this study are in the literature.[11,23] Low-pressure Hg lamps (PCQ-X1, uv-Products Inc.) were used for 254-nm irradiation and medium-pressure Hg lamps (Hanovia) for >300-nm irradiation. For longer wavelengths appropriate Corning filter plates were used to isolate light of the desired wavelengths. For dienes, GLC was used to follow the course of reaction; and for longer polyenes, NMR was used instead. Column conditions and chemical shifts have been described previously.[3,11] The following are representative procedures of direct irradiation at preparative scale.

Retro-γ-ionol (IVb). A 2% ether solution of 7-*cis*-β-ionol was irradiated with 254-nm light in a manner similar to that described for the trans isomer.[7b] The reaction was followed by GLC (6 ft, 3% SE-30, 128 °C) and is usually completed within 2 days of irradiation. The product was isolated by short-path distillation. Its properties are identical with those described in the literature for IVb.[7b]

Retro-γ-ionylideneacetonitrile (V, R = CN) was prepared by irradiation (254 nm) of an ether solution of a mixture of 7-trans (or 7-cis) isomers of β-ionylideneacetonitrile in a similar manner as described above. The NMR data of the products are listed in Table I. When the same triene was irradiated with light >300 nm (Pyrex filters), the final product mixture contained the retro-γ product (77%) and another new compound (23%). Since these compounds cannot be separated by, e.g., column chromatography on silica gel, the characteristic NMR signals of the latter (Table II) were obtained after comparison of the spectrum of the mixture with that of V. Based on these spectral data and other related information (see text) the cyclohexadiene structure VI was assigned to the new product. Upon removal of the Pyrex filters the final product mixture was found to contain only V (R = CN).

β-Ionylideneacetaldehyde (IIIe). A deoxygenated 5% solution of a mixture of *all-trans-* and 9-*cis*-β-ionylideneacetaldehyde in perdeuterated benzene in a NMR sample tube was irradiated with >300-nm light. Formation of the two 7-cis isomers was detected immediately by their characteristic methyl signals. No other new products were detected (by NMR) even after 2 days of irradiation when the solution darkened considerably.

Tetraenenitrile VIIa. The tetraenenitrile, obtained as a four-isomer mixture from Horner reaction of *all-trans-* and 9-*cis*-β-ionylideneacetaldehyde with diethylcyanomethyl phosphonate, was irradiated with >300-nm light and the reaction was followed by NMR. The absence of methyl signals around 1.5 ppm indicated that the 7-cis isomers were not present in significant amounts at any stage of irradiation.[11] Signals in other region were too complex to provide any useful information. After 1 day of irradiation the mixture was separated by column chromatography on silica gel (Biosil) using hexane–benzene (3:1) solvent mixture. The small amounts of unreacted tetraenes were thus separated. Of the products, two useful fractions were collected. One fraction was found to contain primarily one compound. Its spectral properties were discussed in the text and are only consistent with the cyclized structure VIII [ir 2215 (CN), 760 cm^{-1} (cis disubstituted double bond); NMR (Table II)]. The second fraction contained about equal amounts of VIII and a second product which is believed to be the 11-trans isomer of VIII (see text).

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Registry No.—IIa, 79-77-6; IIb, 472-80-0; IIb 7-cis isomer, 35031-11-9; IIc, 40244-29-9; 7-*trans*,9-*trans*-IIIa, 5299-98-9; 7-*trans*,9-*cis*-IIIa, 5299-99-0; 7-*cis*,9-*trans*-IIIa, 40244-68-6; 7-*cis*,-9-*cis*-IIIa, 40244-51-7; IIIa, 58526-71-9.

References and Notes

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(18) Similar to cases in the vitamin D series as discussed in E. G. Havinga and J. L. Schlatmann, *Tetrahedron*, **16**, 146 (1961).

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