We are presently investigating a wide variety of aminium radical cations.

Acknowledgments. We are indebted to Professor N. C. Deno of Pennsylvania State University for suggesting this method of generating the dialkylaminium radicals. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF 5579-AC4), for support of this work. Thanks are also due to Kansas State University for assistance in defraying computing costs.

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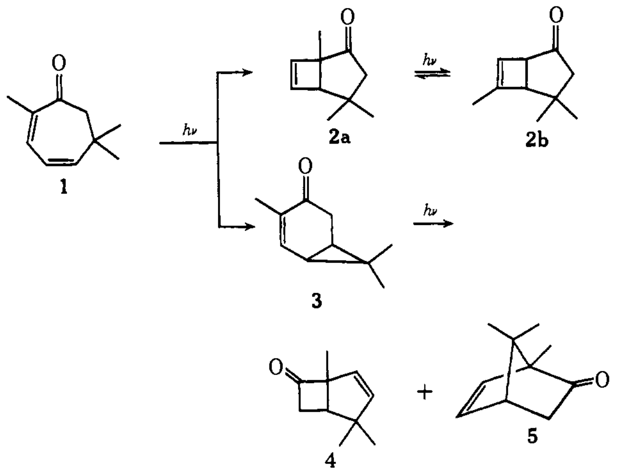
Photoisomerization of 2,7,7-Trimethyl-2,4-cycloheptadienone

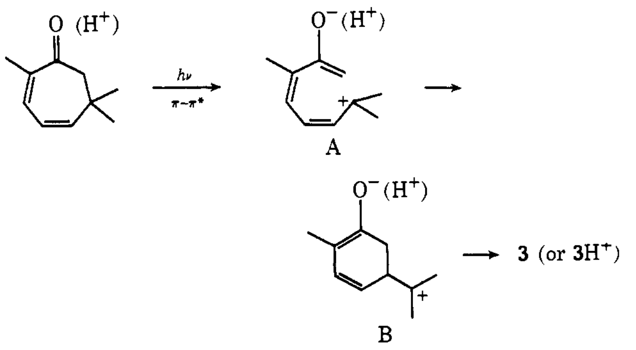
Sir:

We wish to report a previously unobserved type of photoisomerization of conjugated cycloheptadienones, and to call attention to the important role which alkyl substituents may play in determining product structure.

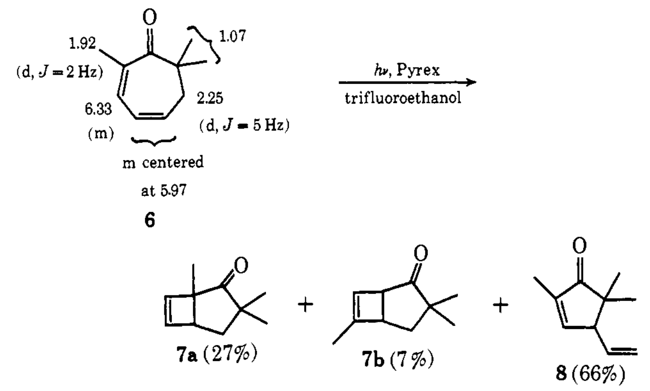
Eucarvone (**1**), long considered the prototype for cycloheptadienone photoisomerizations,[1] rearranges primarily by two paths as shown.[1e] Nonpolar solvents favor **2a** and **2b**, whereas polar solvents favor **3**–**5** suggesting that these two sets of products are derived from two close-lying excited states, $n-\pi^*$ and $\pi-\pi^*$, respectively. Credibility was lent to this suggestion by the finding[1f] that protonated **1** (**1**H$^+$), which of necessity reacts from a $\pi-\pi^*$ excited state, gave mainly **3**H$^+$.



Plausible mechanisms[1e,1f] for the formation of **3** (or **3**H$^+$) from **1** (or **1**H$^+$) involve intermediates (such as A and B) which place a positive charge on the carbon which bears the *gem*-dimethyl group. It seemed possible that **3** and related products were therefore not necessarily characteristic of all cycloheptadienones, but only of those with substituents at C-6 which stabilize carbonium ions. To test this possibility, we synthesized and irradiated a cycloheptadienone with a *gem*-dimethyl group at C-7, rather than at C-6.



2,7,7-Trimethyl-2,4-cycloheptadienone (**6**) was synthesized from cycloheptanone in an unexceptional manner.[2] Irradiation of **6** in cyclohexane through Pyrex (450-W Hanovia lamp) was slow, and gave a mixture of three products, **7a**, **7b**,[3] and **8**,[4] each of which was isomeric with the starting material. No products resulting from α cleavage were observed, despite the



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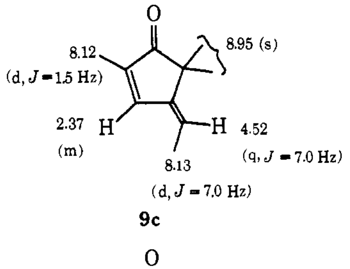
(1) (a) G. Buchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960); (b) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 710 (1963); (c) D. I. Schuster, M. J. Nash, and M. L. Kantor, *Tetrahedron Lett.*, 1375 (1964); (d) D. I. Schuster and D. H. Sussman, *ibid.*, 1657 (1970); (e) T. Takino and H. Hart, *J. Chem. Soc. D*, 450 (1970); *J. Amer. Chem. Soc.*, **93**, 720 (1971); (f) K. E. Hine and R. F. Childs, *ibid.*, **93**, 2323 (1971).

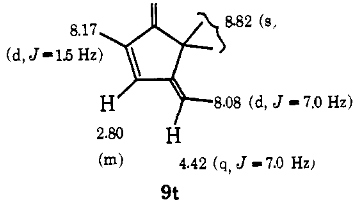
(2) Synthetic, structural, and analytical details will be presented in a full paper.

(3) The structures of **7a** and **7b** rest on their spectra and on their photochemical interconversion.

(4) Ir 1705, 1640 (cyclopentenone), 930 cm^{-1} (terminal methylene); uv 344 nm (ϵ 45), 330 (60), 317 (50), 275 (143), 225 (93,700); nmr δ 0.87, 1.07 (s, 3 H each, *gem*-dimethyls), 1.75 (d of d, 3, J = 1.8, 2.5 Hz, allylic methyl split by protons at C-3 and C-4, respectively), 3.03 (d split into quintets, 1, J = 8.0, 2.5 Hz, methine split by the adjacent proton of the C-4 vinyl group and by the C-2 methyl and C-3 vinyl protons, respectively), 4.6–6.0 (m, 3, protons of the C-4 vinyl group), 6.98 (m, 1, C-3 vinyl proton). Splittings were verified by decoupling. Treatment of **8** with base (1 *M* NaOCH$_3$ in CH$_3$OH) caused isomerization to the fully conjugated dienones **9c** and **9t**.[2]



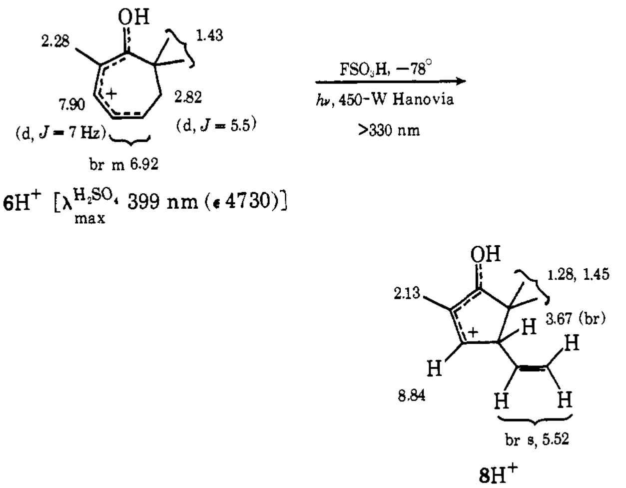
9c



9t

presence of a tertiary α carbon atom. The same products were formed about 10 times faster when the solvent was trifluoroethanol (75% conversion of **6** to **7** and **8** in 2 hr).

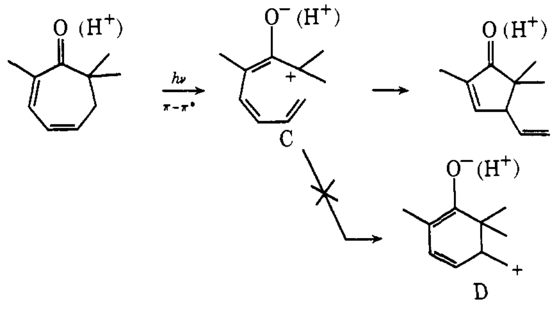
A vinyl cyclopentenone such as **8** has not been observed previously in any cycloheptadienone photoisomerization. Since polar solvents favor its formation, **8** is believed to arise from a π–π^* state of the cycloheptadienone.[5] To test this possibility, **6** was irradiated in FSO$_3$H at −78°. The sole initial photoproduct was **8H**$^+$,[6] which can only arise from a π–π^* state of the protonated cycloheptadienone. This results is in striking contrast with the irradiation of protonated eucarvone.[1f]



6H$^+$ [$\lambda_{\max}^{H_2SO_4}$ 399 nm (ϵ 4730)]

8H$^+$

The results can be rationalized using an intermediate such as C (analogous to A). In contrast with A, C will have the greatest positive charge density at the other end of the unsaturated system because of the different location of the *gem*-dimethyl group. Cyclization to D (analog of A → B) is highly unfavorable, whereas cyclopentenone formation encounters no difficulties.[7]



One may generalize these results and propose that in reactions from the π–π^* state of 2,4-cycloheptadienones (or their protonated forms), substituents which stabilize a positive charge will favor products of the type **3** if located at C-6, and of the type **8** if located at C-7. In preliminary confirmation of this proposal, we have found that a single methyl substituent added to C-7 of eucarvone (*i.e.*, 2,6,6,7-tetramethyl-2,4-cycloheptadienone) is sufficient to divert some of the π–π^* product to the cyclopentenone type.[8]

It is clear that the presence or absence of particular substituents at various ring positions can have a profound effect on the structure of cycloheptadienone photoproducts, and that eucarvone should not be considered a universal model for such systems.[9]

Acknowledgment. We are indebted to the National Institutes of Health (GM 15997) for their generous financial support.

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[5] Preliminary experiments indicate that **7a** arises from an n–π^* state.

[6] The internal reference for the nmr spectra was (CH$_3$)$_4$N$^+$BF$_4^-$, δ 3.10. No thermal isomerization of **6H**$^+$ occurred at −78°. Prolonged irradiations give some **9cH**$^+$, **9tH**$^+$ and an unidentified ion, but these were shown to arise from the slow thermal rearrangement of **8H**$^+$ in FSO$_3$H.

[7] Analogous cyclizations of heptatrienyl cations to cyclopentenyl cations are well known (for examples, see T. S. Sorensen in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 807–835). Cyclization occurs in the most favorable sense, which in the present instance is to give a carbonium ion which is stabilized by the oxygen function.

[8] The addition of a single methyl at C-7 leads to stereoisomeric products; the chemistry of this system will be discussed in a separate paper.

[9] After this paper was submitted, a pertinent related paper appeared on the photoisomerization of 2,4-cycloheptadienone and its 2-methyl derivative [K. E. Hine and R. F. Childs, *J. Chem. Soc. D*, 145 (1972)]. D. I. Schuster and M. A. Tainsky have also studied the unsubstituted dienone (private communication from Professor Schuster). Both groups have independently recognized the atypicality of eucarvone, and the significant role which alkyl substitution can play in the photoisomerization of conjugated cycloheptadienones.

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Prephytoene Pyrophosphate. A New Intermediate in the Biosynthesis of Carotenoids

Sir:

The early steps of the biosynthesis of sterols and carotenoids proceed along nearly identical pathways of head-to-tail terpene condensation, which are followed by the head-to-head condensation of two polyprenyl pyrophosphate moieties. The sterol precursor squalene is the product of a head-to-head condensation of farnesyl pyrophosphate, while phytoene, the first 40-carbon carotenoid, arises from a similar condensation of geranylgeranyl pyrophosphate.[1] Recently, we isolated, characterized, and unambiguously synthesized presqualene pyrophosphate, an intermediate between farnesyl pyrophosphate and squalene.[2–4] Since these two pathways are analogous, a 40-carbon cyclopropylcarbinyl pyrophosphate ester would be anticipated as precursor to phytoene. We now report the isolation, characterization, and synthesis of this precursor **1a**, for which we propose the name prephytoene pyrophosphate.

Geranylgeraniol was prepared by a coupling[5] of **2** and *trans*-**3** in tetrahydrofuran[6] followed by reduction of the initial coupling product with lithium in ethylamine at −78°. The geranylgeraniol so obtained (87% all trans) was further purified by successive recrystallizations of the diphenylurethane derivative,[7]

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[1] (a) T. W. Goodwin, *Biochem. J.*, **123**, 293 (1971); (b) T. C. Lee and C. O. Chichester, *Phytochemistry*, **8**, 603 (1969).

[2] W. W. Epstein and H. C. Rilling, *J. Biol. Chem.*, **245**, 4597 (1970).

[3] H. C. Rilling and W. W. Epstein, *J. Amer. Chem. Soc.*, **91**, 1041 (1969).

[4] L. J. Altman, R. C. Kowerski, and H. C. Rilling, *ibid.*, **93**, 1782 (1971).

[5] J. F. Biellmann and J. B. Ducep, *Tetrahedron Lett.*, 3707 (1969).

[6] E. E. van Tamelen, P. McCurry, and U. Huber, *Proc. Nat. Acad. Sci. U. S.*, **68**, 1294 (1971), and references cited therein.

[7] R. B. Bates, D. M. Gale, and B. J. Gruner, *J. Org. Chem.*, **28**, 1086 (1963).