light absorbed. Potassium ferrioxalate was used as a chemical actinometer. The data were treated by the method of Johns.[5]

Bimolecular Quenching Rate Constants. Bimolecular quenching rate constants with *n*-hexane, cyclohexane, 2-propanol, and naphthalene as quenchers were measured. In each measurement, a series of six samples containing varying amounts of quencher with the same amount of 4-carboxymethylbenzophenone (or benzophenone) were prepared and degassed. Quencher concentration was chosen in such a way that the lifetimes of the samples with quencher were reduced to within the range of 20-80% that of the sample free of the quencher. A measurement of τ as a function of quencher concentration enabled the computation of the rate constant. Data were fit by least squares to eq 3. Correlation coefficients were better than 0.98, and mean deviations in the slopes were less than 5% for individual runs. Since determination of a solvent effect on emission quenching by hexane was particularly important to aspects of this work, duplicate experiments were carried out.

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Photochemistry of Polyenes. IX. Excitation, Relaxation, and Deactivation of Dienes, Trienes, and Higher Polyenes in the Vitamin A Series in the Sensitized Isomerization Reaction[1]

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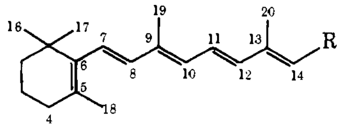
Abstract: In a detailed study of photosensitized isomerization of dienes, trienes, and higher polyenes in the vitamin A series it was found that dienes and trienes behave photochemically differently from the higher members of the series. Not only are the sterically hindered 7-cis isomers present in the photostationary states of the lower members but also under selective sensitization conversion to such isomers becomes quantitative, while for the longer polyenes 7-cis isomers are absent under all conditions of sensitized irradiation. This different photochemical behavior is explained in terms of the expected different structures of relaxed triplets, i.e., perpendicular ones in dienes and trienes and planar ones in higher polyenes. Direct irradiation was also reexamined with emphasis on the nature of the spin states where chemical reactions originate.

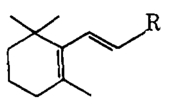
The problem of photochemical geometric isomerization of compounds in the vitamin A (Ia) series has, for many years, attracted the attention of many research groups. The system of retinal (Ib)[3] and related compounds[4] are still of intense current interest. Considering the important role of geometric isomerism in vision, the efforts are well justified.[5]



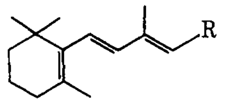
Ia, R = CH_2OH
b, R = CHO
c, R = CH_2OAc
d, R = CN

However, in spite of these efforts, the excited state properties of polyenes are still not well understood especially when compared to the wealth of information available for dienes and other smaller molecules. A major difficulty is to find a reliable analytical tool for systems where large numbers of isomers are expected. Therefore, when we started to investigate the photochemistry of vitamin A related compounds we decided to examine first the chemistry of the lower members of the series in some detail, where a lesser analytical problem is expected. It was hoped that the information so derived would facilitate the study of the chemistry of higher members. Also, it will be interesting to examine the differences, if any, in photochemical properties between polyenes of different length. We have, therefore, prepared the compounds II-IV and studied the photoisomerization reaction in some detail. Earlier we had also studied the photochemistry of several linear trienes with the system 2,5-dimethyl-2,4,6-octatriene (alloocimene) examined in most detail.[6]

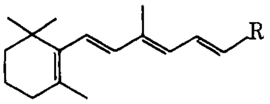
Many reports on direct irradiation of β-ionyl (II), β-ionylidene (III), and higher polyenes in the series are in the literature.[7,8] Largely through the efforts of Mousseron-Canet and co-workers,[7] it became known that the most common reaction in dienes and trienes is the sigmatropic reaction of hydrogen migration from methyl at C-5 to C-8, giving the retro-γ products (V). In one case (ethyl β-ionylideneacetate, IIIa) the formation of the retro products is accompanied by a new set of geometric isomers around the 7,8 double bond, detected spectroscopically during early stages of irradiation.[7] Based on this observation, a general mechanism was proposed in which the retro-γ products are believed to derive entirely from the 7-cis isomers.[7a] β-Ionone is an exceptional case where retro-γ ionone (Va) is only a minor product, the major one being the α-pyran derived from *cis*-ionone.[8]



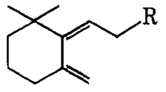
IIa, R = $COCH_3$
b, R = $CHCH_3OH$
c, R = CN
d, R = CO_2H



IIIa, R = CO_2Et
b, R = CO_2H
c, R = CN
d, R = CH_2OH
e, R = H
f, R = CHO
g, R = $COCH_3$



IVa, R = $COCH_3$
b, R = CN



Va, R = $COCH_3$
b, R = $CHCH_3OH$
c, R = CN

No reports on sensitized irradiation of these compounds were in the literature with the exception of several scattered reports on the higher members. Thus, retinal isomerizes efficiently by sensitized irradiation,[3b,c] and vitamin A acetate (Ic) dimerizes under similar conditions.[9]

We have investigated the photochemistry of these compounds with particular emphasis on the triplet-sensitized reaction. During the course of this study we found selective sensitization a synthetically useful technique to prepare the relatively unknown class of sterically hindered 7-cis isomers and other hindered olefins.[10,11] A paper oriented toward the synthetic utility is already in print.[12] The present paper describes aspects of the mechanism of the isomerization reaction under sensitized irradiation,[13] and its relation with reactions under direct irradiation.

Results

Sensitized Irradiation. When irradiated under conditions where only the triplet sensitizer absorbs, all compounds in the series undergo geometric isomerization with no detectable side reactions. Sensitized photodimerization, known to proceed efficiently in linear dienes[15] and trienes,[16] is not a significant side reaction. Therefore, the isomerization reaction frequently can be studied at high concentrations, e.g., sufficient for single sweep NMR analysis, when necessary.

Table I. Photostationary State (PsS) Compositions of β-Ionol by Sensitized Irradiation[a]

Sensitizer[b]	Sensitizer concn, M	% cis at PsS
Acetone	0.5	65.0
Propiophenone	0.5	65.4
	0.01	65.4
Acetophenone	0.1	71.8
p-Methylacetophenone	0.1	73.9
3,4-Dimethylacetophenone	0.1	79.4
4,4′-Dimethoxybenzophenone	0.1	84.1
4,4′-Dimethylbenzophenone	0.5	86.4
	0.1	86.5
	0.01	86.5
	0.1[c]	86.6[c]
	0.1[d]	86.4[d]
Benzophenone	0.1	91.0
Triphenylene	0.01	94.6
2-Acetonaphthone	0.1	100
	0.01	100
1-Naphthyl phenyl ketone	0.1	100

[a] Concentration of β-ionol, 0.1 M in benzene. PsS values determined by GLC analysis, ±1%. [b] For triplet energy of donors, see S. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1974. [c] With 0.001 M of azulene. [d] With 0.01 M of azulene.

With the exception of compounds with large substituents at C-8, all ionyl isomers are sufficiently volatile and stable for analysis by GLC. For the less volatile ones, NMR was used. Pyrex filters were sufficient to ensure exclusive light absorption by sensitizers in most cases, but the use of Corning 0-51 filter (360-nm cutoff) became necessary when unsaturated substituents were present. In general, with a given sensitizer identical photostationary states were obtained starting from both the 7-cis and 7-trans isomers.

For nearly all the β-ionyl derivatives a cutoff point of sensitizer energy can be found below which only the cis is present in the stationary state mixtures. For example, for compounds with saturated substituents at C-8 (such as alkyl and substituted alkyl groups) the cutoff point is approximately 64 kcal/mol. Therefore β-acetonaphthone is a satisfactory sensitizer for complete conversion of trans to cis. For compounds with unsaturated substituents the cutoff point is obviously lower. Therefore with poor to intermediate conjugators (such as ester, acid, nitrile) 9-fluorenone (E_T = 51 kcal/mol) is the highest energy sensitizer for one way isomerization while with good conjugators (such as phenyl, vinyl, and keto groups) benzanthrone (46 kcal/mol) becomes the key sensitizer. A partial list of compounds was reported earlier.[12,14] The list has since been expanded considerably, but only with a few exceptions involving compounds with bulky substituents the above general statements are still valid.

In one case, β-ionol (IIb), the photostationary state compositions were studied in more detail. The values were measured as a function of the nature of sensitizers at different concentrations and in some instances in the presence of azulene, a triplet quencher. The results are listed in Table I.

A similar study with several trienes in this series (β-ionylidene derivatives, III) was also done (Corning 3-70 or 0-51 filters). Because of analytical limitations, the study was not as extensive as in dienes and not as complete as in ionol. GLC is not an acceptable analytical technique because of facile 6e electrocyclization of the 7-cis isomers at temperatures above 80 °C.[12,17] (High-pressure liquid chromatography (HPLC) was not available to us then.) Instead, NMR (HA-100) was used to assay the product mixtures. The spectra are usually quite complex because of the presence of all four geometric isomers. Fortunately the methyls at C-9 (CH_3-19 as in the case

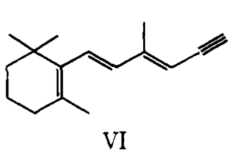
Table II. Photostationary State Composition of Trienes in the Vitamin A Series by Sensitized Irradiation[a]

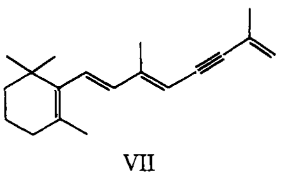
Compd[c]	Sensitizer	All-trans	9-Cis	7-Cis	7,9-Cis,cis[b]
Ethyl β-ionylideneacetate, IIIa	Benzophenone	21	26	30	23
	Benzophenone[d]	22	26	30	22
	1-Naphthyl phenyl ketone	20	26	30	24
	1-Naphthyl phenyl ketone[d]	20	24	30	26
	Benzil	11	16	37	36
	Fluorenone	9	15	39	37
	Benzanthrone	0	0	56	44
	7,12-Dimethylbenzanthracene	0	0	58	42
β-Ionylideneacetic acid, IIIb	Benzophenone	23	15	22	40
	Naphthyl phenyl ketone	22	16	22	40
	Benzil	13	12	36	38
	Fluorenone	16	12	39	33
	Benzanthrone	0	0	50	50
β-Ionylideneacetonitrile, IIIc	Benzanthrone	0	0	100[e]	
β-Ionylideneethanol, IIId	Fluorenone	0	0	100[e]	
β-Ionylidenemethane, IIIe	β-Acetonaphthone	45		55	
	Fluorenone	0		100	
β-Ionylideneacetaldehyde, IIIf	Fluorenone	66	34	0	0
	Benzanthrone	65	35	0	0
	Dimethylbenzanthracene	64	36	0	0
	Benzpyrene	67	33	0	0
β-Ionylideneacetone, IIIg	Fluorenone	58	42	0	0
	Benzanthrone	57	43	0	0
	Dimethylbenzanthracene	57	43	0	0

[a] >360 nm, $CDCl_3$ as solvent. [b] Analysis by NMR, based on peak heights of CH_3-19; error limit ±3%. [c] All results obtained from 7-cis as well as 7-trans isomers. [d] In the presence of 0.01 M azulene. [e] Sum of the two 7-cis isomers.

of vitamin A) for the four isomers usually have sufficiently different chemical shifts (see the Experimental Section) that their relative peak heights provide the desired information. The method clearly is not highly accurate as reflected by the larger estimated errors. The results (Table II) can be summarized as follows: for compounds with saturated (R = H, alkyl, and substituted alkyls) and weakly conjugating substituents (cyano and carboxyl) at C-10, benzanthrone is a satisfactory sensitizer for "one" way isomerization to the two 7-cis isomers. Compounds with good conjugative substituents (keto, phenyl, and vinyl) give no 7-cis isomers under any conditions of sensitized irradiation.

For tetraenes (IV) and pentaenes (I) in this series, again NMR was used to assay isomer compositions. With a large number of possible geometric isomers (8 for tetraenes and 16 for pentaenes) one might think the technique close to being totally uninformative. In an attempt to reduce the complexity of the problem we first prepared VI and VII as model compounds for the longer polyenes, each containing a manageable number of four geometric isomers. Also, later it became apparent that the information of interest is the relative ratio of the sum of 7-cis isomers vs. the sum of 7-trans (see below) which can be obtained from the relative intensities of the CH_3-18 (methyl at C-5) resonances in the product mixture; the signals of CH_3-18's of all 7-cis isomers resonate ~0.2 ppm above those of 7-trans.[18] Therefore a cursory examination of the relative intensity of these signals provided the desired information even for the complex vitamin A derivatives. The problem was further simplified when we found no 7-cis isomers of any tetraenes or pentaenes were present at any stage of irradiation regardless of the nature of sensitizers (light >400 nm, Corning 3-70 filters). Results for these higher polyenes are summarized in Table III.


VI


VII

In the case of retinal, we have recently verified the above conclusion from NMR analysis[19] by using the more accurate method of HPLC analysis.[20] For example, irradiation of 7-*cis*-retinal in hexane produced a mixture containing only the all-trans, 13-cis, and small amounts of 9-cis and possibly 9,13-cis,cis isomers.

Direct Irradiation. Direct irradiation of compounds in the vitamin A series is known to produce products (retro-γ derivatives, V) derived from sigmatropic 1,5-hydrogen migration from CH_3-18 to C-8 sometimes accompanied by geometric isomerization during the initial period of irradiation.[7] We have reinvestigated several systems. Here the initial geometric isomerization will be discussed. Subsequent stable product formation will be examined in a separate paper.[21]

Similar to an earlier report, irradiation (254 nm) of a hexane solution of *trans*-β-ionol did not give detectable amounts of *cis*-ionol at any stage of irradiation; nor, did we find *trans*-ionol from *cis*-ionol. The only product in both cases was *retro*-γ-ionol (Vb). On the other hand, irradiation (254 nm) of β-cyclocitrylideneacetonitrile (IIc), cis or trans, in a quartz vessel resulted in geometric isomerization accompanied by accumulation of the retro-γ product (Vc). When a Pyrex filter was introduced (0-54, >300 nm), irradiation of the trans isomer of IIc in $CDCl_3$, CD_3OD, CD_3CN, C_6D_6, or *n*-butyl bromide gave identical mixtures of *cis*-IIc (35%) and Vc (65%). At these wavelengths only the trans isomer absorbs. Similarly, the reported geometric isomerization and sigmatropic reaction of *trans*-β-ionone and β-cyclocitrilydeneacetic acid (IId) were also found to take place when the cis isomers of ionone (in equilibrium with its α-pyran) and the acid were irradiated.

For β-ionylidene derivatives we confirmed the observations of formation of retro-γ products being accompanied by geometric isomerization in the case of ethyl β-ionylideneacetate and not in β-ionylideneethanol.[7] However, we also found at least in one case other photochemical reactions previously not observed in such systems. For example, with the nitrile IIIc 6e electrocyclization[22] as well as geometric isomerization ac-

Table III. Photostationary State Compositions of Tetraenes and Pentaenes in the Vitamin A Series by Sensitized Irradiation[a]

Compd[c]	Sensitizer (E_T)	All-trans	9-Cis	11-Cis	9,11-Cis,cis	7-Cis[b]
C_{16} hydrocarbon, VI	Fluorenone	69	31			0
	Fluorenone	71	29			0
	Benzanthrone	68	32			0
	Benzanthrone	70	30			0
	9,10-Dibromoanthracene	72	28			0
C_{18} tetraene ketone, IVa	Benzanthrone	70	10	20	0	0
C_{17} tetraene nitrile, IVb[d]	Benzanthrone	47	23	18.	12	0
	Dimethylbenzanthracene	46	22	19	15	0
	Benz(α)pyrene	44	22	20	14	0
	9,10-Dibromoanthracene	47	22	19	12	0
	9-Phenylanthracene	44	23	20	13	0
C_{19} hydrocarbon, VII	Benzanthrone	73	27			0
		74	28			0
	Benzpyrene	74	26			0
		77	23			0
	9,10-Dibromoanthracene	75	25			0
Retinyl acetate, Ic	Benzanthrone[f]		100[e]			0
	9,10-Dibromoanthracene[f]		100[e]			0
Retinonitrile, Id	Benzanthrone		100[e]			0
	Benzpyrene	100[e]			0	
Retinal, Ib	Benzanthrone[g]		100[e]			0
	Benzpyrene[g]		100[e]			0

[a] >400 nm, $CDCl_3$ solvent. [b] Analysis by NMR. Error limit ±5%. [c] Unless specified, all measurements were made starting from both 7-trans and 7-cis isomers. [d] From 7-trans isomers only. [e] Sum of all 7-trans isomers. [f] Accompanied by dimerization: C. Giannotti, *Can. J. Chem.*, **46**, 3025 (1968). [g] About 50% light absorption by sensitizer.

company formation of the retro-γ products. On the other hand the aldehyde IIIf and ketone IIIg only undergo geometric isomerization upon direct irradiation without giving any retro-γ products. Thus, irradiation (>290 nm) of 7-cis or 7-trans isomers of IIIf gave a photostationary state mixture consisting of 35% 7-cis and 65% 7-trans isomers (by NMR), while IIIg gave 40% 7-cis and 60% 7-trans. This is particularly interesting when one considers that sensitized irradiation of these compounds did not give any amounts of the 7-cis isomers.

Discussion

The use of sensitizer energy to control the photostationary state composition of a geometric isomerization reaction is an established technique. In particular the papers by Hammond, Saltiel, and others[23] and Herkstroeter and Hammond[24] showed the importance of the excitation ratio in determining the product composition. The systems described in this paper differ at least in two ways from those reported earlier: in some cases low-energy sensitizers can selectively produce mixtures containing a single isomer (hence the name selective one-way sensitized isomerization) while in others the same set of geometric isomers (the 7-cis isomers) is missing under all conditions of sensitized irradiation. Previously only enrichment of one isomer was observed.[25] In the following paragraphs we shall attempt to rationalize the different photochemical behavior of the systems reported here and also to discuss other points related to properties of excited polyenes.

Selective One-Way Sensitized Isomerization. An obvious structural difference between our systems and other earlier reported ones is that the 7-cis isomers of vitamin A analogues are sterically severely crowded making the chromophore impossible to exist in a planar conformation for maximum resonance stabilization. In fact at one time they were thought to be too unstable for preparation.[26] Now with the preparation of many such isomers,[12,27] this notion can be completely dismissed.

That these isomers exist in a highly skewed conformation has been shown in a separate study of long range coupling constants between H-7 and the allylic hydrogens at C-4 and CH_3-18 of several dienes in the series, the ring-chain dihedral angle about the 6-7 single bond being around or above 40°.[17,28] By the same method it was shown that the corresponding angles for the less hindered trans isomers are around 25° or less.[16,28] Since the triplet excitation energy is a function of the cosine of the dihedral angle, the small deviation from planarity of the trans isomer is not expected to increase significantly its excitation energy from that of a common planar analogue, while a much larger increase is expected for the cis. This difference in excitation energies between pairs of isomers certainly is expected to have a profound effect on the overall photochemistry.

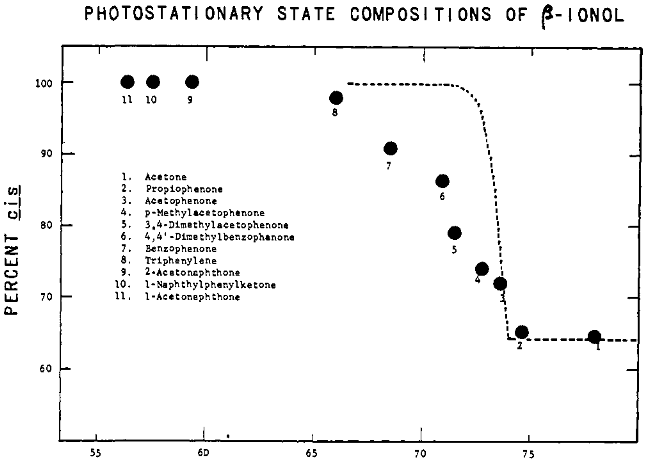


Figure 1. Photostationary state compositions of β-ionol as a function of sensitizer excitation energy. The dashed line is that of calculated compositions based on excitation involving ground state activation only (see text).

In the case of β-ionol (IIb) the triplet excitation energy of the cis isomer can be obtained from a plot of photostationary state compositions vs. donor excitation energies (Figure 1). The horizontal portion of the curve in the high-energy region reflects the lack of selectivity of energy transfer to either isomer;

hence only the decay ratio determines the stationary state composition. Similar to the stilbenes and other olefin systems, decay to cis is slightly favored ($k_{\text{d-cis}}/k_{\text{d-trans}} = 1.86$). The point of inflexion near 74 kcal/mol must then be the triplet excitation energy of *cis*-ionol, below which transfer to cis becomes inefficient and affects the product mixtures accordingly. This value is significantly higher than the corresponding values for conjugated dienes which generally fall within the range of 55-60 kcal/mol.[30,31] The excitation energy of *trans*-ionol, on the other hand, cannot be deduced from the plot. The second point of inflexion (around 64 kcal/mol) merely reflects the rate of transfer to cis being now insignificantly small as compared to that to trans ($^1/_{54}$, assuming the limit of detection of *trans*-ionol is 1% and taking into consideration the favored decay rate to cis). Unfortunately heavy-atom (ethyl iodide) perturbed S_0-T_1 absorption spectrum gave an enhanced but structureless tail. Thus it was not possible to locate the 0-0 line. But from the observation that the relative quantum yields of isomerization of *trans*-ionol to cis are not significantly different when sensitized by benzophenone or β-acetonaphthone (68.5 and 59.3 kcal/mol, respectively), we see no reasons to suspect its value being higher than those of common linear dienes. Therefore, the difference in excitation energies between the two isomers is of the order of 15 kcal/mol, an exceptionally large value for a pair of isomers but in view of the difference in their conformation not an unreasonable one. The system is therefore ideally set-up for one-way selective sensitized isomerization.

A closer examination of the slope of the line between 74 and 64 kcal/mol reveals a "nonclassical" behavior[24] of endothermic energy transfer to *cis*-ionol. In this region, rates of energy transfer to trans should remain constant and close to diffusion controlled (exothermic by more than 3 kcal/mol). The change of photostationary state composition must then be solely due to a change of transfer rates to the cis. If endothermic energy transfer rates were "classical", i.e., a simple activated process where $\Delta E^{\ddagger}$ in the Arrhenius equation is supplied entirely by thermal energy of the acceptor, one would expect a sharp decline of transfer rates and predict proportional rapid rise of cis (dashed line in Figure 1). The actual values clearly deviate significantly from the predicted. This trend of course has been observed in the stilbenes.[23,24] They all suggest that an activated process based on ground state activation alone is inadequate in discussing the endothermic energy transfer process.[32] Among other possibilities it may be viewed in the following way.[33]

The ground and excited (triplet) torsional potential curves around the 7,8 bond of ionol probably take the general shape of the lines sketched in Figure 2. The ground state cis is at least 5 kcal/mol higher than the trans[34] while the triplet cis, after adding the excitation energy difference, is almost 20 kcal/mol higher than the trans! That a minimum exists in the excited potential curve is suggested by the lack of azulene-quenching, sensitizer-concentration effects (Table I) and the ability of the triplet to decay to both cis and trans. Results from calculation also agree with the presence of a minimum (see below). But because of the difference in stability of the planar triplets the two parts of the curve around the minimum are expected to be highly unsymmetrical.

With this picture in mind, we suggest that endothermic energy transfer to cis involves *vertical excitation* of vibrationally excited ground state molecules. The dashed line in Figure 2 depicts such a possibility. Clearly, the excitation energy gap is lowered not only by the vibrational energy in the ground state but *also a simultaneous lowering of the excited potential curve* near planar cis by an amount of ΔE_c. This is analogous to hot-band transitions in absorption spectroscopy which are usually significantly red shifted for the same reasons. It is then clear that an analysis of endothermic energy transfer based on activation of the ground state molecules alone should not be able to account for the results. On the other hand, such an analysis may be applicable to rigid acceptors where vertical excitation of hot ground state molecules receives no benefit from lowering of the excited state energy. *trans*-Stilbene happens to fit in the latter category.

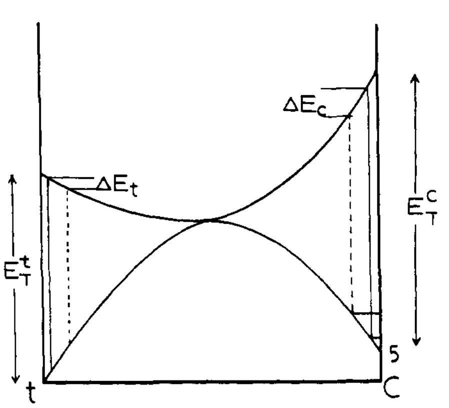


Figure 2. Idealized torsional potential curves of the ground and the triplet states of β-ionol. Excitations involving exothermic (solid lines) and endothermic (dashed lines) energy transfers are depicted (see text).

Examination of the trans side of the potential curves reveals that "hot band excitation" by energy transfer can also reach potential surfaces lower in energy than the planar. But because of the smaller slope of the curve from t* to the perpendicular triplet, the amount of energy lowered is much smaller (ΔE_t). In terms of Hammond and Herkstroeter, *trans*-ionol is more of a "classical acceptor" approaching but not quite *trans*-stilbene like. Unfortunately, Figure 1 does not provide any information on endothermic energy transfer to trans. It will certainly be of interest to determine directly rates of energy transfer to this isomeric pair (as in stilbenes)[24] as a test for the rationale presented above.

The data for the triene derivatives (Table III), though less complete due to analytical difficulties, essentially show photochemical behavior parallel to diene triplets (except in trienal, trienone, and higher polyenes which will be discussed in the next section). Based on photostationary state compositions upon variation of sensitizers we estimate that the triplet excitation energies of the 7-cis isomers are probably around 50 kcal/mol for ethyl β-ionylideneacetate (IIIa) and 54 kcal/mol for the unsubstituted hydrocarbon IIIe, higher than those of simpler trienes (~47 kcal/mol for 1,3,5-hexatriene[35] and 43 kcal/mol for a trienal).[36]

The Tetraenes and Pentaenes. The results in Table III clearly show that the higher polyenes photochemically behave differently from the lower members in that they do not produce any amounts of the 7-cis isomers regardless of the nature of the sensitizers. Trienes with good conjugating substituents at C-10 (IIIf and IIIg) behave in the same way as the tetraenes, hence they should be considered together in this group. From the following observations, we believe this preferential formation of the 7-trans isomers is indeed a general property of the triplets of these higher polyenes.

To rule out the possibility that the results might be caused by an unusual effect on the part of the sensitizer, the system of dehydrodemethyl-β-axerophtene, VII,[37] was examined in more detail. Possible involvement of the singlet state of the sensitizer in the observed photochemistry was ruled out by the following experiment; VII was irradiated with 9,10-dimethylbenz(α)anthracene or benz(α)pyrene as donor to examine the effect of VII on fluorescence intensity of the donors and the photostationary state compositions. Results are summarized in Table IV. Clearly, the pentaene (up to 5×10^{-3} M) has a negligible effect on the fluorescence intensity of the donors. Yet, with a mixture of the two 7-cis isomers of VII, either

Table IV. Fluorescence Intensity of Sensitizers in the Presence of Dehydrodemethylaxerophtene (VII)[a]

Sensitizer	[VII]	$[I_0/I]$
Dimethylbenz(α)anthracene	0	1
	1×10^{-4}	1.08
	5×10^{-4}	1.06
	1×10^{-3}	1.10
	5×10^{-3}	1.08
Benz(α)pyrene	0	1
	1×10^{-4}	1.01
	5×10^{-4}	1.03
	1×10^{-3}	1.06
	5×10^{-3}	1.09

[a] Measured on a Hitachi Perkin-Elmer MPF-II spectrometer. Excitation wavelength, 400 nm. Solvent, benzene. [b] Sensitizer concentration, 5×10^{-4} M.

sensitizer produced mixtures containing only the two 7-trans isomers with a slight preference for the 9-cis, and with *all-trans*-VII, 7-cis are not produced although isomerization around the 9,10 bond proceeded as usual giving an identical mixture as from 7-cis. The triplets of VII clearly are capable of isomerization in both directions around the 9,10 bond and only toward the trans around the 7,8 bond.

The Relaxed Triplets of Conjugated Polyenes. A plausible explanation for the different photochemical behavior of the higher polyenes from lower member dienes and trienes is found from consideration of the shape of the excited state torsional potential curves of these molecules. By extended HMO calculation, Hoffmann[38] concluded, "... In the first excited state, the hexatriene preferred a conformation twisted 90° around the central bond to a planar one ... octatetraene preferred retention of planarity in the first excited state. Presumably all higher polyenes will also remain planar." Therefore, only in dienes and trienes a common triplet intermediate exists (possible involvement of isomeric triplets is discussed in a later section), i.e., the minimum energy species is one with an orthogonal structure (same as in Figure 1). Deactivation from this common triplet gives either cis or trans in stationary state mixtures. On the other hand, tetraenes and higher polyenes do not have a single triplet intermediate. The lowest energy species are the planar structures from which deactivation will originate. With different reacting species, there are no reasons to suspect identical photochemical behavior of polyene triplets as compared to those of dienes and trienes.

That isomerization does take place readily at room temperature indicates that the barriers separating the planar triplets of polyenes are small so that the thermal energy is sufficient to allow crossing within the triplet lifetimes. The recent observations of identical transient absorption of retinal when starting with four different geometric isomers (all-trans, 11-cis,[39] 7-cis, and 7,9-cis,cis)[19] also suggest low barriers separating the planar triplets. In fact the 5 kcal/mol activation energy of trans to cis isomerization of retinal under direct irradiation as reported by Kropf and Hubbard[3a] may be a good indication of the approximate maximum height of the barriers.

With these low barriers in mind it is clear then that the planar triplets should rapidly equilibrate within the triplet lifetime of the polyenes. Their relative amounts should be controlled by the relative energy differences of the planar species. Unfortunately, these energy differences are not accurately known for any set of polyene isomers simply because of the absence of experimental data on S_0–T_1 transition energies of a set of isomers of polyenes. However, some calculated results are available in the literature, and also from simple energy considerations, one may make a rough estimation of the ordering of planar triplets, especially the hindered 7-cis and 11-cis relative to the unhindered ones.

For example, several attempts have been made to calculate the triplet torsional potential curves of retinal.[40] Although there are some disagreements as to the exact magnitudes of the barriers and energy differences between isomers, they generally agree that the hindered 11-cis is much higher in energy than the unhindered all-trans, 9-cis, and 13-cis, and that there are low barriers connecting the planar species. However, just as by the synthetic chemists in the past, the 7-cis isomers were neglected by the theoretical chemists. But it is reasonable to expect that the 7-cis triplets should behave in the same way as the hindered 11-cis in that it should be much higher in energy than the unhindered triplets. Incidentally, from simple energy consideration as we have done in the previous section with the dienes, a similar ordering of the planar triplets is concluded. Since the energy difference between the hindered and unhindered isomers is much greater than 3 kcal/mol, when equilibrated, the planar 7-cis (also 11-cis) is simply not expected to be present in any significant amounts. We therefore suggest that the photochemistry of the polyenes takes place completely during the process of equilibration of the planar triplets. Radiationless decay only takes the form of vertical deactivation from the planar triplets. The absence of planar 7-cis triplets then accounts for the absence of such isomers during the course of photoisomerization of all the polyenes.

In agreement with this model, we have recently demonstrated with retinal isomers that one photon can effect the isomerization of more than one double bond (e.g., 7,9-cis,cis directly to 13-cis).[19] For additional support one would have to await accurate quantum yield measurements of the sensitized isomerization reactions in order to demonstrate the presence of, effectively, a common intermediate. Low-temperature photochemical and flash photolytic studies clearly should be explored in order to provide information about the barriers in the excited state.

The Triene Triplets. The above results show that the reversal of the role of planar and twisted triplets as the relaxed triplets occurs somewhere between trienes and tetraenes. There is some experimental evidence which further pin-points this reversal taking place closer to the triene series. First, the photostationary data in Tables II and III clearly show that triene chemistry is very sensitive to the nature of substituents at C-10. Better conjugative groups stabilize the planar structures making the triene behave like a tetraene. Compounds with less effective conjugative substituents apparently have higher planar triplets, consequently with chemistry dominated by those from the twisted species. Also results from quenching experiments appear to indicate that the planar trans triplet must be very close in energy with the twisted in trienes. Table II shows that the triplets from ethyl β-ionylideneacetate (IIIa) are not quenchable in that its photostationary states are not affected by the presence of azulene. On the other hand, the triplets from linear trienes such as alloocimene[6b,c] and 1,2-bis(1,1′-cyclopentenyl)ethylene[41] undergo rapid secondary energy transfer to lower energy acceptors. A dramatic increase of central trans isomers in the photostationary states upon introduction of small amounts of azulene has been observed. In the latter cases, the planar trans triplets must be very close in energy to the twisted triplets. In the absence of a quencher, chemistry from the twisted intermediate predominates; in the presence of azulene, energy transfer from the planar triplets predominates. For ethyl β-ionylideneacetate, the steric interaction induced ring-chain nonplanarity about the 6,7 single bond[29] is apparently sufficient to raise the energy of the planar trans triplet to the extent that it is no longer present in sufficient amounts for participation in secondary energy transfer processes.[42]

Geometric Isomerization in Direct Irradiation. The absence of retro-γ products (V) and cyclohexadienes in sensitized irradiation indicates that the sigmatropic and electrocyclization processes in direct irradiation must originate from the S_1 states. This is not unexpected for such normally concerted processes. However, since geometric isomerization appears to be the exclusive reaction from the triplet state, it is tempting to attribute the same reaction observed under direct irradiation also to a T_1 process, i.e., after intersystem crossing. The following observations, however, negate this possibility.

First for β-ionylideneacetaldehyde (IIIf) and β-ionylideneacetone (IIIg) under direct irradiation geometric isomerization is the only important photoreaction leading to mixtures containing sizable amounts of the 7-cis isomers while triplet sensitized irradiation failed to give any amounts of such isomers (Table II). Different reactive states (probably correspondingly S_1 and T_1) under these two conditions must be involved. In other simpler dienones[43] and 3,4-dehydro-β-ionone[44] differences in photochemical properties of S_1 and T_1 states have been documented. Second, that the ratio of products of *cis*-β-cyclocitrilydeneacetonitrile (IIc) and the retro-γ analogue (Vc) remained constant upon direct irradiation of the trans isomer in a variety of solvents including *n*-BuBr is inconsistent with the view that the two products originate from two different states. The brominated solvent known to enhance intersystem crossing efficiency of solutes[45] certainly would have enhanced the geometric isomerization process should it originate from the triplet state. Hence, we conclude only the excited singlet states are responsible for all the observed photochemistry from direct irradiation.

Isomeric Diene Triplets. In simple diene systems, the presence of nonequilibrating isomeric diene triplets (around formal single bonds) is known to affect the photochemical properties of the systems. For example, their presence is reflected in different product formation in cycloaddition reactions[15,31,46] and in different decay properties in isomerization reactions.[47] For β-ionone derivatives, the preferred ground state conformation appears to be the twisted cisoid from which the twisted transoid is not too much higher in energy.[29] It is possible that isomeric diene triplets are also present in these systems, but their photochemical properties must not be sufficiently different to show in the stationary state studies. Possibly, accurate quantum yield measurements might reveal their presence.

Experimental Section

Material. The syntheses of all the lower member 7-cis isomers used in this study were described in an earlier paper.[12] Procedures to prepare the corresponding 7-trans isomers were either discussed or references were cited in the same paper. In separate papers the synthesis of 7-cis isomers of retinal[26,48] and dehydrodemethyl-β-axerophtene, VII,[37b] were described.

Irradiation Procedures. All samples were irradiated in a "Merry-go-round" apparatus[49] with a 550 W Hanovia medium pressure Hg lamp. Appropriate Corning filter plates, or combination of filter plates, were used to isolate light of desired wavelength. All samples were thoroughly degassed before irradiation. For higher polyenes, NMR tubes were used instead of the usual 13-mm test tubes.

Analytical Procedures. The β-ionol mixtures were analyzed by GLC on a Varian 2800 unit equipped with a flame-ionization detector. A 6 ft 5% SE-30 column was used. The cis has a shorter retention time. For trienes and higher polyenes, NMR (HA-100) was used to assay product mixtures. Intensities of the methyl signals were used to judge the relative amounts of the isomers. A detailed listing of the signals of 7-cis[12] as well as the 7-trans[50] isomers is in the literature. As an example those of ethyl β-ionylideneacetate are shown below. Characteristically the CH_3-19 is deshielded by the cis carbonyl group (trans around the 9,10 bond) and CH_3-18 by the polyene side chain when the 7,8 bond is cis.[12]

	Chemical shift	
Isomer	CH_3-18	CH_3-19
All-trans	1.64	2.29
7-Cis	1.44	2.10
9-Cis	1.72	1.98
7,9-cis,cis	1.44	1.79

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Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. III.[1] Arylation of Aromatic Hydrocarbon Cation Radicals

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Abstract: Aromatic hydrocarbon cation radicals undergo electrophilic attack on aromatic compounds such as anisole, toluene, benzene, and chlorobenzene to give the corresponding arylated compounds. The reactions were studied in media containing trifluoroacetic acid, and in some cases trifluoroacetoxylation of the cation radicals were significant competing processes. The radical ions studied most thoroughly were those from 9-phenylanthracene (PA) and anthracene (A). The reaction of PA with anisole (AN) obeys the rate law $-d[PA\cdot^+]/dt = k_{app}[PA\cdot^+]^2[AN]/(2.36 \times 10^{-3} + [PA])$. The data are consistent with a mechanism involving initial complex formation between the cation radical and AN followed by electron transfer to a second $PA\cdot^+$. The value of the constant in the denominator of the rate law is of such magnitude that the linear anisole dependence was used to conclusively rule out an alternate reaction mechanism involving the disproportionation of $PA\cdot^+$. As expected, the corresponding dications of the aromatic hydrocarbons were found to react at much greater rates with the aromatic compounds. The latter reactions are most likely simple bimolecular processes. Convincing support of the proposed reaction mechanism was obtained from experiments in which equal concentrations of $PA\cdot^+$ and dibenzodioxin (DBO) cation radical were allowed to react with AN and a large rate enhancement was observed as predicted by the mechanism considering the higher oxidation potential of DBO.

Electrophilic reactions of aromatic cation radicals have been studied in numerous cases.[1-9] The most common reactions result in the formation of carbon-heteroatom bonds although one case, the cyclization of the tetraphenylethylene cation radical which proceeds via disproportionation to the dication, involves carbon-carbon bond formation and has been studied in detail.[1a] Cation radicals have been implicated in other electrophilic reactions of anodically generated intermediates, for example, the trimerization of anthracene[10] and in the anodic arylation of naphthalene with alkyl benzenes.[11,12] The latter studies involved only product determinations and little is known regarding the mechanisms of the reactions.

We have recently observed that several cation radicals of aromatic compounds react with simple aromatic compounds such as benzene, toluene, chlorobenzene, and anisole. Some of the reactions take place at rates convenient for kinetic studies. Previous papers in this series[1] describe the kinetics and mechanisms of various cation radical reactions and suggest a general mechanism for such reactions which involves an initial complexation of the radical ion with the other reactant (eq 1). Depending upon the reactivity of the initial complex, a first-order reaction leading to products (eq 2) or a bimolecular electron transfer reaction with a second radical ion leading to a dication complex (eq 3) which dissociates leading to products (eq 4) may occur. In some cases it has been possible to control the proportion of reaction following the first- and the second-order pathways by suitable adjustment of the cation radical concentration. In this paper we further demonstrate the generality of the complexation mechanism and report the new reactions: arylation of aromatic hydrocarbon cation radicals.

$$\pi\cdot^+ + \mathrm{NUC} \rightleftharpoons (\pi/\mathrm{NUC})\cdot^+ \tag{1}$$

$$(\pi/\mathrm{NUC})\cdot^+ \rightarrow \text{products} \tag{2}$$

$$(\pi/\mathrm{NUC})\cdot^+ + \pi\cdot^+ \rightleftharpoons (\pi/\mathrm{NUC})^{2+} + \pi \tag{3}$$

$$(\pi/\mathrm{NUC})^{2+} \rightarrow \text{products} \tag{4}$$

Results

Structures and identifying symbols of the aromatic compounds are summarized in Scheme I.

Reactions of Anthracene Cation Radical with Aromatic Compounds. The cation radical of anthracene (A) is readily observable by voltametric and spectrophotometric techniques during anodic oxidation of anthracene in dichloromethane containing trifluoroacetic acid anhydride (TFAn) and trifluoroacetic acid (TFA).[13] Solutions of $A\cdot^+$ in the above medium prepared by anodic oxidation of A were found to react with anisole (AN), benzene (BE), toluene (TO), and chlorobenzene (CB). Since the lifetime of $A\cdot^+$ was limited by reaction with TFA, it was inconvenient to prepare reaction products by first oxidizing A and then admitting the aromatic compounds. The method of choice was to oxidize A in the presence of the aromatic compound. The products of the reactions, 9,10-diarylanthracenes, were readily identified by their voltametric behavior and from the visible absorption spectra of the corresponding cation radicals.

Exhaustive constant current coulometry[14] on 1 mM solutions of A in CH_2Cl_2-TFA-TFAn (90:5:5) containing the aromatic compound (100 mM) resulted in the consumption of 5.0 faradays/mol and the formation of the cation radical of