

visual pigments should await the outcome of present work and will be put forth at some future time.

Experimental Section

Polynes. *all-trans*-Retinyl acetate was obtained crystalline from Distillation Products Industries in vacuum-sealed ampoules which were stored at Dry Ice temperature in the dark. Opened ampoules were stored under nitrogen in the dark at Dry Ice temperature. All studies were performed in red light. *all-trans*-Retinol was treated as given above. Anhydroretinol [3,7-dimethyl-9-(2,6,6-trimethyl-2-cyclohexan-1-ylidene)-1,3,5,7-nonatetraene] was prepared and characterized according to the procedures outlined by Shantz and coworkers.¹⁴

Acids. Sulfuric acid was dried by adding a sufficient amount of fuming sulfuric acid to react with the water.¹⁵ Trichloroacetic acid was purified by recrystallization and was dried in a drying pistol.

Solvents. All solvents were dried and stored over molecular sieves in a nitrogen atmosphere. Methanol, ethanol, 1,2-dichloroethane, chloroform, carbon tetrachloride, cyclohexane, *n*-heptane, and isooctane were dried by the methods set forth by Wiberg.¹⁶ Acetic acid was dried by treatment with triacetyl borate which reacts with the water to form acetic acid and insoluble boric acid.¹⁷

Generation and Observation of the Retinylic Cation. Variations in experimental conditions were necessary for the generation and detection of retinylic cations. Conditions were dictated by the acid-solvent system employed and the kind of information sought. Low temperatures were always necessary to stabilize the cation; the exact temperature was determined by solvent and the acid concentration. Also experimental conditions were dependent on whether the λ_{\max} or ϵ_{\max} of an absorption band was to be measured.

(14) E. M. Shantz, J. D. Cawley, and N. D. Embree, *J. Amer. Chem. Soc.*, **65**, 901 (1943).

(15) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 2nd ed, Longmans, Green and Co., New York, N. Y., 1951, pp 171-172.

(16) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 240-252.

(17) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 281.

Absorption Maximum. The following procedure performed in the dark was used most extensively. Two milligrams of retinyl acetate were weighed, placed in a 10-ml volumetric flask, and diluted to the mark. A 0.3-ml aliquot (1.83×10^{-7} mol of retinyl acetate) of this solution was mixed quickly with 25 ml of a cooled (approximately -35°) sulfuric acid-solvent mixture using a magnetic stirrer. The acid-solvent ratio can be varied considerably; but 10 ml of sulfuric acid and 15 ml of solvent were used most often. After formation of a homogeneous blue color, a portion of the solution at about -50° was quickly transferred to a 1-cm cuvette and its spectrum was scanned from 800 to 400 $m\mu$. The spectrophotometer was set to scan this region repetitively at a rapid rate so that spectral changes could be recorded as a function of time.

When trichloroacetic acid was used as the protonating agent, the carbonium ion solution was maintained at a temperature above 0° to avoid precipitation. A constant-temperature cell was employed for most measurements.

Molar Absorptivity. Experimental conditions for determination of molar absorptivity of the retinylic cation were chosen to ensure maximum concentration of the cation. Although the same procedure was used as described above, it was necessary to: (1) use acid-solvent proportions known to give the highest absorbance (*i.e.*, 50-60 mol % sulfuric acid), (2) mix the components as completely as possible, and (3) freeze the carbonium ion mixture in Dry Ice-acetone immediately after mixing to retard its decay to other products.

Measurements. All spectral measurements in the visible and ultraviolet regions were obtained in 1-cm matched quartz cells with the Beckman DK-2A ratio recording spectrophotometer equipped with a Beckman temperature-regulated cell holder. When lower temperatures were required, the cell holder was cooled either by ice water or by methanol at -78° . For temperatures lower than 0° , dry nitrogen was flushed across the optics of the spectrophotometer and the cells to eliminate condensation. Because of the rapid scanning speed, it was necessary to add a correction of 8 $m\mu$ to the measured absorptions to compensate for instrument time lag.¹⁸

(18) The value of 8 $m\mu$ should be added to all values reported in ref 9.

The Role of Singlet and Triplet Excited States in the Photochemistry of 3,5-Cycloheptadienone¹

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Abstract: The photolysis of 3,5-cycloheptadienone in ethyl ether, hexane, and ethanol solutions gives solely carbon monoxide and a mixture of *cis*- and *trans*-1,3,5-hexatrienes. This reaction cannot be quenched using either piperylene (1,3-pentadiene) or naphthalene. Photolysis of 3,5-cycloheptadienone sensitized by either benzophenone (in ether) or acetone (neat) gives exclusively the valence tautomer, bicyclo[3.2.0]hept-6-en-3-one. Product mixtures were analyzed spectroscopically and by gas-liquid partition chromatography with direct comparison with authentic samples of products and possible intermediates. It is concluded that the direct photolysis occurs exclusively *via* a singlet excited state, and that the efficient concerted fragmentation to carbon monoxide and the hexatrienes, in contrast to facile valence tautomerizations in related systems, can be understood on the basis of the symmetry properties of the dienone. Relationships with the previously proposed modes of fragmentation of diazenes are discussed. The sensitized reaction *via* the triplet state is seen possibly as another example of conversion of a *cis,cis*-1,3-diene to the *cis,trans* isomer followed by thermal conversion to the cyclobutene derivative.

In 1961 and 1962 Chapman and his coworkers reported the photolysis of 3,5-cycloheptadienone (**1a**) and its 2-methyl homolog (**1b**) in ether solution.⁴

(1) Part XIII of a series on the photochemistry of unsaturated ketones in solution. Part XII: D. I. Schuster and D. F. Brizzolara, *Chem. Commun.*, 1158 (1967).

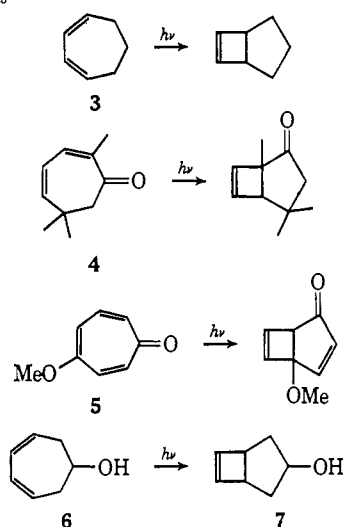
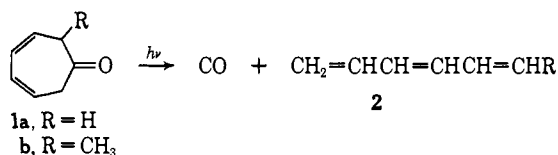
(2) Fellow of the Alfred P. Sloan Foundation.

These ketones on irradiation with a broad spectrum lamp in Pyrex vessels give carbon monoxide (95% in the

(3) Abstracted in part from the A.B. Honors Thesis of B. R. S., University College, New York University, 1967, and the Ph.D. Dissertation of F.-T. H. L., New York University, 1966.

(4) (a) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); (b) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

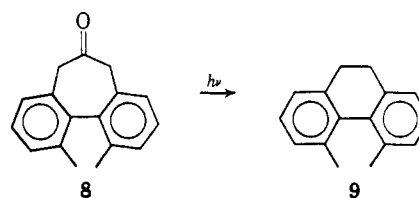
case of **1b**) and isomeric hexatrienes **2a** and **2b**, respectively. Decarbonylation of cyclic ketones is a well-known reaction in the vapor phase, but only few examples are known in condensed phases. The reactions of **1a** and **1b** are therefore truly unusual, as has been pointed out previously.⁴⁻⁹ The ring opening reaction in **1a** and **1b** is especially in contrast to the well-known general photochemical reaction of 1,3-cycloheptadienes to give valence tautomeric bicyclo-[3.2.0]hept-6-ene derivatives.⁴⁻⁹ From the abundant literature in this area,⁴⁻⁹ four well-known examples are shown below in the transformations of 1,3-cycloheptadiene (**3**),^{4,10} eucarvone (**4**),¹¹ γ -tropolone methyl ether (**5**),¹² and 3,5-cycloheptadienol (**6**)⁴.



The anomalous behavior of **1a** and **1b** has been attributed^{4b,9} to the unusual geometry of the ground state, which has been presumed to be the geometry of the reactive excited state. As pointed out by Chapman,^{4b} Dreiding models indicate that the ground-state molecule is severely twisted such that the two carbon-carbon double bonds are not coplanar, as in 2,4-cycloheptadienones.^{4b} The dihedral angle between the planes of the two double bonds has been estimated as 45°.^{4b} The low-wavelength ultraviolet absorption maximum of **1a** found at 213 m μ (log ϵ 3.77) agrees well with that reported^{13,14} and is evidence of the lack of coplanarity of the diene system. The system thus behaves spectroscopically as expected for a nonconjugated rather

than a conjugated diene.^{4b} This is not, however, a satisfying rationalization for the photochemistry of **1a** and **1b**, and it was decided that additional studies to probe the mechanism of the decarbonylation reaction were in order, particularly to determine the multiplicity of the reactive excited state and the sequence of intermediates involved in the reaction.

One other investigation bears on this problem. Mislow and Gordon¹⁵ investigated the photochemistry of the optically active biphenyl derivative **8** which is a dibenzo derivative of 3,5-cycloheptadienone. They found that irradiation of **8** in ether with or without Pyrex filters led to decarbonylation to give the dihydrophenanthrene **9** and partial racemization of the starting material **8**, with decarbonylation about four to five times as fast as racemization. As noted,¹⁵ the light absorbed, corresponding to over 90 kcal/mol of energy, is more than sufficient to effect racemization ($E_{\text{act}} = 36$ kcal/mol), yet the preferred pathway of the excited state is bond cleavage



One essential difference between 3,5-cycloheptadienones **1a**, **1b**, and **8** and 2,4-cycloheptadienones such as eucarvone (**4**) is that the former group possesses a twofold symmetry axis with respect to either the entire molecule or the dienone chromophoric system, and this axis passes through the carbonyl group.¹⁵ This symmetry element is missing in the 2,4-cycloheptadienones. Since the decarbonylation can be effected using the carbonyl $n \rightarrow \pi^*$ transition, there is the interesting possibility that the unusual reactivity of **1a** might be related, as in many recent examples, to its symmetry. That this relationship is a real one is indicated by the results below.

Results

Synthesis of 3,5-Cycloheptadienone. In the earlier phases of this work, the synthesis of **1a** from cyclohexanone as described by Parham and his coworkers^{14,16} was used. The material as obtained was impure as indicated by gas-liquid partition chromatography (glpc) and ultraviolet (uv) spectroscopy and was purified *via* the sodium bisulfite addition compound, although the recovery was poor. The procedure in our hands was found to be tedious and a shorter route was sought. Chapman, *et al.*, had reported that lithium aluminum hydride reduction of tropone gave mixtures of 3,5-cycloheptadienone (**1a**) and 3,5-cycloheptadienol (**6**).¹⁷ We investigated this interesting reaction and reported that the reaction proceeds in three steps.¹⁸ Conjugated addition of hydride to tropone **10** gives the enolate **11**,

(15) K. Mislow and A. J. Gordon, *ibid.*, **85**, 3521 (1963).

(16) W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Amer. Chem. Soc.*, **84**, 1755 (1962). We are grateful to Professor Parham for sending us the full details of this preparation in advance of the full publication of his work.

(17) O. L. Chapman, D. J. Pasto, and A. A. Griswold, *ibid.*, **84**, 1213 (1962).

(18) D. I. Schuster, J. M. Palmer, and S. C. Dickerman, *J. Org. Chem.*, **31**, 4281 (1966).

(5) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(6) O. L. Chapman, *ibid.*, **1**, 323 (1963).

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966.

(8) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, p 53 ff.

(9) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 43 ff.

(10) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

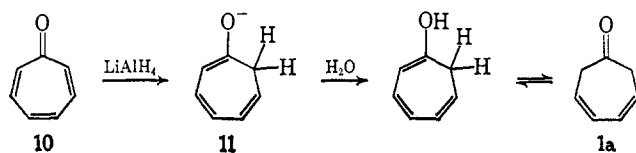
(11) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

(12) O. L. Chapman and D. J. Pasto, *ibid.*, **80**, 6685 (1958); **82**, 3642 (1960).

(13) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *ibid.*, **77**, 4401 (1955).

(14) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncel, and R. M. Dodson, *ibid.*, **87**, 321 (1965).

which gives ketone **1a** on hydrolysis. The alcohol **6** is formed predominantly if not totally by reduction of ketone **1a** with residual hydride during the hydrolysis work-up procedure.¹⁸ The yield of ketone **1a** was



substantially increased relative to that of alcohol by inverse addition of the hydride reaction mixture to acetic acid with rapid stirring in the hydrolysis step.¹⁸ An even better procedure,¹⁹ which gives ketone **1a** almost totally free of alcohol **6** and which is experimentally more simple than that described earlier,¹⁸ involves adding ethyl formate to the hydride reaction mixture to destroy any residual hydride before hydrolysis with aqueous sodium hydroxide. The procedure is simple, can be carried out on a large scale, and gives ketone **1a** in high purity after a single distillation.

The infrared and uv spectra and refractive index of **1a** are in excellent agreement with those previously reported,^{13,14,16,17} but there are some minor discrepancies in the nmr spectrum discussed in the Experimental Section. The long-wavelength uv spectrum of 3,5-cycloheptadienone in ether consisted of a shoulder at 352.5 m μ (log ϵ 5.90) and a maximum at 372.5 m μ (log ϵ 4.57). At the two wavelengths of principal interest for photolysis, 313 and 366 m μ , extinction coefficients of 73.6 and 4.1, respectively, were observed.

Direct Photolysis of 3,5-Cycloheptadienone (1a). Irradiations were carried out in dilute solutions in ether (6.1×10^{-2} to 8×10^{-3} M) with a Hanovia 450-W high-pressure mercury lamp with and without Pyrex filters. The reaction flask was equipped such that aliquots could be withdrawn at any desired stage of the reaction. In a typical run with 1.03 g of **1a** in 300 ml of ether, analysis by glpc indicated 25% of unreacted **1a** after 5 hr without a Pyrex filter. Close to 24 hr of irradiation was required for complete disappearance of **1a**. Relatively crude measurements of the amount of carbon monoxide generated in the reaction were in the range of 73–91% of theoretical, based on complete decarbonylation of **1a**. Chapman⁴ reported that **1b** on photolysis gave 95% of the theoretical amount of carbon monoxide.

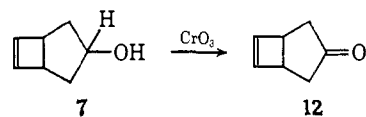
The reaction mixture at various stages of photolysis of **1a** was examined, and compared directly with samples of 1,3-cyclohexadiene, mixtures of *cis*- and *trans*-1,3,5-hexatrienes (**2a**), and bicyclo[3.2.0]hept-6-en-3-one (**12**). The trienes were prepared by irradiation of 1,3-cyclohexadiene,^{20,21} and material isolated by glpc had infrared and ultraviolet spectra in excellent agreement with those reported in the literature.²² In particular, the series of uv maxima at 246, 256, and 266 m μ ²² were particularly useful in analysis. The bicyclic ketone **12** was prepared as described previously^{1b,23} and its

(19) Adapted from a procedure described by J. A. Marshall, N. H. Andersen, and A. R. Hochstetler, *J. Org. Chem.*, **32**, 113 (1967).

(20) R. J. de Kock, N. G. Minnaard, and E. Havinga, *Rec. Trav. Chim.*, **79**, 922 (1960).

(21) D. I. Schuster, F.-T. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965).

(22) G. F. Woods and L. H. Schwartzman, *J. Amer. Chem. Soc.*, **70**, 3394 (1948); J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *ibid.*, **82**, 2537 (1960).



properties agree with those reported. Gas chromatographic analysis of the photolysate of **1a** on three different columns under a variety of conditions demonstrated conclusively that neither 1,3-cyclohexadiene nor the bicyclic ketone **12** were present at any stage of the photolysis. Two hours after photolysis had begun (conditions as described above), the characteristic set of uv maxima at 246, 256, and 266 m μ due to the trienes **2a**²² could be seen above the tail due to residual ketone **1a**. Two new peaks appeared in the gas chromatograms which corresponded exactly (by coinjection) with the mixture of the *cis*- and *trans*-trienes **2a** isolated as above. These were the only new peaks seen by glpc, although we cannot eliminate the possibility of traces of additional materials produced by further photochemical isomerization of the trienes.²⁴

Photolyses of **1a** in *n*-hexane and 95% ethanol were briefly studied, with results similar to those obtained as above in ethyl ether. Again, the only products observed (uv and glpc analysis) were the trienes **2a**, although some white apparently polymeric solid material was observed on concentration of the hexane photolysate.

Effect of Quenchers. Photolyses of ketone **1a** in ether solution in the presence of naphthalene and piperylene as possible triplet quenchers were studied. In Table I are given the per cent conversions of ketone

Table I. Photolyses of 3,5-Cycloheptadienone (**1a**) in the Presence of Possible Quenchers^a

Quencher	Concn, M	% disappearance of 1a ^b
Set 1		
None		42.2
Piperylene	2.7×10^{-4}	47.5
Piperylene	2.7×10^{-2}	47.3
Piperylene	2.7	48.8
Piperylene	Solvent (10.0)	62.1
Set 2		
None		31.5
Naphthalene	2.7×10^{-4}	35.6
Naphthalene	2.7×10^{-2}	27.6
Naphthalene	2.7×10^{-1}	30.2

^a All tubes contained an aliquot of a single prepared solution (2.7×10^{-2} M) of **1a** in ethyl ether. The Pyrex tubes were contained in a rotating turntable surrounding a 450-W, high-pressure mercury lamp; the irradiation time was 2.0 hr. ^b The internal standard, bromobenzene, used in the glpc analyses was added after irradiation. Analyses were as described in the Experimental Section.

1a in the presence of varying amounts of naphthalene and piperylene as found in a series of competitive irradiations using a standard "merry-go-round" apparatus.²⁵ Analyses were by glpc using an internal standard.

(23) J. Meinwald, P. Anderson, and J. J. Tufariello, *ibid.*, **88**, 1301 (1966).

(24) J. Meinwald and P. H. Mazzocchi, *ibid.*, **88**, 2850 (1966).

(25) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

The extinction coefficients of piperylene are 0.014 at 313 $m\mu$ and 0.000 at 366 $m\mu$, while those for naphthalene are 236 and 0.000 at these two wavelengths, respectively. Thus, it can be calculated that piperylene is not absorbing any appreciable portion of the incident light over the range of concentrations used, involving a variation of over five orders of magnitude. The results indicate no quenching by piperylene of the photolysis of **1a**. The increase in the per cent conversion of **1a** in solvent piperylene is probably beyond experimental error, and is tentatively attributed to a chemical reaction between piperylene and **1a** (e.g., adduct formation) in this solution.

In the naphthalene solutions, the change in concentrations involves a variation in per cent of the light absorbed at 313 $m\mu$ by naphthalene from <3% to >97%. The major portion (>75%) of the incident light is at 366 $m\mu$ due to the characteristics of the lamp and the Pyrex filter, and only dienone **1a** absorbs at this wavelength. However, due to the low concentrations of **1a** used, light absorption at 366 $m\mu$ is incomplete, on the order of 25%. Nevertheless, despite the fact that naphthalene is absorbing a substantial portion of the incident radiation in the more concentrated solutions, no significant change in the per cent conversion of **1a** was noted. Clearly, no quenching by naphthalene is being observed; indeed, naphthalene must be sensitizing this reaction. That this sensitization must be singlet sensitization became clear from the results found below from triplet sensitization with benzophenone and acetone. The triplet energies for naphthalene, *trans*-piperylene, and *cis*-piperylene are 61, 59, and 57 kcal/mol, respectively.²⁶

Sensitized Photolyses of 1a. Benzophenone sensitization of the photolysis was tested by competitive irradiation through Pyrex of an ether solution of **1a** and two ether solutions of **1a** containing enough benzophenone to absorb respectively 89.1% and >99.9% of the incident radiation. Analysis by glpc indicated a single new component in the reaction mixture which had the same retention time (coinjection) as the bicyclic ketone **12** on two different columns. This component was not produced on irradiation of benzophenone alone under the same reaction conditions. Irradiation of **1a** in acetone solution through Pyrex was also studied under concentration conditions where essentially all the light (>99%) was absorbed by acetone. The same new product was detected by glpc, with analysis again on two different columns. After complete disappearance of **1a**, the new component was isolated by removal of acetone and had the same infrared and nmr spectra as an authentic sample of the bicyclic ketone **12**.^{4b,23} Extended irradiation, direct or sensitized, leads to disappearance of **12** and formation of a very complex reaction mixture.²⁷

A large-scale photolysis in acetone was examined for the presence of trienes **2a** using glpc (direct comparison with authentic trienes) and uv spectroscopy. Work-up of a parallel photolysis in ether easily showed the presence of the trienes by both techniques, while none could

be detected from the acetone-sensitized photolysis. It is conservatively estimated from known extinction coefficients (see Experimental Section) that <5% of trienes would have been easily detected in the ultraviolet spectra. It is therefore concluded that, within the small experimental error, sensitized photolysis of **1a** does not give trienes **2a**.

It was also observed that the rate of benzophenone-sensitized disappearance of **1a** was about seven times that of disappearance of **1a** on direct photolysis in ether while the rate of acetone-sensitized disappearance of **1a** was about twice as slow as the unsensitized rate. This is probably due to differences in the efficiencies of light capture in the various tubes.

The fact that the bicyclic ketone **12** is not observed as a product in the irradiations conducted in the presence of naphthalene, which as shown above must involve sensitization by naphthalene in the more concentrated solutions, requires that naphthalene is not acting as a triplet sensitizer. Singlet energy transfer from naphthalene to ketones has been demonstrated previously in the case of 4,4-diphenylcyclohexadienone.²⁸ From the data in Table I, it seems that such singlet energy transfer from naphthalene to 3,5-cycloheptadienone must be particularly efficient. Further discussion is deferred until more suitably controlled experiments are performed.

Discussion

The experiments described above conclusively demonstrate that the direct photolysis of 3,5-cycloheptadienone (**1a**) proceeds exclusively through the lowest singlet n, π^* state to give as primary products carbon monoxide and hexatrienes **2a**. The sensitized photolysis proceeding through a triplet excited state takes an entirely different course which does not involve decarbonylation, to give the valence tautomer bicyclo-[3.2.0]hept-6-en-3-one (**12**). This is therefore one of the very few cases in which both the singlet and triplet excited states of a ketone are chemically reactive but lead to entirely different products.

In the direct photolysis, the same reaction takes place on excitation of the n, π^* transition (Pyrex filters) or of the π, π^* transition (no filters). Since the product of the sensitized photolysis is not seen under these conditions, one must conclude that the decarbonylation reaction of the singlet state competes totally efficiently with intersystem crossing to the triplet manifold. Intersystem crossing rates for ketones are generally in the range of 10^7 – 10^{10} sec^{-1} while corresponding rates for aromatic hydrocarbons and derivatives as well as for aliphatic dienes are much lower by several orders of magnitude.^{29,30} 1,3-Dienes for all practical purposes do not undergo intersystem crossing from the singlet to triplet excited states on direct photolysis, as their photochemistry on direct and sensitized irradiation is usually entirely different.^{7,29} There can be no question but that the excitation of **1a** is being introduced primarily through the carbonyl group. However, the lowest singlet state of **1a** may have a great deal of the

(26) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964); G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964); R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

(27) B. R. Skolnick and J. M. Palmer, unpublished results from this laboratory.

(28) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

(29) For abundant data and references to original work, see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965; N. J. Turro, *Chem. Eng. News*, **84** (May 8, 1967).

(30) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

characteristics of a diene singlet state, which would account for the low efficiency of intersystem crossing. In many β,γ -unsaturated ketones, spectroscopic studies and molecular orbitals calculations^{15,31-33} indicate that there is substantial interaction between the β,γ double bonds and the carbonyl group, which results in mixing of the n,π^* and π,π^* transitions. Such an interaction is indicated for **1a** from its ultraviolet spectrum, and is reasonable on examination of molecular models.

In any case, the decarbonylation of the lowest singlet excited state of **1a** must be an extremely facile process. As far as can be determined experimentally, the decomposition to carbon monoxide and hexatriene **2a** (almost surely only the *cis*-hexatriene is produced initially) is totally concerted.³⁴ This is in marked contrast with the behavior of tropone derivatives and 2,4-cycloheptadienone derivatives.⁴⁻¹² The fragmentation of **1a** can be understood in terms of the very elegant and extraordinarily useful theory developed by Woodward and Hoffman relating reaction modes and symmetry properties of molecules.³⁵ In particular, the fragmentation of **1a** is related to the decomposition of diazenes, discussed by Lemal and McGregor.³⁶ There are two fragmentation modes of the five-ring diazene **13**, as generated by treatment of 3-pyrrolines with nitrohydroxylamine.³⁶ These two modes, represented by

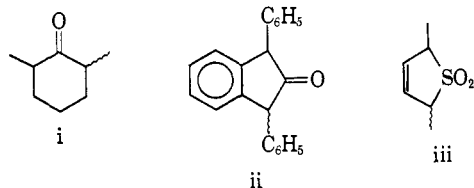
(31) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

(32) A. Moscovitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).

(33) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., Sect. B*, 215 (1967).

(34) We recognize that these results do not exclude the possibility of a two-step mechanism, involving initially a simple α cleavage. A definitive distinction between one- and two-step processes must await further stereochemical studies with substituted derivatives of **1a**. However, the fact that a mechanism for photodecomposition of **1a** via the singlet state competes completely efficiently with a totally different reaction via the triplet state argues in favor of a special mechanism for the singlet reaction. Thus, we have chosen to interpret the results at this time solely in terms of a concerted fragmentation mechanism which is especially favorable in this particular system.

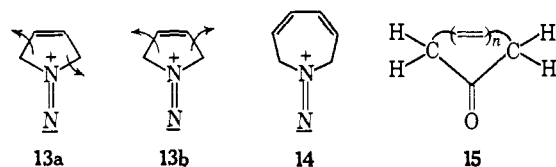
A referee has raised the question of the relevance of this work to the apparent nonstereospecificity observed in the decomposition of some related systems, which seem to be best interpreted in terms of a two-step cleavage process. The most definitive results are those of ketone i [R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965)] which gives the same mixture of *cis*- and *trans*-1,2-dimethylcyclopentanes from photolysis of either the *cis*- or *trans*-dimethylcyclohexanone in the gas phase. The results require a diradical intermediate and rule out a concerted mechanism in this case. On the basis of results with added oxygen the authors suggest the relative unimportance of triplet states in this process, although triplet contributions cannot be definitively ruled out.⁵ Similarly, the decarbonylation of ketone ii is not completely stereospecific [G. Quinkert, K. Opitz, W. Wiersdorff, and M. Finke, *Ann.*, **693**, 44 (1966)], nor is the extrusion of sulfur dioxide on sensitized photolysis of the *cis*- and *trans*-sulfolenes iii [J. Saltiel and L. Metts, *J. Amer. Chem. Soc.*, **89**, 2232 (1967)], although these processes show some stereoselectivity. However, these reactions which proceed wholly or in part via excited triplet states may follow quite different reaction pathways compared with the decarbonylation in solution of **1a** exclusively via the singlet state. Srinivasan⁶ favors an interpretation involving concerted processes for the gas-phase decarbonylations of cyclic ketones and also for the ring contractions of cyclic ketones observed in the liquid phase [R. Srinivasan and S. E. Cremer, *ibid.*, **87**, 1647 (1965)].



(35) R. B. Woodward and R. Hoffman, *ibid.*, **87**, 395, 2511 (1965); R. Hoffman and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(36) D. M. Lemal and S. D. McGregor, *ibid.*, **88**, 1335 (1966).

13a and **13b**, are termed axisymmetric and sigmasymmetric, respectively, to denote, for concerted fragmenta-



tion, transition states possessing a twofold or higher symmetry axis or a mirror plane, respectively. Lemal and McGregor³⁶ demonstrated using methyl-substituted derivatives that the thermal decomposition of **13** into nitrogen and substituted 1,3-butadiene proceeds exclusively sigmasymmetrically, in accord with predictions based on orbital symmetry arguments. These arguments can be extended to the seven-ring diazene **14** which is predicted³⁶ to decompose thermally exclusively by the axisymmetric mode. **14** is of course isoelectronic with ketone **1a**, and it is expected that they should behave in much the same way, in the absence of other perturbing effects. If the excited state of **1a** which undergoes reaction maintains the geometry of the starting material, the system is then constrained to react via an axisymmetric mode analogous to the ground state of diazene **14**. In a planar geometry for **1a**, the sigmasymmetric mode of reaction seems to be preferred for the first excited singlet state.³⁷ At any event, the symmetrical nature of the system allows for a concerted reaction path for **1a** via the spin-paired singlet state, leading to decarbonylation, which is not allowed for the unsymmetrical 2,4-dienones. Similar considerations rationalize the conversion of **8** to **9**.¹⁵ The exact stereochemistry of the ring opening of **1a** is of much interest, and is under study in other laboratories.³⁸

It is clear that this type of photodecarbonylation via the singlet state ought to be a general reaction of ketones of the general formula **15** which possess either a C_2 axis or a plane of symmetry.

The sensitized photolysis of **1a** leading exclusively to the bicyclic valence tautomer **12** is very interesting. This reaction must pass through a triplet state of **1a**; whether this is a diene-like π,π^* or a ketone-like n,π^* triplet state cannot be assigned with absolute confidence, although the former seems more likely (see below). It is well known that the triplet states of dienes are generally less than 60 kcal/mol above the ground state, compared with much higher energies (65-83 kcal/mol) for ketone n,π^* triplet states in most cases studied.^{26,29} Generally, the triplet states of simple olefins are of higher energy than ketone n,π^* triplets. The energy of the lowest triplet for the twisted diene configuration of **1a** should be intermediate between that for cisoid planar dienes (e.g., cyclohexadiene $E_T = 54$ kcal/mol)^{39,40} and for simple olefins (between 70 and 82 kcal/mol).^{39,40} It is therefore not unexpected that triplet transfer can occur from benzophenone ($E_T = 68.5$ kcal/mol)^{7,26,29} and acetone ($E_T \sim 82$ kcal/mol)^{29,41} to give initially a twisted diene triplet of

(37) These arguments depend on the assumption that the lowest antibonding molecular orbital is the π^* orbital of the carbonyl group.

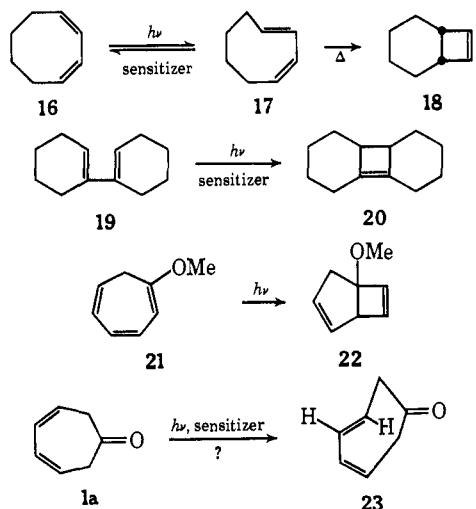
(38) Professor D. M. Lemal of Dartmouth College has prepared the *cis*- and *trans*-2,6-dimethyl-3,5-cycloheptadienones and is studying the stereochemistry of their photodecarbonylation.

(39) Reference 29, pp 214-220.

(40) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

1a. The behavior and character of this triplet state may well be independent of the presence of the carbonyl group, although this interpretation is not necessary for the balance of the discussion.⁴²

Before proceeding further, it is well to consider some recent investigations of the mechanism of valence tautomerizations. Liu⁴⁵ has made the very important observation that the photosensitized conversion of *cis,cis*-1,3-cyclooctadiene (**16**) to bicyclo[4.2.0]oct-7-ene (**18**) is a two-step process involving first sensitized isomerization of the diene to its *cis,trans* isomer **17**, followed by thermal closure of **17** to **18** as previously found by Fonken.⁴⁶ Liu suggests that the direct photoconversion of **16** to **18** may not involve **17** as an intermediate. The photosensitized conversion of **19** to **20** has also been reported⁴⁷ and Liu⁴⁵ suggests that this may also take place by way of a *cis,trans* intermediate. A number of examples are known in which formation of cyclobutene derivatives on photolysis of cyclic and acyclic dienes and trienes almost surely involves only singlet excited states.^{47,48} A very recent example is the photoconversion of **21** to **22** described by Chapman and his coworkers.⁴⁹ These reactions most likely do not occur



through vibrationally excited ground-state molecules produced by internal conversion from the excited singlets, in agreement again with orbital symmetry considerations.^{35,49}

The course of the conversion of the excited triplet of **1a** to the bicyclic valence tautomer **12**, by analogy with the results of Liu,⁴⁵ may occur by isomerization of the

twisted triplet to the *cis,trans*-3,5-cycloheptadienone (**23**), which then closes to **12** in a thermal (dark) reaction. Compound **23** with five trigonal atoms in a seven-membered ring would be even more strained, and hence more reactive, than *trans*-2-cycloheptenone which has been described by Corey⁵⁰ and Eaton.⁵¹ Experiments are in progress to obtain evidence for the intermediacy of **23** in this reaction using the kind of techniques which were successful in the identification of *trans*-2-cycloheptenone.^{50,51}

Experimental Section⁵²

Synthesis of 3,5-Cycloheptadienone (1a). Details of the synthesis according to the procedure of Parham^{14,16} can be found elsewhere.⁵³ The procedure described below is a further modification of the reaction originally reported by Chapman¹⁷ as first modified by Schuster, *et al.*¹⁸

In a typical run, 15 g (0.14 mol) of tropone⁵⁴ in 300 ml of anhydrous ether was added dropwise to a stirred suspension of 2.69 g (0.284 equiv) of lithium aluminum hydride in 380 ml of anhydrous ether. After 30 min of stirring at room temperature, 42.1 g (0.57 equiv) of ethyl formate in 275 ml of ether was added dropwise to the reaction flask cooled in an ice-water bath. After 30 min, the mixture was hydrolyzed by the addition of 5.4 ml of water and 4.3 ml of 10% sodium hydroxide solution. The mixture was stirred until the salts became granular, whereupon it was filtered and the salts were washed three times with ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and filtered and the solvent removed at reduced pressure. Spinning-band distillation of the residue gave 5 g (30% of theory) of pale yellow liquid, bp 52–54° (9.5 mm). Analysis by glpc indicated the material was contaminated by traces (1% or less) of 3,5-cycloheptadienol (**6**). Infrared spectra of the material were in excellent agreement with those of ketone **1a** prepared by the method of Parham^{14,16} and with available literature data.^{13,14,16,17} The ultraviolet spectrum is reported in the text, and was notable for the absence of a peak at 290 m μ which had characterized earlier samples⁵³ and which has been attributed by Parham¹⁴ to contamination by 2,4-cycloheptadienone. The nmr spectrum shows a sharp doublet (4 H) at 2.60 and 2.68 ppm (relative to external TMS) and an unsymmetrical multiplet (4 H) between 5.2 and 6.0 ppm for a neat sample of **1a**. This spectrum is substantially shifted from that reported by Parham:¹⁴ doublet at 2.97 and 3.06 ppm and vinyl hydrogen multiplet at 5.58–6.43 ppm for a 10% solution in CCl₄. The discrepancy may be due to differences in the state of the sample or to errors in calibration in the earlier spectrum.¹⁴ We have found that the spectrum does shift in CCl₄ solution but by no more than 0.2 ppm from that of the neat sample. The *N*-phenylmaleimide derivative of **1a** was identical with that reported earlier.^{13,14,17}

Bicyclo[3.2.0]hept-6-en-3-one (12). The bicyclic ketone **12** was prepared by the method of Chapman, *et al.*,^{4b} by photochemical conversion of the 3,5-cycloheptadienol **6** to the bicyclic alcohols **7** and subsequent Jones oxidation to the ketone. The modifications of Meinwald, *et al.*,²³ were used in the last step. The infrared spectrum of **12**, which has not been reported previously in full, shows bands at 3040, 2970 (broad), 2880 (s), 1750 (s) (lit.^{4b} 5.73 μ), 1450 (w), 1410 (m), 1380 (w), 1310 (m), 1240 (w), 1028 (m), 885 (m), 825 (m), 790 (w), and 750 cm⁻¹ (s). The nmr spectrum (neat sample, external tetramethylsilane) shows a sharp singlet for the vinyl protons (2 H) at 5.92 ppm, a doublet (2 H) ($J = 7$ Hz) centered

(50) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

(51) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

(52) Infrared spectra were obtained on a Perkin-Elmer grating Infracord spectrophotometer Model 337 and ultraviolet spectra on a Cary 15 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60 spectrometer with tetramethylsilane as an internal (or occasionally external) reference. Gas-liquid partition chromatography (glpc) was carried out in the direct photolyses on a Perkin-Elmer Model 154 gas chromatograph and in the sensitized photolyses and the attempted quenching studies on an F & M 700 gas chromatograph, all using thermal conductivity detection.

(53) F.-T. H. Lee, Ph.D. Dissertation, New York University, 1966.

(54) Prepared by the procedure of P. Radlick, *J. Org. Chem.*, **29**, 960 (1964), from 1,3,5-cycloheptatriene. We gratefully acknowledge generous gifts of cycloheptatriene from the Shell Chemical Corporation.

(41) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(42) The acetophenone-photosensitized valence tautomerization of 1,3-cycloheptadiene (**3**) to bicyclo[3.2.0]hept-6-ene has been reported by Frey and his coworkers.⁴³ We wish to thank Dr. Frey for calling this article to our attention. Liu has also observed sensitization of this tautomerism reaction with acetophenone and xanthone,⁴⁴ and has found that the reaction is much slower than similarly sensitized photolyses of 1,3-cyclooctadiene.⁴⁵

(43) G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **62**, 659 (1966).

(44) R. S. H. Liu, private communication.

(45) R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).

(46) K. M. Shumate, P. N. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965).

(47) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *ibid.*, **88**, 2742 (1966).

(48) R. Srinivasan, *ibid.*, **84**, 3432, 4141 (1962); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964), and numerous other references cited therein.

(49) G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *J. Amer. Chem. Soc.*, **89**, 2979 (1967).

at 3.23 ppm which is split extensively further, and a multiplet (4 H) between 1.7 and 2.3 ppm. These data are all consistent with the structure for **12**.

Photolysis of Ketone 1a. The ethyl ether used as solvent in these experiments was anhydrous grade and was freshly distilled from lithium aluminum hydride before use. The reaction vessel and the nitrogen purification train have been previously described.⁵⁵ Solutions of 0.3–2.0 g of **1a** in 300 ml of ether were irradiated at room temperature with a 450-W Hanovia high-pressure mercury lamp for varying periods of time with and without Pyrex filter sleeves surrounding the lamp. Evaporation of ether was minimized by maintaining a positive nitrogen pressure in the system without bubbling nitrogen through the solution. Solutions were purged with nitrogen for 40–60 min before irradiation. Aliquots were withdrawn periodically through a stopcock at the bottom of the flask and examined by glpc and ultraviolet spectroscopy. Where necessary, solutions were concentrated under nitrogen before analysis. Control samples of the solution were always put aside and kept in the dark during the irradiation, and were analyzed along with the photolysate after irradiation.

For the glpc analyses, Perkin-Elmer column C (20% DC-200 silicone oil on GC-22) at 100° was used initially to separate ketones **1a** and **12** and column K (Carbowax 1500) at 58° was used to separate the trienes from 1,3-cyclohexadiene. Most of the analyses were made on a 6-ft stainless steel column of Dow 710 silicone oil 25% on 60–80 mesh Chromosorb P. Hydrocarbon analyses were made at 70° and ketone analyses at 100°.

For runs in which carbon monoxide evolution was measured, no aliquots were withdrawn during the reaction. The outlet at the top of the condenser attached to the photolysis flask was connected to a gas buret *via* a Dry Ice-acetone trap to condense any solvent vapor carried out during the reaction. The total change in gas volume, corrected to standard conditions, was taken as the volume of carbon monoxide evolved. The final reading was taken when the change of volume was either zero or 2–5 ml over a period of 1 hr or more. The values obtained, as per cent of theory based on the amount of ketone used, were 74 and 88% in ethyl ether photolyses, 73% in a hexane run, and 91% in an ethanol run.

Attempted Quenching Studies. Diethyl ether and piperylene (K & K Laboratories) were freshly distilled prior to use. Dienone **1a** (450 μ l, 462.6 mg) was dissolved in 50 ml of ethyl ether. To each of five Pyrex tubes⁵⁶ was added 5 ml of the above solution. To three of the tubes was added, respectively, 0.4 μ l, 42.7 μ l, and 4.27 ml of piperylene, and the five tubes were brought to 15 ml with ether (density of piperylene is 0.683 g/ml). One tube without any added piperylene was set aside as a control, and the four tubes were placed in a turntable surrounding a 450-W Hanovia high-pressure mercury lamp in a quartz immersion well. The turntable was rotated slowly and the tubes were irradiated for 2 hr. At the end of this time, 20 μ l of bromobenzene was added to each of the tubes, and the solvent was removed at reduced pressure at room temperature until the residual volume was about 1 ml. The mixture was analyzed by glpc on a 6-ft 20% DC-200 silicone oil on 60–80 mesh Chromosorb P column at an oven temperature of 125° and a helium flow rate of 50–60 cc/min. The areas under the peaks due to the standard (bromobenzene) and dienone **1a** were measured using a planimeter after triangulation. Each set of chromatograms was measured twice in this way, and the results were converted to per cent reaction based on starting dienone **1a** and are given in Table I.

A set of tubes was prepared as above with naphthalene instead of piperylene. The naphthalene was recrystallized from petroleum ether, dried under vacuum before use, and added to each of three tubes to the extent of 0.5, 54.8, and 548.9 mg. The procedure otherwise was identical with that described above using piperylene.

Benzophenone-Sensitized Photolyses of 1a. For the 450-W Hanovia high-pressure mercury lamp, 80.3% of the spectral distribution in the presence of Pyrex filters occurs at 3130 and 3600 Å. The extinction coefficients for ketone **1a** at these two wavelengths in ether solution are 73.6 and 4.1, respectively, and for benzophenone 58.8 and 68.0, respectively. To each of four Pyrex tubes was added a solution containing 47.7 mg of **1a** (4.4×10^{-4} mol). Benzophenone was added to two tubes to the extent of 0.485 and 2.6305 g, and the total volume of all tubes was brought up to 15 ml with

ether. In the two tubes containing benzophenone, it is calculated that benzophenone is absorbing respectively 89.1% and > 99.9% of the incident light. One tube without benzophenone was set aside as a control, and the three remaining tubes were irradiated as described in the quenching studies for 2.25 hr and then were analyzed by glpc on the 20% DC-200 column at 140° with bromobenzene as internal standard. Retention times of **1a** and bromobenzene were 3.00 and 2.27 min, respectively, at a flow rate of 60 cc/min. A new peak appeared in the chromatogram at 2.37 min, which was the retention time for bicyclic ketone **12**, which on coinjection with **12** was enhanced with no separation. A single peak was also observed on coinjection with **12** on a 4-ft 10% Carbowax 20M on Chromosorb P column at 111°.

Quantitative estimates by glpc of the extent of reaction in benzophenone-sensitized *vs.* unsensitized photolyses of **1a** in ether are difficult because of tailing of the peak due to the ketone **1a** and incomplete separation of the peaks due to **1a** and bicyclic ketone **12**. It can be roughly estimated that after 1 hr of competitive photolysis, about 70% reaction had occurred in the tube containing benzophenone compared with about 10% in the tube without benzophenone.

Acetone-Sensitized Photolyses of 1a. Competitive photolyses of **1a** in ether and acetone were carried out in Pyrex tubes on the merry-go-round apparatus for 2 hr using the 450-W Hanovia lamp. In a typical run, there was 24 mg of **1a** in a total volume of 20 ml of either acetone or ethyl ether. The measured extinction coefficient of acetone (in benzene solution) is 6.8 at 3130 Å and 0.24 at 3660 Å. Under the photolysis conditions, well over 99% of the incident light is being absorbed by acetone in the acetone solutions. Bromobenzene (15 μ l) was added to each tube as an internal standard for glpc analysis as described above. As in the benzophenone-sensitized reactions, a new peak appeared in the chromatograms which was identical in retention time with that of the bicyclic ketone **12** (coinjection) on the 6-ft DC-200 column and the 4-ft Carbowax 20M column. After 2 hr, the amount of **1a** which had reacted in the acetone solution was 34% compared with 60% in the ether solution photolyzed concurrently, while after 3 hr 56% **1a** had been consumed in the acetone solution while all had undergone reaction in the ether solution. These numbers are admittedly crude, because of the incomplete separation of peaks due to the standard, bromobenzene, and bicyclic ketone **12**. However, there can be no doubt that the rate of disappearance of ketone **1a** is about twice as fast in the ether as compared with the acetone solution.

A larger scale photolysis, 0.510 g of **1a** in 500 ml of acetone, was carried out in the reaction vessel described originally.⁵⁵ The system was purged with nitrogen before photolysis, and aliquots were withdrawn frequently for glpc analysis. After 35 min, the ketone **1a** had completely disappeared. The solvent was removed to give a residue of 0.67 g (containing some acetone). Analysis of the residue by glpc indicated there was only one major component, identical by coinjections on the columns mentioned above with authentic **12**. The infrared and nmr spectra of the crude residue were identical with that of **12** in every respect, except for some infrared absorption in the hydroxyl region and a few minor extraneous shoulders elsewhere. The over-all agreement is excellent, suggesting the product is at least 95% **12**, in accord with the glpc results.

In another competitive merry-go-round experiment, at concentrations as described above, ether and acetone photolysates after 2 and 3 hr (separate tubes) were diluted 1:500 with ether and examined by uv spectroscopy. The ether photolysate showed the set of maxima at 246, 256, and 266 $m\mu$ characteristic of the trienes **2a**, as seen above. The extinction coefficients for a mixture of trienes at these wavelengths are reported as 35,000, 48,000, and 39,000, respectively.²² The diluted acetone photolysate showed in this region only a symmetrical peak centered at 277.5 $m\mu$, due to acetone. The extinction coefficient of acetone at this wavelength is 15, from which one can calculate that the absorbance of the trienes **2a** at 256 $m\mu$ would have been 0.7 relative to that of acetone (0.45) at 278 $m\mu$ if the trienes had been produced quantitatively from **1a**. In fact, no shoulders at all are seen at 246, 256, and 266 $m\mu$ on the acetone peak, which is nearly superimposable on that of pure acetone at the same dilution. This is strong evidence that there is no triene **2a** in the acetone photolysate. Supporting evidence is obtained by glpc analysis⁵⁷ of the concentrated ether and acetone photolysates on the 25% DC-710 on Chromosorb P column at 70°. The ether photolysate clearly shows two peaks at retention times corresponding to that of the triene **2a** while no such peaks

(55) D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **88**, 1722 (1966).

(56) In this and the following experiments, no attempt was made to check the uniformity of the Pyrex tubes. This may account, to some extent, for some of the minor differences in the data reported in Table I.

(57) These analyses were carried out on a F & M Model 810 gas chromatograph using flame ionization detection, under conditions of very high sensitivity.

can be seen in the concentrated acetone photolysate after 2 and 3 hr.

Acknowledgment. This work was supported through grants from the U.S. Army Research Office, Durham,

which we gratefully acknowledge. Some preliminary studies were supported in part by an Institutional Grant to New York University by the National Science Foundation.

Steroids. CCCXVII.¹ Photochemical Cycloadducts. III.² Addition of Ethylene and Maleic Anhydride to a Linear Dienone

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Contribution from the Institute of Steroid Chemistry, Syntex Research, Palo Alto, California. Received July 31, 1967

Abstract: The photochemical addition of ethylene to 17 β -acetoxyandrosta-4,6-dien-3-one (I) gave approximately equal amounts of the 4 β ,5 α - and 4 α ,5 α -ethylene adducts II and III, and a small amount of the 6 β ,7 β adduct IV. Photochemical addition of maleic anhydride to I produced a mixture of the 4 α ,5 α , 6 α ,7 α , and 6 β ,7 β adducts in yields of 15, 19, and 57%, respectively. The 6,7-maleic anhydride adducts were converted *via* the corresponding diacids Vb and VIb to the 6,7-vinylene adducts VIII and IX. A correlation between the maleic anhydride and ethylene additions is described. The structures of the compounds are deduced mainly from their nmr and ORD spectra.

Recently several reports of photochemically induced intermolecular cycloadditions of olefinic compounds to unsaturated carbonyl systems have been published.⁴ The method is of considerable utility for the preparation of cyclobutane compounds bearing a wide variety of substituents. In the course of our investigations of the photochemistry of steroids,^{2,5} it became of interest to examine the addition of certain olefins to an $\alpha,\beta,\gamma,\delta$ -unsaturated ketone. 17 β -Acetoxyandrosta-4,6-dien-3-one (I) was chosen as a model unsaturated ketone and ethylene and maleic anhydride as addition substrates. It has been previously reported⁶ that dienones of this type will undergo dimerization when irradiated, but the addition of different olefinic compounds has apparently not been studied.

Bubbling a stream of ethylene through an irradiated benzene solution of I, for a period of 6 hr, resulted in a slow cycloaddition to give the *trans*-fused adduct 17 β -acetoxy-4 β ,5 α -ethyleneandrost-6-en-3-one (II) in 7% yield, and the corresponding *cis*-fused adduct, 17 β -acetoxy-4 α ,5 α -ethyleneandrost-6-en-3-one (III), was isolated in 5% yield. In addition, *ca.* 1% of the 6,7 cycloadduct 17 β -acetoxy-6 β ,7 β -ethyleneandrost-4-en-3-one (IV) and *ca.* 30% of recovered starting material were also isolated. The remainder of the material was accounted for by several very polar products whose isolation and characterization were not attempted.

(1) Steroids. CCCXVI: L. Cuellar, H. Martinez, and P. Crabbé, *Steroids*, in press.

(2) For part II see P. Sunder-Plassmann, P. H. Nelson, L. Durham, J. A. Edwards, and J. H. Fried, *Tetrahedron Letters*, 653 (1967).

(3) Syntex Postdoctoral Fellow, 1965-1966.

(4) See, for example, E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966); Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966); J. J. McCullough and J. M. Kelly, *J. Amer. Chem. Soc.*, **88**, 5935, (1966).

(5) P. Sunder-Plassmann, J. Zderic, and J. H. Fried, *Tetrahedron Letters*, 3451 (1966).

(6) H. C. Thronsdon, G. Carnelli, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2342 (1962); M. B. Rubin, G. E. Hipps, and D. Glover, *J. Org. Chem.*, **29**, 68 (1964).

In order to obtain a larger proportion of addition to the γ,δ double bond, we next studied the photochemical addition of maleic anhydride to I, in the expectation that excited maleic anhydride would add preferentially to the more electron-rich 6,7 double bond of the ground-state dienone. Irradiation of an equimolar mixture of I and maleic anhydride under the same conditions as above led to rapid addition with only a trace of starting material being detectable after 40 min. The composition of the resulting mixture of anhydride adducts had to be determined after conversion to the corresponding diesters by mild alkaline hydrolysis followed by diazomethane methylation, since the primary products of addition were too easily hydrolyzed to be chromatographed.

The major product, obtained in 55% yield, was 17 β -acetoxy-6 β ,7 β -ethyleneandrost-4-en-3-one-6'-*exo*-7'-*exo*-dicarboxylic acid dimethyl ester (Va). The corresponding 6 α ,7 α isomer VIa was isolated in 19% yield, and the product resulting from addition to the 4,5 double bond, 17 β -acetoxy-4 α ,5 α -ethyleneandrost-6-en-3-one-4'-*exo*-5'-*exo*-dicarboxylic acid dimethyl ester (VII), was obtained in 15% yield, in addition to *ca.* 5% of recovered starting material.

Degradation of the 6,7-anhydride adducts appeared to be a useful route to the epimeric 6,7-vinylene and 6,7-ethylene adducts, as well as providing an opportunity to identify the minor product from photoaddition of ethylene to I, which had not been obtained in large enough amounts or in sufficient purity⁷ for conventional structure determination. The diacids Vb and VIb were isolated by preparative tlc of the crude mixture of diacids obtained by mild hydrolysis of the total reaction product⁸ from maleic anhydride addition to I. The

(7) This compound was contaminated with an impurity which could not be removed by recrystallization or chromatography. The nature of the impurity will be discussed later.

(8) The more abundant diacid Va could also be obtained by direct crystallization of the crude hydrolysis mixture, or by hydrolysis of its