29179-14-4; **23**, 29179-15-5; **24**, 29246-55-7; **25**, 29179-16-6; **26**, 29179-17-7; **27**, 29179-18-8; **28**, 29179-19-9; **29**, 29179-20-2; **30**, 29179-21-3; **31**, 29179-22-4; **32**, 29179-23-5; **33**, 29179-24-6; **34**, 29179-25-7; **35**, 29179-26-8; **36**, 79-77-6; **37**, 29179-27-9; **38**, 29179-28-0; **39**, 29179-29-1; **40**, 29179-30-4; **41**, 16326-91-3; **42**, 29179-32-6; **43**, 29179-33-7; **44**, 29179-34-8; **45**, 29179-35-9.

Acknowledgments. We thank Professor Kenneth L. Williamson of Mt. Holyoke College for running a 100-MHz nmr spectrum and decoupling experiments on compound **6** and Mr. William Nason for running several infrared and ultraviolet spectra. The nmr spectrometer used in this work was purchased with funds from a research instruments grant of the National Science Foundation.

Photoisomerization Products of Conjugated Dienones

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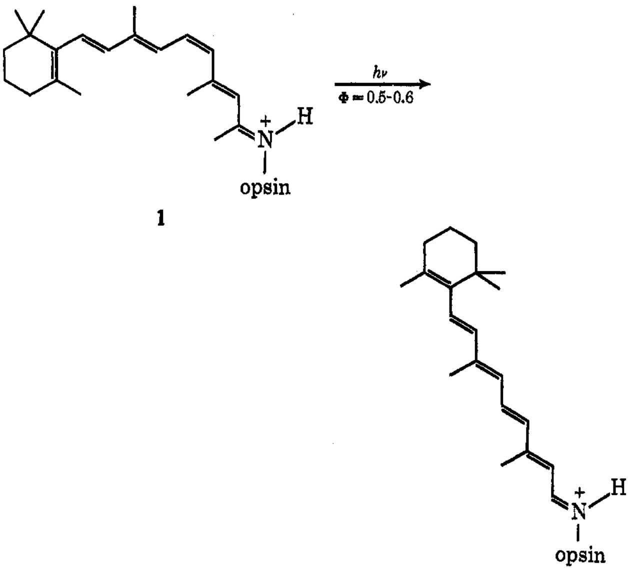
Received September 28, 1970

Irradiation of dilute (10^{-2}–10^{-4} *M*) diethyl ether solutions of conjugated dienones rapidly produces photostationary-state mixtures of the all-trans, cis,trans, and trans,cis isomers. Exceptions are 4-methyl-3,5-heptadienone (**21**), which undergoes isomerization only about its α,β double bond, and the 1-aryldienones **44**, **46**, and **47**, which seem to undergo only γ,δ photoisomerization. α-Pyran formation occurred on irradiation of 4,6-dimethyl-3,5-heptadienone (**24**) and 5-methyl-3,5-heptadienone (**27**) as the result of ring closure of the respective α,β-*cis*-dienones in what are possibly dark reactions. Failure to detect any cis,cis photoisomers has been tentatively attributed to their rapid conversion to α,β-cis-γ,δ-trans isomers *via* the valence isomeric α-pyrans in the dark.

The initial chemical event in vision is a remarkably specific cis to trans photoisomerization of the 11 double bond of the visual pigment rhodopsin (**1**).[2] This isomerization, which triggers but does not constitute in itself the visual process, occurs in an 11-*cis*-retinal unit which is bound to the protein opsin *via* a protonated Schiff base linkage and fits snugly into the protein surface. The specificity of 11 isomerization could be an electronic property of the protonated retinylidene imine chromophore or might arise because alternative isomerizations are geometrically prohibited by the fit with the protein surface. Photoisomerization of *all-trans*-retinal itself (**2**) has been variously reported to give a mixture of isomers in which all-trans predominates[3] and to give the 13-cis isomer specifically.[4,4a] In a program designed to investigate the properties of excited states which are electronically similar to those of rhodopsin and retinal, we have examined the relatively simple dienones which have two isomerizable double bonds and a carbonyl group in conjugation.



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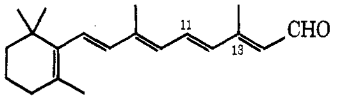

2

In contrast to the extensive studies of cross-conjugated dienones,[5] investigations of the photochemistry of conjugated dienones have been relatively rare. Early reports showed that conjugated dienones bearing aromatic groups gave photodimers both in solution and solid phases.[6,7] Irradiation of some steroidal dienones resulted in formation of cyclobutane-type dimers.[8] *trans*-β-Ionone (**3**) gave pyran **4**[9–11] and smaller amounts of the unconjugated dienone **5**.[12] In an

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[1] (a) NSF Cooperative Fellow, 1965–1969; (b) Alfred P. Sloan Foundation Fellow, 1969–1971.

[2] For a summary of knowledge of the molecular basis of vision, see E. W. Abrahamson and S. E. Ostroy, *Progr. Biophys. Mol. Biol.*, **17**, 179 (1967); C. B. D. Bridges, *Compr. Biochem.*, **27**, 31 (1967); G. Wald, *Science* **162**, 230 (1968).

[3] R. Hubbard, R. I. Gregerman, and G. Wald, *J. Gen. Physiol.*, **36**, 415 (1953); G. Wald, P. K. Brown, and R. Hubbard, *Proc. Nat. Acad. Sci. U. S.*, **41**, 438 (1953); P. K. Brown and G. Wald, *J. Biol. Chem.*, **222**, 865 (1956).

[4] M. Mousseron-Canet, *Advan. Photochem.*, **4**, 219 (1966).

[4a] NOTE ADDED IN PROOF.—For a recent quantitative study involving four photoisomers of retinal, see A. Kropf and R. Hubbard, *Photochem. Photobiol.*, **12**, 249 (1970).

[5] *Cf.* K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

[6] (a) H. Stobbe and C. Rücker, *Chem. Ber.*, **44**, 869 (1911); (b) H. Stobbe, A. Hensel, and W. Simon, *J. Prakt. Chem.*, **110**, 129 (1925).

[7] A more recent study has confirmed dimer formation but has resulted in revision of some noncyclobutane structures proposed earlier (see ref 46): D. J. Zepka, Ph.D. Thesis, University of Massachusetts, 1969.

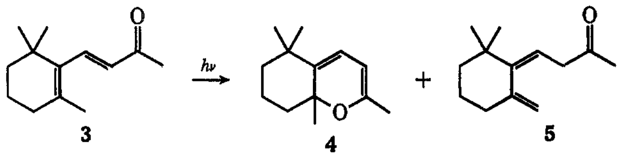
[8] H. C. Throndsen, G. Cianelli, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2342 (1962); M. B. Rubin, D. Glover, and R. G. Parker, *J. Org. Chem.*, **29**, 68 (1964); *Tetrahedron Lett.*, 1075 (1964); and A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969).

[9] G. Büchi and N. C. Yang, *Chem. Ind. (London)*, 355 (1955); *J. Amer. Chem. Soc.*, **79**, 2318 (1957).

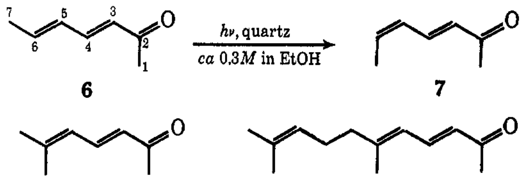
[10] Pyran **4** is in thermal equilibrium with a small amount of the valence isomeric dienone.[9]

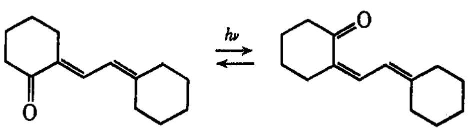
[11] E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *ibid.*, **88**, 619 (1966).

[12] P. de Mayo, J. B. Stothers, and R. W. Yip, *Can. J. Chem.*, **39**, 2135 (1961).



attempt to develop a general pyran synthesis, Büchi and Yang irradiated several other aliphatic dienones (**6**–**9**).[9] Compound **6** gave a photoisomer to which they assigned structure **7** plus polymer, while **8** and **9** were reported to give only polymer. One example of a clean geometrical photoisomerization, that of **10**, has been reported.[13]





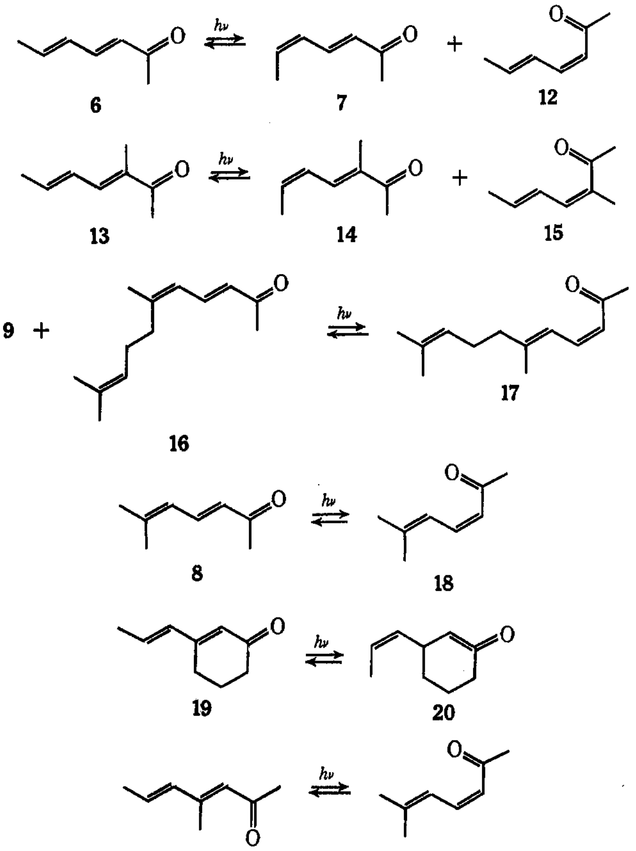
Results

We chose to study the conjugated dienones as 10^{-2} to 10^{-4} M solutions in diethyl ether. The volatile diethyl ether did not interfere with glpc analysis and showed no propensity to react with dienones under irradiation. In these solutions geometrical isomerization is much more efficient than bimolecular reactions such as dimer and polymer formation. Typically irradiation led rapidly to photostationary-state mixtures of all the possible geometrical isomers except cis,cis. Under our conditions (*e.g.*, relatively short irradiation times) no other monomeric photoproducts such as unconjugated dienones or photoreduction products could be detected.

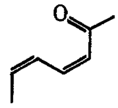
A thorough study of conjugated dienones was undertaken using infrared, nmr, and uv spectroscopy; and correlations between spectra and molecular structure are reported in the preceding paper.[14] Structures of new compounds are based on these data except where noted.[15] Most analytical and preparative separations were accomplished using glpc, and here also useful general correlations between structure and physical properties emerged. For a given aliphatic dienone, retention times increased in the order cis,trans[16] $<$ trans,cis $<$ all-trans, the last two isomers being closely spaced. For δ-phenyldienones the order of elution of cis,trans and trans,cis isomers was reversed.

CHART I

PHOTOISOMERIZATION OF ALIPHATIC DIENONES IN Et_2O



Aliphatic Dienones.—Photoisomerizations of aliphatic dienones are shown in Chart I. Irradiation of **6**, which is typical, gave a photostationary-state mixture (see Table I) of **6**, **7**, and **12**. The glpc purified isomers exhibited spectral properties uniquely consistent with these structures.[18] No evidence was found for the presence of the cis,cis isomer (**23**) in the photolysate.



23

Extended irradiation of a 10^{-2} M solution of **6** in diethyl ether at 254 nm to give a photostationary-state mixture caused loss of only 12% of the total dienone to a nonvolatile fraction. Photoisomerization of dienones **8** and **19** proceeded in a similar fashion, the products being identified spectroscopically.[14] 3-Methyl-3,5-heptadienone (**13**) rapidly gave two photoisomers whose glpc elution pattern paralleled that of the 3,5-heptadienone isomers **7** and **12**. They were assigned the (*E*,*Z*) and (*Z*,*E*) structures **14** and **15**, respectively, on this basis alone. Only one photoisomer could be detected from irradiation of **21** under glpc conditions which resolve **6** and **7**. The infrared, uv, and nmr spectra of this material were identical with those of the authentic (*Z*,*E*) isomer (**22**) prepared by sodium

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[13] I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 837 (1958).

[14] A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1977 (1971).

[15] Structures of starting trans,trans isomers are known from previous work in many cases. Nevertheless, we have in every case made a thorough spectroscopic study to prove their stereochemistry.[14]

[16] The configuration of the double bond nearest the carbonyl group is specified first. When the terms cis and trans are ambiguous the isomers will be labeled (*E*,*E*) and (*E*,*Z*), etc.[17]

[17] J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

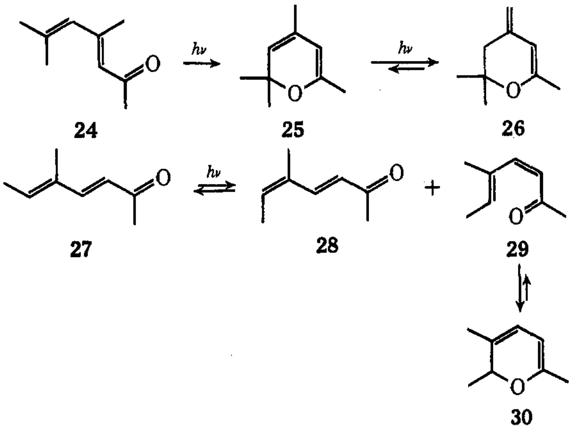
[18] Büchi and Yang[9] reported isolation of **7** by irradiation of **6** and subsequent distillation of the photolysate. We find, however, that **6** and **7** are so similar in volatility that a 30-ft glpc column is necessary for their separation. The uv absorption reported by Büchi and Yang for their "**7**" is virtually identical with that of our isomer **12**,[14] and, owing to its high volatility, **12** could have been separated from a crude photolysate by distillation. Thus Büchi and Yang's photoproduct is the α,β-cis isomer **12**.

borohydride reduction of 2,4,6-trimethylpyrilium perchlorate.[19] Owing to separation difficulties, a mixture of the (*E,E*) and (*E,Z*) isomers of pseudoionone **9** and **16**, respectively, was irradiated. The structure of the third isomer which appeared at a shorter glpc retention time was assigned tentatively on the basis of the nmr spectrum of partially purified photolysate (see Experimental Section).

Two aliphatic dienones gave α-pyrans upon irradiation (Chart II). Irradiation of (*E*)-4,6-dimethyl-3,5-heptadienone (**24**) gave a fraction with a much shorter glpc retention time. Under proper conditions this peak could be partially resolved showing that at least two photoproducts were present; however, separation under preparative conditions was not possible. These photoproducts were shown to be **25** and **26** by comparison of an nmr spectrum of a mixture with published values for **25** and **26**.[20] Further, an authentic mixture produced by treatment of 2,4-6-trimethylpyrone with methylmagnesium chloride[21] exhibited nmr and glpc properties which were identical save for a minor variation attributable to a difference in isomer ratio. Disappearance of **24** was first order to at least 87% reaction,[22] and at long irradiation times **24** is completely consumed. Therefore conversion of **24** to **25** is not reversible under our conditions. The longer the irradiation time is the higher the ratio of **26** to **25**; so **26** probably arises from **25** in a second photoreaction. Irradiation of **27** resulted in rapid production of two components with shorter glpc retention times, and continued irradiation gave a photostationary state. The first eluted component was shown to be an equilibrium mixture of 87% α-pyran **30** and 13% its dienone valence isomer **29**.[14] The second eluted component was assigned the (*E,Z*) structure **28**.[14]

CHART II

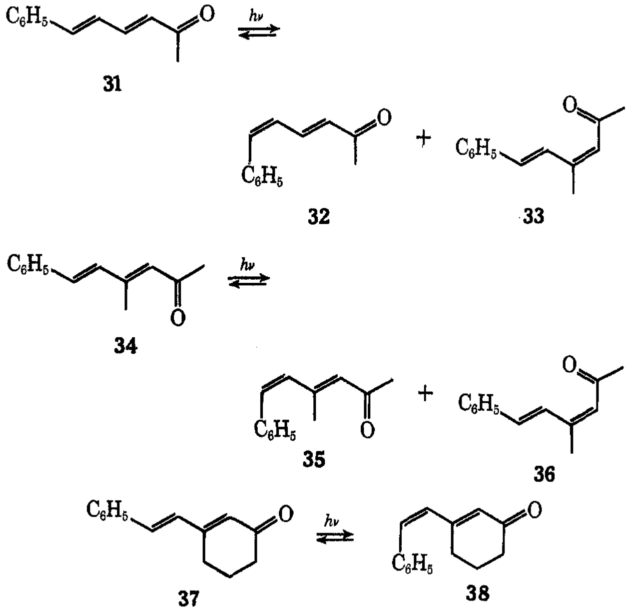
PYRAN FORMATION

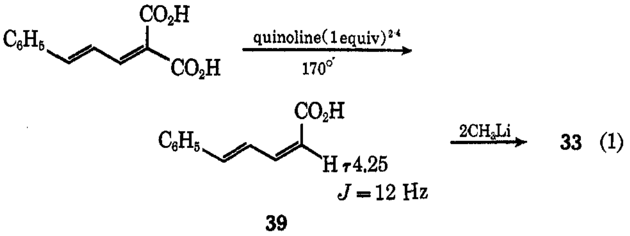


δ-Phenyldienones.—Black light[23] irradiation of δ-phenyldienones causes isomerizations similar to those observed for most aliphatic dienones (Chart III). Three isomers of 6-phenyl-3,5-hexadienone (**31**, **32**, and **33**) are formed. The cis,trans isomer (**33**) was identical in all respects with material prepared as shown in eq 1.

CHART III

PHOTOISOMERIZATION OF δ-PHENYLDIENONES IN Et_2O





(*E,E*)-4-Methyl-6-phenyl-3,5-hexadienone (**34**) gave **35** and **36**. The latter gave mixtures of **34** and **36** on glpc collection because of the high temperature required for separation. Thus, its structure was proven by independent synthesis as shown in Scheme I. A separation of the potassium salts was achieved in the hydrolysis stage. The α,β-cis (*Z*) configuration of acid **42** was revealed by the long-range deshielding of H_γ (τ 1.5, doublet, J = 16 Hz) by the carboxyl carbonyl.[14,25] The glpc retention time of synthetic **36** was identical with that of the second eluted photoisomer, and irradiation of **36** in ethyl ether gave the same photostationary-state mixture produced from **34**. Spectral properties of **36** are entirely consistent with its assigned structure.[25a]

1-Phenyldienones.—Irradiation of crotonylideneacetophenone (**44**) and two related dienones resulted in geometric isomerization that was apparently specific for the γ,δ double bond. Our work in this series was not extended to isolation and characterization of the photoisomers because of difficulty in achieving glpc

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[19] A. T. Balaban, G. Makai, and C. D. Nenitzescu, *Tetrahedron*, **18**, 257 (1962).

[20] A. Hinnen and J. Dreux, *C. R. Acad. Sci.*, **255**, 1747 (1962).

[21] R. Gompper and O. Christmann, *Chem. Ber.*, **94**, 1784 (1961). These authors assigned structure **25** to the product but Hinnen and Dreux[20] showed that it was a mixture of **25** and **26**.

[22] This experiment was performed under conditions in which there was a large excess of light and most photons were not absorbed by dienone.

[23] A broad spectrum of wavelengths between 300 and 400 nm with a maximum intensity at 366 nm.

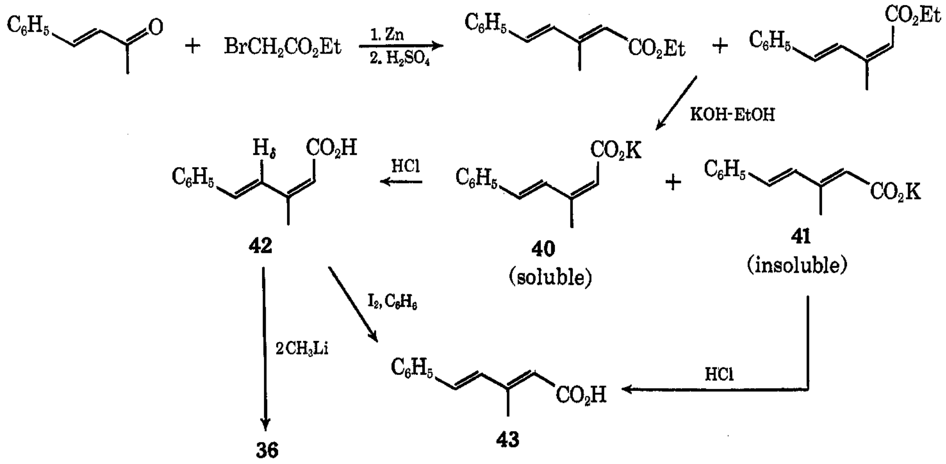
[24] C. Liebermann, *Chem. Ber.*, **28**, 1438 (1895).

[25] See G. Englert, *Z. Anal. Chem.*, **181**, 447 (1961), for a similar effect in dienoic esters.

[25a] NOTE ADDED IN PROOF.—We have recently detected a second photoproduct as a shoulder on the leading edge of the glpc peak of the all-trans isomer. Thus failure to observe α,β isomerization in phenone derivatives may be only the result of inadequate analytical methods: R. A. Gaudiana, unpublished work.

SCHEME I

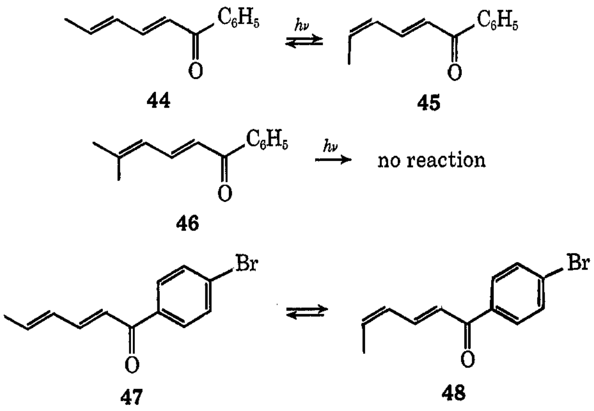
PREPARATION OF (*Z*,*E*)-4-METHYL-6-PHENYL-3,5-HEXADIENONE (**36**)



separations. The photoreactions are shown in Chart IV. Irradiation of **44** gave a photoisomer of shorter glpc retention time. The percentage of this isomer in the photostationary-state mixture was estimated from the partially resolved glpc peaks as 30 to 40%. The uv spectrum of the photostationary-state mixture shows a 3-nm bathochromic shift from λ_{max} of **44** with 95% of the original absorption intensity. Assuming that λ_{max} for **44** and its photoisomer are coincident and that 40% photoisomer is present, we estimate the absorption intensity of the photoisomer as 88% of that of **44**.[26] This estimate and the near-identity of the glpc retention times for **44** and the photoisomer are in accord with a γ,δ-cis structure (**45**) for the photoisomer. Irradiation of **46** gave no photoisomers as judged by glpc analysis. This is in accord with the idea that **44** undergoes only γ,δ isomerization, since in the case of **46** γ,δ isomerization is degenerate. 1-(*p*-Bromophenyl)-2,4-hexadienone (**47**) gave an isomer which is tentatively assigned as **48** (see Experimental Section).

CHART IV

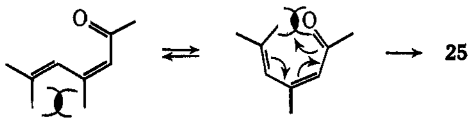
PHOTOISOMERIZATION OF 1-PHENYLDIENONES IN Et_2O



Discussion

These results show that geometric isomerization is the primary mode of photoreaction for conjugated dienones. Excellent material balance at the photostationary states shows that polymerization does not compete effectively, and analysis of the volatile products shows that the reactions are clean photoisomerizations. Several potentially meaningful generalizations can be drawn from the data. In no case did we succeed in detecting a *cis,cis*-dienone among the photoproducts. However, the aliphatic and the δ-phenyldienones gave all of the other possible geometric isomers. The sole exception to this is **21** which does not undergo γ,δ isomerization. In contrast, 1-phenyldienones appear to undergo γ,δ isomerization exclusively.

Two dienones, **24** and **27**, appear unusual in that they give pyrans on irradiation. In fact, the photoisomerization of these dienones is entirely normal. α-Pyrans exist only in cases where their valence isomeric α,β-*cis*-dienones possess no stable planar conformations.[14] Thus, irradiation of **24** almost certainly gives the sterically destabilized dienone **49**. Closure of **49** to



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give pyran **25** is the inexorable consequence of themodynamics. Irradiation of **27** gives a (*Z*,*E*) isomer that is in thermal equilibrium with the valence isomeric pyran **30**.[14] Whether closure to pyrans is light-catalyzed under our conditions cannot be deduced. Marvell, *et al.*, have shown that dark interconversion of *cis*-β-ionone and its corresponding α-pyran is sufficiently rapid to account for our observations.[11] Formation of the methylenetetrahydropyran **26** from **25** can be formulated as a photochemical [1,3] sigmatropic shift of hydrogen for which the suprafacial pathway is allowed.[27]

One of the most striking aspects of our data is the complete absence of *cis,cis*-dienones from the photolysates. Isomerization of cis,cis isomers during glpc analysis could be the cause. However, the crude photolysates exhibited no significant nmr or ir absorption which could not be accounted for on the basis of the isolated isomers. Furthermore in the case of 6-phenyl-

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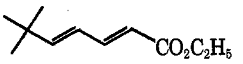
[26] The fact that the first condition is not quite met means that we will tend to underestimate the absorption intensity of the photoproduct.

[27] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 122.

3,5-hexadienones (**31–33**) a semicarbazone mixture prepared directly from the crude photolysate was resolved into only three components by tlc. This could be a consequence of nonformation of cis,cis isomers. However, we can think of no obvious reason for this. In the closely related isomerization of the dienonic ester **50**, evidence for four geometric isomers has been obtained.[28] Owing to their predictably low uv absorption intensities,[14] cis,cis isomers would be expected to be major components of the photostationary states. Alternatively, the absence of cis,cis isomers can be interpreted in terms of their rapid disappearance *via* dark reactions. Facile interconversion of *α,β-cis*-dienones and *α*-pyrans could afford such a pathway. Scheme II shows that *cis,cis*- and *cis,trans*-dienones could be equilibrated *via* the *α*-pyran **51** which is valence isomeric to both. A ΔF° value of −1.8 kcal/mol for conversion of **23** to **12** would correspond to *ca.* 5% **23** at equilibrium near room temperature, an amount undetectable by our ir and nmr analyses.[29] 1,3 Methyl–hydrogen interactions similar to that in **23** have been estimated as 1.6 kcal/mol.[30]



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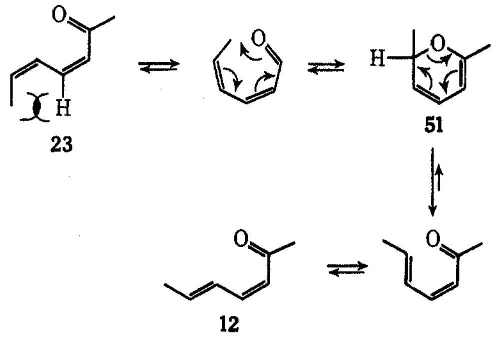
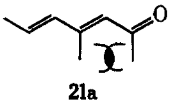
SCHEME II

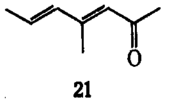
EQUILIBRATION OF *cis,cis*- AND *cis,trans*-DIENONES



Only tentative explanations can be advanced to account for lack of *γ,δ* isomerization of 4-methyl-3,5-heptadienone (**21**). Owing to steric destabilization of the s-trans conformer (**21a**), this compound exists exclusively as an *s-cis*-enone (**21**).[14] Except for **8**, which cannot undergo *γ,δ* isomerization, **21** is unique among our aliphatic dienones in this regard. Compounds **13** and **19**, which have conformationally homogeneous *s-trans*-enone units,[14] undergo normal isomerization. Should the unique conformation of **21** lead to rapid photoenolization to the exclusion of normal photoisomerization, exclusive *α,β* isomerization could be explained as shown in Scheme III. However, for simple enones geometric isomerization is faster than photoenolization.[28,31] Furthermore, no unconjugated products (*e.g.*, **52**), which are characteristic of enone photoenolization, were detected. Alternatively, lack of *γ,δ* isomerization could be a property peculiar to s-cis excited states. The other aliphatic dienones could undergo *γ,δ* isomerization *via* s-trans excited states populated by Franck–Condon excitation of s-trans ground-state conformers. Different reactivity of the s-cis and s-trans excited states of dienes has been recognized for some time,[32] and similar behavior has been suggested in the case of enones.[33] Neither of the above proposals provides an obvious basis for explaining the lack of isomerization specificity for 4-methyl-6-phenyl-3,5-hexadienone (**34**) which also has a conformationally homogeneous *s-cis*-enone unit.



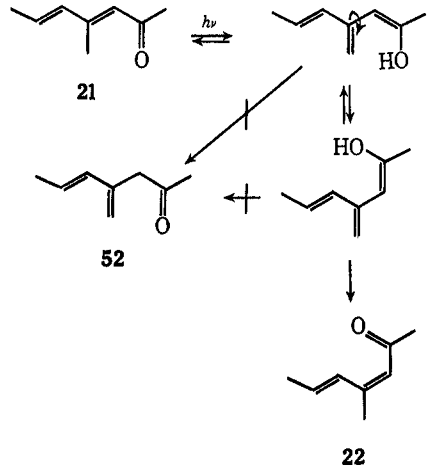
21a



21

SCHEME III

PHOTOENOLIZATION OF 4-METHYL-3,5-HEPTADIENONE



Work on the mechanism of photoisomerization of 3,5-heptadienones (**6**, **7**, and **12**) has revealed moderately efficient isomer interconversion $\Phi = 0.12$–0.36 and has demonstrated that a common excited state is not involved.[34] We are conducting further experiments designed to clarify the role of cis,cis isomers and to test for photoenolization and for conformational dependence of photoreactivity.

Experimental Section

General.—Glpc analysis was performed using an F & M Model 609 instrument with a flame ionization detector, with 0.25-in. columns. Analytical columns were AC-1 copper, 6 ft, 30% DC-200 on 60–80 mesh Chromosorb W; AC-2 copper, 10 ft, 10% FFAP on 60–80 mesh Chromosorb W; and AC-3 copper, 20 ft, 5% FFAP on 60–80 mesh Anakrom AB. A Varian Aerograph Autoprep A-700 glpc unit was used for preparative work. The following $^3/_8$-in.-diameter preparative columns were employed: PC-1 aluminum, 20 ft, 30% SE-30 on 60–80 mesh Chromosorb W; PC-2 aluminum, 10 ft, 25% DC-200 on 60–80 mesh Chromosorb W; PC-3 aluminum, 20 ft, 30% FFAP on 60–80 mesh Chromosorb W; PC-4 aluminum, 20 ft, 30% QF-1 on 60–80 mesh Chromosorb W; and PC-5 copper, 30 ft, 0.25-in. diameter, 25% FFAP on 60–70 mesh Anakrom AB.

For analytical irradiations a stoppered 1-cm path length fused silica uv cuvette was placed flush with the window of an ultraviolet hand lamp. This lamp, a Black-Ray Model X4 obtained

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[28] M. J. Jorgenson, *J. Amer. Chem. Soc.*, **91**, 6432 (1969); see Experimental Section, p 6443.

[29] At the temperature of glpc analysis, 100–110° interconversion could easily be too rapid to allow resolution.[11]

[30] J. Packer, J. Vaughan, and E. Wong, *ibid.*, **80**, 905 (1958).

[31] M. J. Jorgenson and N. C. Yang, *ibid.*, **85**, 1698 (1963); N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964).

[32] R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

[33] R. A. Schneider and J. Meinwald, *ibid.*, **89**, 2023 (1967).

[34] A. F. Kluge and C. P. Lillya, *ibid.*, **92**, 4480 (1970), and paper in press.

from Scientific Glass Apparatus Co., Inc., Bloomfield, N. J., emitted a broad spectrum λ 300–400 nm with a maximum intensity at 366 nm (black light). Preparative irradiations were performed with either a Hanovia immersion apparatus employing a 450-W medium-pressure mercury arc (679A-36) and Corex filter sleeve or with a Rayonet photochemical reactor equipped with 16 RPR 3500A or RPR 2537A lamps. Solutions irradiated in the Rayonet reactor were contained in an 800-ml quartz vessel equipped with a reflux condsnser. Deaeration had no observable effect on the reactions.

Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory directed by Mr. Charles Meade. Spectrophotometric equipment and infrared, uv, and nmr spectral data are described in detail in the preceding paper[14] and are not reproduced here.

Photostationary-State Compositions.—Dilute solutions of the dienones in ether were irradiated until their compositions no longer changed. Analysis was performed using glpc by injecting the ether solutions directly into the chromatograph. Light sources are 300–400 (see hand lamp above), "2537" Rayonet RPP-2537A lamps whose main output is at 253.7 nm but also emits energy at 313 and 366 nm; 313 and 254 nm refer to monochromatic light of the designated wavelength obtained by passing the output of a medium-pressure mercury arc through a series of filter solutions and plates.[35] The results are presented in Table I.

TABLE I

PHOTOSTATIONARY-STATE COMPOSITIONS IN DIETHYL ETHER

		% composition		
Compd[a]	Light source	All-trans or (*E*,*E*)	Trans,cis or (*E*,*Z*)	Cis,trans or (*Z*,*E*)
6	300–400	49.1	25.2	25.7
	"2537"	32.6	20.7	46.7
	313	48.0	30.0	22.0
	254	28.4	20.4	51.2
8	300–400	74.8		25.2
	"2537"	47.4		52.6
	254	46.6		53.4
9	300–400	46	31	23
13	300–400	41.5 ± 3	19 ± 3	39.5 ± 3
19	300–400	55.8	44.2	
21	300–400	51.2		48.8
27	300–400	19 ± 3	13 ± 3	68 ± 3[b]
31	300–400	40[c]	50[c]	10[c]
34	300–400	37[c]	27[c]	36[c]
37	300–400	36[d]	64[d]	

[a] The all-trans or (*E*,*E*) compound. [b] Exists as 13% dienone and 87% α-pyran. [c] Values approximate owing to incomplete resolution of (*E*,*E*) and (*E*,*Z*) isomers and isomerization during glpc analysis. [d] Values approximate owing to isomerization during glpc analysis.

Preparation of Dienones from Dienoic Acids.—The Tegnér reaction[36] was found to be a generally efficient and completely stereospecific method of preparing methyldienones from their corresponding dienoic acids. To a three-neck, round-bottom flask equipped with reflux condenser, nitrogen inlet, magnetic stirring bar, and rubber stopple were added from 2 to 20 mmol of dienoic acid and from 40 to 300 ml of ether. The system was purged with nitrogen and 2 equiv of another solution of methyllithium was added with a syringe. The solution was heated at reflux for 30 min, then cooled. Water (20–50 ml) was added and the layers were separated. The ether layer was separated, washed with additional water, and dried (Na_2SO_4). Removal of solvent gave the crude dienone, containing small amounts of alcohol impurity. The crude dienone was filtered through activated alumina (3–20 g) with a suitable solvent such as hexane or benzene. Removal of solvent gave the alcohol-free dienone which could be obtained in very pure form by micromolecular distillation or sublimation.

Irradiation of *all-trans*-3,5-Heptadienone (6).—Compound **6** was prepared according to the method of Attenburrow, *et al.*[37] Material prepared according to this procedure contained approximately 15% of the trans,cis isomer **7**. The two isomers were separated using PC-5 at 130°. It was found that the best method for the preparation of isomerically pure **6** was through treatment of *all-trans*-sorbic acid with methyllithium (*vide supra*) which gave **6** in 75% yield. Analysis by glpc (AC-3,110°) showed less than 0.1% of **7** as the only impurity. Five irradiations were performed in an Hanovia apparatus using approximately 0.3 g of **6** in 600 ml of ether (*ca.* 5×10^{-3} *M*). Each solution was irradiated for 12 min at which time glpc analysis revealed three components: **12** (T_r[38] 14.4 min, 27%), **7** (T_r 18.4 min, 27%), and **6** (T_r 19.2 min, 46%). Solvent was removed by careful distillation, and the cis,trans isomer **12** was isolated by glpc as a light yellow oil using PC-1 at 120°. The trans,cis isomer **7** was isolated using PC-5 at 130°.

It was found that **12** could be prepared in greater quantities by irradiation in the Rayonet reactor. A solution of 2.5 g of **6** (containing 15% of **7**) in 500 ml of ether (4.55×10^{-2} *M*) was irradiated with RPR 2537A lamps. After 4 hr the photomixture contained approximately 40% **12**. The loss of monomer to polymer at this concentration was still small.

Irradiation of *trans*-6-Methyl-3,5-heptadienone (8).—The procedures of Kuhn and Hoffer[39] and Fischer and Lowenberg[40] were followed for the preparation of **8**. The reaction product was purified in each case by preparative glpc (PC-1, 150°). A solution of 0.0842 g of **8** in 500 ml of ether (1.36×10^{-3} *M*) was irradiated in a Rayonet reactor equipped with RPR 3500A lamps. Analytical glpc (AC-1, 110°) showed two components: **18** (T_r 16.4 min) and **8** (T_r 24 min). The irradiation was terminated after 20 min, at which time the percentage composition of **8** was *ca.* 25%. Two similar irradiations were run, and solvent was carefully removed from each mixture. The *cis* isomer **18** was isolated by preparative glpc as a light yellow oil using PC-1 at 150°. Isomer **18** could be prepared in greater quantity by irradiation with RPR 2537A lamps. A solution of 2.5 g of **8** in 600 ml of ether (3.36×10^{-2} *M*) when irradiated for 6 hr gave a mixture that was approximately 50% **18**. Losses to polymerization were small.

Irradiation of *trans*-3-Propenyl-2-cyclohexenone (19).—The procedure of Crison and Normant was used to prepare **19**.[41] An ether solution 2.46×10^{-2} *M* in **19** was irradiated in a 1-cm path length with a uv hand lamp, and the reaction was followed by glpc (AC-2, 140°). At zero time there was a single component, **19** (T_r 36 min). As the irradiation progressed, a new isomer **20** (T_r 24.4 min) appeared and in 20 min built up to a stationary concentration of 44%. In a preparative run 1.34 g of **19** in 500 ml of ether (1.98×10^{-2} *M*) was irradiated for 1 hr in a Rayonet reactor equipped with RPR-3500A lamps. The isomer mixture was approximately 40% **20**. The solvent was removed leaving a yellow oil. Cis isomer **20** was isolated by preparative glpc using PC-1 at 180°. In contrast to **19** it exhibits only weak ir absorption in the 980-cm^{-1} region.

Irradiation of (*E*,*E*)-4-Methyl-3,5-heptadienone (21).—Compound **21** was prepared in 81.7% yield through treatment of (*E*,*E*)-3-methyl-2,4-hexadienoic acid[39] with methyllithium. The 2,4-dinitrophenylhydrazone derivative melted at 172–173° (cor) (lit.[41] 172°). Compound **21** was further purified by preparative glpc using PC-3 at 130° to give a clear oil. A cyclohexane solution 3.62×10^{-3} *M* in **21** was placed in a 1-cm path length uv cuvette and was irradiated with a uv hand lamp. Analysis by glpc (AC-2, 100°) showed starting material (T_r 26.8 min) and a new isomer, **22** (T_r 22.4 min). At 56 min a photostationary state consisting of only these two isomers was reached. In a preparative run a solution of 0.5 g of **21** in 500 ml of ether (8.07×10^{-3} *M*) was irradiated for 1 hr with RPR 3500A lamps. Glpc showed the isomer mixture was 40% **22**. After the volume of this solution was reduced to *ca.* 4 ml, the (*Z*,*E*) isomer **22** was isolated by preparative glpc using PC-3 at 130°. This material exhibited ir, nmr, and uv absorption as well as a glpc retention time that was identical with that of authentic (*Z*,*E*)-4-methyl-3,5-heptadienone (**22**).[19]

Irradiation of Pseudoionone.—Pseudoionone was prepared according to the "Organic Syntheses" procedure.[42] Further

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[36] C. Tegnér, *Acta Chem. Scand.*, **6**, 782 (1952).

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[38] Glpc retention time.

[39] R. Kuhn and M. Hoffer, *Chem. Ber.*, **65**, 651 (1932).

[40] F. G. Fischer and K. Lowenberg, *Justus Liebigs Ann. Chem.*, **494**, 279 (1932).

[41] C. Crison and H. Normant, *Bull. Soc. Chem. Fr.*, 1451 (1957).

[42] A. Russell and R. L. Kenyon, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1951, p 747.

purification was effected by preparative glpc using PC-1 at 190°. Pseudoionone prepared by this procedure is a mixture of two isomers (derived from geranial and neral which together constitute citral). The first eluted isomer constituted approximately one-third of the isomer mixture. The nmr spectra of the two isomers are very similar. The uv max (C_6H_{12}) for both isomers was 283 nm. The ϵ_{max} for the isomer of shorter retention time was 18,200 and that for the other was 18,900. On the basis of the uv spectra and the glpc retention times (γ,δ-cis isomers have shorter retention times than all-trans isomers), the isomer of shorter retention time is assigned (*E,Z*) stereochemistry (**16**), and the other isomer is assigned (*E,E*) stereochemistry (**9**). A solution of 0.0031 g of pseudoionone (mixture of **9** and **16**) in 4 ml of ether (4×10^{-3} *M*) was added to a 1-cm path length uv cuvette, and the solution was irradiated with a uv hand lamp.

Analysis by glpc (AC-1, 160°) showed, in addition to **16** (T_r 30.8 min) and **9** (T_r 38 min), a new component, **17** (T_r 27.6 min). The isomerization was slow compared to other systems. In a preparative run, 0.41 g of pseudoionone in 500 ml of ether (4.27 $\times 10^{-3}$ *M*) was irradiated for 23 hr in a Rayonet reactor equipped with RPR 3500A lamps. Solvent was removed to give a yellow oil. Analysis by tlc (silica gel, $CHCl_3$) showed three spots very near starting material (R_f 0.5), one minor spot at R_f 0.75, and several spots near the application point. The three components of R_f 0.5 were separated from the rest of the reaction mixture by preparative tlc using two 20 × 20 cm plates coated with an 0.5-mm layer of uv-indicating silica gel. The plates were developed twice with $CHCl_3$ and were visualized by uv. A band from 5 to 15 cm along the plates was scraped off. The removed silica gel was shaken with 100 ml of $CHCl_3$ and the slurry was filtered by suction. Solvent was removed leaving 0.3 g of a yellow oil. Analysis by glpc showed the following isomer composition: **9**, 46%; **16**, 31%; **17**, 23%. The base line was irregular leading up to the first peak (**17**) suggesting decomposition. The nmr spectrum of the isomer mixture exhibited a new signal at τ 3.37 (J = 12 Hz) which was assigned to H_4 of the (*Z,E*) isomer (**17**). Integration of this signal gives an estimate of **17** as 26 ± 4% (glpc estimate 23%).

Irradiation of (*E,E*)-3-Methyl-3,5-heptadienone (13).—Compound **16** was prepared by treating (*E,E*)-2-methyl-2,4-hexadienoic acid[43] with methyllithium (*vide supra*) and was isolated in 51% yield as a clear oil. Spectral properties are tabulated in the preceding paper and are in full accord with structure **13**.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.40; H, 9.70.

An ether solution 1×10^{-3} *M* in **13** was placed in a 1-cm path length uv cuvette and was irradiated with a uv hand lamp to give a photostationary state after 1 hr. Analysis by glpc (AC-3, 130°) showed **13** (T_r 9.5 min) at zero time. As the irradiation progressed two new isomers appeared at T_r 6.6 and 8.5 min. These isomers are respectively assigned (*Z,E*) and (*E,Z*) stereochemistry by analogy of their retention times with those of **6**, **7** and **12** on the same column.

Irradiation of (*E*)-4,6-Dimethyl-3,5-heptadienone (24).—Dienone **24** was prepared in 47% yield by treatment of (*E*)-3,5-dimethyl-2,4-hexadienoic acid[44] with methyllithium (*vide supra*). The resulting clear oil gave a 2,4-dinitrophenylhydrazone derivative, mp 149–150° (lit.[41] mp 148°).

Irradiation of a 4.93×10^{-3} *M* methanol solution of **24** in a uv cuvette was followed by glpc (AC-1,110°). In addition to **24** (T_r 38.2 min) a new peak (T_r 12 min) appeared and after 46 min accounted for 84% of the total area under the two peaks. A plot of log [**24**] *vs.* time for this reaction gave a straight line. In a preparative run 0.5 g of **24** in 500 ml of ether (7.25×10^{-3} *M* was irradiated for 2 hr with RPR 3500A lamps. Glpc showed conversion of **24** to product was essentially complete. After removal of the solvent the photoproduct was collected by preparative glpc (PC-4,100°). This product exhibited glpc retention times (AC-1 and AC-2) and nmr absorptions which were identical with those of an authentic mixture of **25** and **26**.[21] In our hands **25** and **26** exhibited identical glpc retention times and the amount of **26** was determined to be 45% by nmr integration. A second run made under the same conditions but irradiated for only 90 min gave only 90% conversion of starting dienone, and the photoproducts contained only 25 ± 2% **26**.

Irradiation of (*E,E*)-5-Methyl-3,5-heptadienone (27).—A 3.4 $\times 10^{-3}$ *M* ether solution of **27**, prepared according to Dautwitz,[45] was irradiated in a uv cuvette, and progress of the reaction was monitored by glpc (AC-2). Elution at 75° gave a single peak (**29** and **30**) after which the column temperature was increased to 130° (9°/min) causing elution of **28** and **27** in that order. The photostationary state was reached after 94 min. In a preparative run 2.40 g of **27** in 500 ml of ether (3.87×10^{-2} *M*) was deaerated by bubbling nitrogen through the solution for 30 min. The solution was maintained under an atmosphere of nitrogen while it was irradiated with RPR 3500A lamps for 9 hr. Removal of solvent left a yellow oil which was separated into its components by preparative glpc (PC-4,140°). The second eluted component was identified as the (*E,Z*) isomer **28** while the first eluted component was a mixture of **29** and **30**:[14] ir (film) 1695 (sh), 1666, 1622, 1042 cm^{-1}; nmr (see ref 14); uv max (C_6H_{12}) 284 nm (ϵ 3920), 211 nm (ϵ 2320). The mixture of **29** and **30** was air sensitive and elemental analysis had to be performed immediately on glpc purified material which was further purified by molecular distillation.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.30; H, 9.70.

The semicarbazone had mp 165–166° dec.

Anal. Calcd for $C_9H_{15}N_3O$: C, 59.65; H, 8.34; N, 23.18. Found: C, 59.60; H, 8.27; N, 23.00.

Irradiation of *all-trans*-6-Phenyl-3,5-hexadienone (31).—Compound **31** was prepared by the procedure of Plati, *et al.*[46] The light yellow crystals, mp 66.5–67°, could be obtained in colorless form by sublimation (0.05 mm, 50°), which left the melting point unchanged. A solution of 0.05 g of **31** in ether was irradiated with RPR 3500A lamps for 4 hr. The photostationary state was reached sometime after 2 hr. Ten more runs were made under identical conditions with an irradiation time of 20 min which gave a composition of 35% **32**, 5% **33**, and 60% **31**. The combined products were dissolved in the minimum amount of methanol and separated by preparative glpc (PC-1,200°). The first eluted compound was **32**, the trans,cis isomer, a yellow oil. The cis,trans isomer **33** was eluted next; however, collected samples were contaminated with **31** owing to isomerization of the column or detector block.

Irradiation of *cis,trans*-6-Phenyl-3,5-hexadienone (33).—Compound **33** was obtained as a yellow paste in 93% yield by treatment of *cis,trans*-5-phenyl-2,4-pentadienoic acid[24] with methyllithium (*vide supra*). When analyzed by glpc (AC-1, 175°) a neat sample showed 92% **33** and 8% **31**, while a 10^{-3} *M* ether solution showed 23% **33** and 77% **31**. Irradiation of a 1.16 × 10^{-3} *M* solution of **33** with RPR 3500A lamps for 2 hr gave the same photostationary-state isomer mixture produced by irradiation of **31**.

Synthesis of (*E,E*)-3-Methyl-5-phenyl-2,4-pentadienoic Acid (43) and (*Z,E*)-3-Methyl-5-phenyl-2,4-pentadienoic Acid (42).—A mixture of ethyl esters (51 g) prepared according to Kuhn and Hoffer[39] was hydrolyzed in a solution of 20 g of potassium hydroxide in 40 ml of water and 300 ml of ethanol. The potassium salt of the (*E,E*) acid (**41**) was collected by filtration from the cooled hydrolysate. Reprecipitation from 200 ml of hot water by addition of concentrated hydrochloric acid and subsequent recrystallization from benzene gave 14.5 g of **43** as white crystals: mp 163–163.5° (lit.[39] 160°). The basic filtrate was diluted with 700 ml of water, treated with decolorizing charcoal, filtered, and acidified with concentrated hydrochloric acid. The resulting precipitate was collected and dried. Reprecipitation from 100 ml of hot benzene by addition of 500 ml of pentane gave 8.4 g of the (*Z,E*) acid (**42**) as white crystals: mp 157°; nmr (acetone) τ 4.17 (s, broad, 1, H_2), 2.93 (d, 1, J_{45} = 16 Hz, H_6), 1.50 (d, 1, J_{45} = 16 Hz, H_5), 2.35–2.7 (m, 5, C_6H_5).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.50; H, 6.25.

A sample of **42** was isomerized to **43** by treatment with iodine in benzene.

Irradiation of (*E,E*)-4-Methyl-6-phenyl-3,5-hexadienone (34).—Dienone **34** was prepared by treatment of the corresponding dienoic acid (**43**) with methyllithium (*vide supra*) and isolated as yellow crystals, mp 57–58° (lit.[47] 53°); phenylsemicarbazone derivative, mp 190–191° (cor) (lit.[47] 190°).

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An ether solution 5.16×10^{-3} *M* in **34** was irradiated in a uv cuvette. Analysis by glpc (AC-1, 180°) showed **35** (T_r 14.2 min), **36** (T_r 25.2 min), and **34** (T_r 26.8 min). In addition there was an unidentified component at T_r 20.8 min, which comprised less than 1% of the total mixture and did not change in percentage composition over the course of the irradiation. In a preparative run, 0.476 g of **34** in 500 ml of ether (5.45×10^{-3} *M*) was irradiated for 45 min with RPR 3500A lamps. Removal of solvent left a yellow oil. Isomer **35** was collected by preparative glpc (PC-2, 180°) as a yellow oil.

Irradiation of (*Z,E*)-4-Methyl-6-phenyl-3,5-hexadienone (36).—Dienone **36** was prepared by treating **42** with methyllithium (*vide supra*) to give a yellow oil. An ether solution 1.7×10^{-3} *M* in **36** was irradiated in a uv cuvette. Glpc analysis (AC-1, 180°) revealed **34**, **35**, and **36** identical in retention times and photostationary-state concentrations with the three components obtained from irradiation of **34**.

Irradiation of *trans*-3-Styryl-2-cyclohexenone (37).—Compound **37** was prepared according to the general method of Crison and Normant.[41] A solution of 0.0805 g of **37** in 500 ml of ether (8.13×10^{-4} *M*) was irradiated with RPR 3500A lamps. After 10 min, the uv absorption maximum had decreased in intensity by a factor of 2 and shifted 15 nm to shorter wavelengths. Removal of solvent left pasty yellow solid. In another run, a solution of 0.2103 g of **41** in 500 ml of ether (2.12×10^{-3} *M*) was irradiated. Analysis by glpc (AC-1, 200°) of the photomixture showed **38** (T_r 19.6 min) and **37** (T_r 36.4 min). A steady state was reached after 10 min. Removal of solvent again gave a yellow paste from which **38** was isolated by preparative glpc (PC-2, 200°). Compound **38** was a yellow oil. Analysis by glpc showed the isomeric purity to be 92%.

Irradiation of *all-trans*-1-Phenyl-2,4-hexadienone (44).—To a 100-ml, round-bottom flask equipped with a reflux condenser were added 4.8 g (12.6 mmol) of benzoylmethylenetriphenylphosphorane,[48] 5 g of crotonaldehyde, and 50 ml of benzene. The solution was heated at reflux for 24 hr. Removal of solvent left a tan solid that was washed with two 20-ml portions of ether. The remaining solid (triphenylphosphine oxide) was discarded. Evaporation of the ether and sublimation (60°, 0.05 mm) gave 1.541 g (71%) of crude **44**, a yellow solid. Recrystallization from 20 ml of hexane gave light yellow crystals, mp 47–48.5° (lit.[49] 47–48°).

A solution of 0.0436 g of **44** in approximately 500 ml of ether (*ca.* 5×10^{-4} *M*) was irradiated with RPR 3500A lamps. A tenfold dilution with cyclohexane was made for uv samples.

Time, min	λ_{max}	Absorbance at λ_{max}
0	288	1.20
10	291	1.14
15	291	1.15
20	291	1.14

The samples were analyzed by glpc (AC-1, 175°). At zero time there appeared one trace at T_r 27.6 min (**44**). As the irradiation progressed, there appeared a trace assigned to **45** at T_r 26.4 min.

Irradiation of *trans*-1-Phenyl-5-methyl-2,4-hexadienone (46).—A solution of 4.8 g (12.6 mmol) of benzoylmethylenetriphenylphosphorane, 5 g of 3-methyl-2-butenal,[50] and 75 ml of dry benzene was heated at reflux for 24 hr in a nitrogen atmosphere. Removal of solvent left an amber mass which was washed with two 50-ml portions of ether. The remaining solid (triphenylphosphine oxide) was discarded. Evaporation of the washings left an amber oil which was filtered through 30 g of alumina with 100 ml of benzene-hexane (1:1). Removal of solvent and distillation gave 0.8 g (34%) of **46**, bp 113° (1 mm), as yellow crystals. Recrystallization from two 10-ml portions of hexane gave **46** as yellow crystals, mp 44.5–45°.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.80; H, 7.50.

A solution of 0.0328 g of **46** in 500 ml of ether (3.54×10^{-4} *M*) was irradiated with RPR 3500A lamps. Analysis by glpc (AC-1, 175°) at zero time showed **39** (T_r 45.6 min) and a barely detectable trace at 20.4 min. After 20 min of irradiation time the trace at T_r 20.4 min was somewhat more defined than at zero time, but it contributed less than 3% to the total area under the two peaks. The uv spectrum of the solution did not change during irradiation.

Irradiation of *all-trans*-1-(*p*-Bromophenyl)-2,4-hexadienone (47).—A solution of 10 g (21.7 mmol) of *p*-bromobenzoylmethylenetriphenylphosphorane,[51] 5 g of crotonaldehyde, and 100 ml of dry benzene was heated at reflux for 24 hr. Removal of solvent left a tan solid which was washed with two warm 50-ml portions of benzene–hexane (1:1). The remaining solid was filtered through 50 g of alumina with 150 ml of benzene–hexane (1:1). Removal of solvent and recrystallization from two 50-ml portions of hexane gave **47** as 2.241 g (32.4%) of off-white plates, mp 109–110°.

Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.39; H, 4.41; Br, 31.82. Found: C, 57.65; H, 4.70; Br, 31.60.

A solution of 0.151 g of **47** in 600 ml of deaerated ether (1×10^{-3} *M*) was irradiated with RPR 3500A lamps. An inert atmosphere was maintained throughout the irradiation. Analysis by glpc (AC-1, 200°) showed that at zero time there was **47** (T_r 20.8 min) and an impurity at T_r 15.6 min (*ca.* 3%). As the reaction proceeded, a new component assigned structure **48** appeared at T_r 20 min. An apparent photostationary state containing 10–20% **48** was set up between **47** and **48** after 10 min. The uv spectrum of this mixture in cyclohexane exhibited λ_{max} at 298 nm with 92% of the original intensity and shoulder at 292 nm (**47** exhibits two maxima of equal intensity at 298 and 292 nm). Within limits of error the area for the 15.6-min trace did not change during the irradiation. There was a slow decrease in total trace area for **47** and **48** over the course of the irradiation (equal injection volumes) such that after 30 min the total area was approximately 65% of the original area for **47**. Analysis of the reaction mixture by tlc (CCl_4) showed two spots at approximately R_f 0.5 (**47** and **48**), a small spot at R_f 0.8, and two small spots near the application point. Removal of solvent left a brown solid. The color and the low R_f components and the loss of volatile material (glpc) are indicative of decomposition and/or polymerization.

Registry No.—**6**, 18402-90-9; **8**, 16647-04-4; **13**, 29179-01-9; **19**, 29179-03-1; **21**, 29178-97-0; **24**, 29179-02-0; **27**, 29178-99-2; **29**, 29168-56-7; **29** semicarbazone, 29168-57-8; **30**, 29168-58-9; **31**, 29179-13-3; **33**, 29179-15-5; **36**, 29179-18-8; **37**, 29179-20-2; **42**, 20430-09-5; **44**, 29179-22-4; **46**, 29179-23-5; **47**, 29179-24-6; pseudoionone, 141-10-6.

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