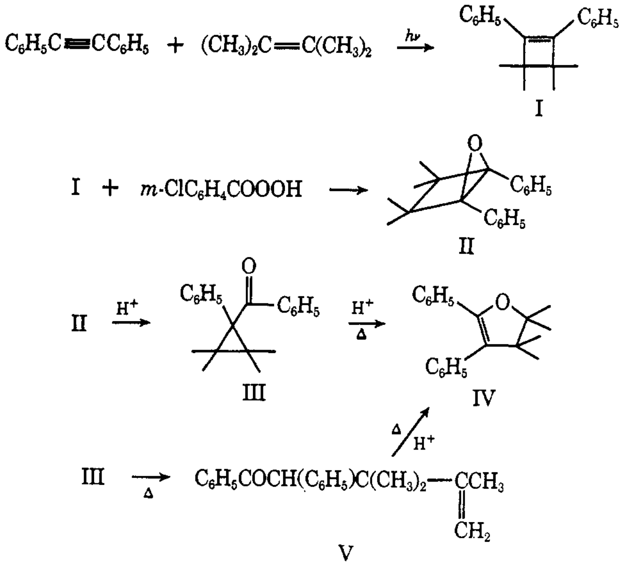
Photochemical and Thermal Reactions of 5-Oxabicyclo[2.1.0]pentane Characteristic of the Carbonyl Ylide

Sir:

Photolysis and pyrolysis of three-membered rings frequently yields products derived from the intermediate 1,3 diradicals or 1,3 dipoles.[1] If the three-membered ring is incorporated in a fused ring system where strain is relieved upon bond homolysis or heterolysis, the resulting cyclic 1,3 diradical or 1,3 dipole will be more stable, relative to the starting material, than in the analogous acyclic system.[2] Furthermore, ring closure of a cyclic 1,3 diradical or 1,3 dipole by a symmetry-allowed conrotatory process[3] results in *trans*-fused rings which in the smaller systems is clearly impossible. Thus, to the extent that a conrotatory process is favored, these intermediates may be stable. We are interested in applying these principles to the heterobicyclic[2.1.0]pentanes and have previously described some characteristics of the 2,3-diazabicyclo[2.1.0]pentane system which we attribute to a 1,3 diradical.[4] We report here the extension of this work to a 5-oxabicyclo[2.1.0]pentane (II) where a 1,3 dipole (carbonyl ylide) is involved. The behavior of II is contrasted to that of monocyclic aryloxiranes[5] and other 5-oxabicyclo[2.1.0]pentanes.[6]

Oxidation of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (I), prepared by the reported procedure,[7] with *m*-chloroperbenzoic acid gave II[8] after chromatography on silica gel: mp 118–120°; mass spectrum (70 eV) *m/e* 278 (19), 263 (64), 77 (100); ir (KBr) 8.0, 11.3, 13.1 μ (epoxy); nmr (CDCl$_3$), δ 1.14 (s, 6 H), 1.18 (s, 6 H), 7.25 (s, 10 H); uv (hexane) (no maxima < 210 nm)[9] 295 (ε 100), 270 (700), 250 (4000), 230 (12,200), 220 (14,300). Once pure, II is stable for months at room temperature; however, a trace of acid catalyzes its rearrangement to the cyclopropyl ketone III[8] [mp 120°; nmr (acetone-d_6) δ 1.28 (s, 6 H), 1.35 (s, 6 H), 7.23–7.83 (m, 8 H), 8.06–8.37 (m, 12 H); mass spectrum (70 eV) *m/e* 278 (56), 263 (100), 105 (54); ir 6.03 μ (C=O)] which upon heating rearranges further to the dihydrofuran IV[8] [mp 42–46°; mass spectrum (70 eV) *m/e* 278 (35), 263 (100); nmr (benzene-d_6), δ 0.97 (s, 6 H), 1.35 (s, 6 H), 7.17 (s, 10 H)]. These rearrangements involve the cyclobutyl–cyclopropylcarbinyl carbonium ion and have ample precedent.[6a–d] Thermal rearrangement (190° in diglyme) of the cyclopropyl ketone III yields the terminal olefin V[8] [mp 59–60°; nmr (CDCl$_3$), δ 1.12 (s, 3 H), 1.32 (s, 3 H), 1.76 (s, 3 H), 4.80 (s, 2 H), 4.90 (s, 1 H), 7.16–8.00 (m, 10 H); ir (KBr) 5.93 μ (C=O), 11.20 μ (>C=CH$_2$)] presumably *via* a concerted 1,6-hydrogen migration.[10] The terminal olefin V, upon treatment with acid, yields the hydrofuran IV.



Solutions of II in diglyme or benzene become visibly colored (purple) when heated to 100° or when irradiated (2537 Å) at room temperature. The visible absorption spectrum of the colored species is essentially the same (Table I) whether generated thermally or photochemically and is undoubtedly due to the same species. The color disappears from the irradiated solutions with first-order kinetics ($t_{1/2}$ (benzene) 8 min, $t_{1/2}$ (diglyme) 16 min at 22.2°) and from the heated solutions upon cooling. The oxide II can be recovered almost quantitatively from a benzene solution kept at 115° for 50 hr, and solutions can repeatedly be made colored by irradiation with little loss of II. On the basis of these

Table I. Visible Absorption Spectra Assigned to the Carbonyl Ylide VI[a]

Solvent	22°, nm[b]	125°, nm
Diglyme	544	535 ± 5
Benzene	550	
Decalin	546	538 ± 3

[a] Some influence of temperature on the solvent is expected. [b] Color formed upon irradiation.

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(1) G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, **87**, 3256 (1965); G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968); W. L. Carter and R. G. Bergman, *ibid.*, **90**, 7344 (1968); R. Huisgen, W. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967); A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, **4**, 118 (1967); H. Nozaki, S. Fujita, and R. Noyori, *Tetrahedron*, **24**, 2193 (1968).

(2) For example, thermal bond homolysis of the central bond of bicyclopentane requires *ca.* 20 kcal mol^{-1} less energy than bond homolysis in dimethylcyclopropane; J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, **A257**, 122 (1960).

(3) R. Hoffman, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); B. G. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

(4) A. B. Evnin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968); D. R. Arnold, A. B. Evnin, and P. H. Kasai, *ibid.*, **91**, 784 (1969).

(5) (a) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, *ibid.*, **89**, 3357 (1967); (b) R. S. Becker, J. Kolc, R. O. Bost, H. Kietrich, P. Petrellis, and G. Griffin, *ibid.*, **90**, 3292 (1968).

(6) (a) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, *Tetrahedron Lett.*, 5855 (1968); (b) R. Criegee and K. Noll, *Ann.*, 627, 1 (1959); (c) J.-L. Ripoll and J.-M. Conia, *Tetrahedron Lett.*, 979 (1965); (d) J.-L. Ripoll and J.-M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965); (e) W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 11M; (f) L. A. Paquette, A. A. Youssef, and M. L. Wise, *J. Amer. Chem. Soc.*, **89**, 5246 (1967); (g) A. C. Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962); (h) E. E. van Tamelen and D. Carty, *ibid.*, **89**, 3922 (1967); (i) D. L. Garin, *J. Org. Chem.*, **34**, 2355 (1969); (j) G. Maier, *Chem. Ber.*, **96**, 2238 (1963); (k) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Amer. Chem. Soc.*, **80**, 5505 (1958); (l) A. Padwa, *ibid.*, **87**, 4205 (1965).

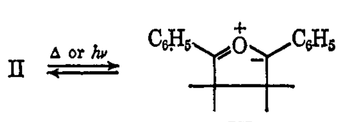
(7) O. J. Chapman and W. R. Adams, *ibid.*, **90**, 2333 (1968).

(8) Satisfactory elemental analyses were obtained for all new compounds reported here.

(9) L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *J. Org. Chem.*, **31**, 3976 (1966).

(10) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965); R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, **87**, 2282 (1965).

data and by analogy to similar systems[11] we assign the carbonyl ylide structure VI to the colored species.

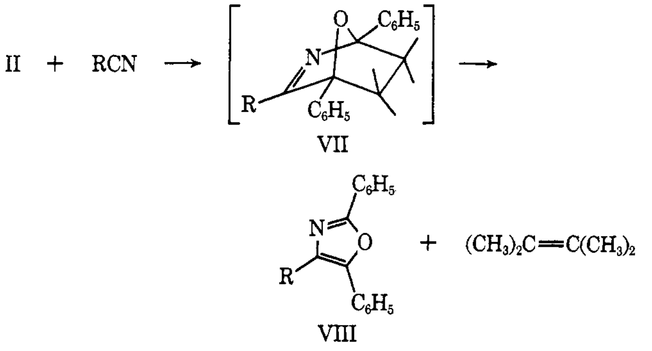


VI

The nmr spectrum of II shows two singlets for the methyl groups, one pair *endo*, the other *exo*. Since the carbonyl ylide structure VI has C_{2v} symmetry, these methyls must be exchanging environment at higher temperatures when the solution of the oxide is colored. There was, however, no evidence of broadening of these signals up to 170° (tetraglyme). (The width of both peaks at half-peak height is 1.0 Hz at 170°; at 40° the lower field signal is 1.3 Hz, and the high-field signal is 1.1-Hz wide at half-peak height.) This requires an exchange rate $<\pi$ sec^{-1} for the methyl groups of II (*i.e.*, 2 × lifetime^{-1} of II).

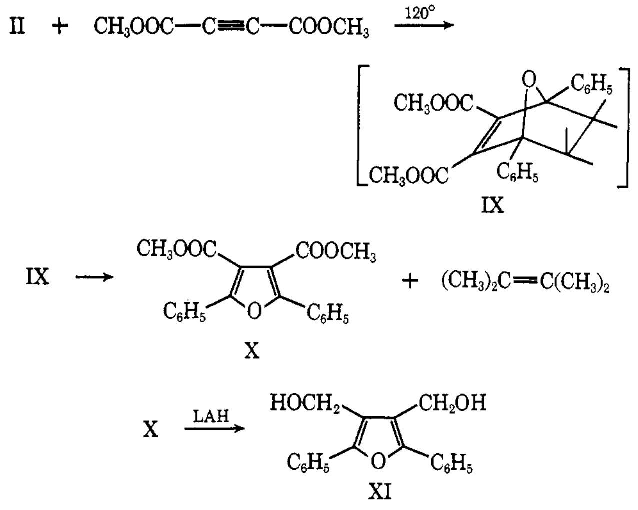
We have looked for an esr signal from the products obtained upon irradiation of II and conclude that VI is not paramagnetic. However, VI is precursor to a species which has a stable esr signal. These results are to be reported elsewhere.

When II is heated to 120° in cyanobenzene, no color is observed, and after 50 hr the oxide has disappeared with formation of triphenyloxazole[12] VIIIa and tetramethylethylene. Similarly reaction of II with *p*-methylcyanobenzene affords 2,5-diphenyl-4-*p*-toluoloxazole, VIIIb[8] [mp 115–115.5°; nmr ($CDCl_3$), δ 2.31 (s, 3 H), 7.0–8.3 (m, 14 H)]. Addition of the nitrile between the carbon and oxygen would have resulted in formation of 4,5-diphenyl-2-*p*-toluoloxazole[13] [mp 127–129°; nmr ($CDCl_3$), δ 2.41 (s, 3 H), 7.16–7.82 (m, 14 H)].

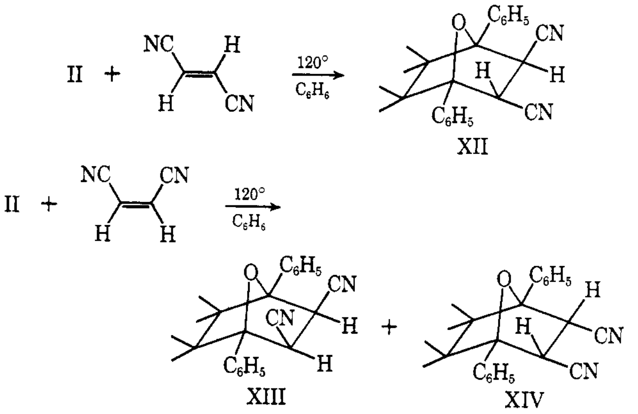


R = C_6H_5, *p*-$CH_3C_6H_4$

When II is heated to 120° with dimethylacetylenedicarboxylate, 2,5-diphenyl-3,4-dicarbomethoxyfuran[14] (X) and tetramethylethylene are formed. The structure of X was confirmed by reduction with lithium aluminum hydride to the known diol[15] XI (ir identical, mixture melting point undepressed).



Reaction of II with the isomeric 1,2-dicyanoethylenes gave the adducts in a stereospecific reaction. The single adduct obtained from reaction with fumaronitrile had the four nonequivalent methyl groups and two coupled hydrogens required for structure XII [mp 221.5–223°; nmr ($CDCl_3$), δ 0.62 (s, 3 H), 0.66 (s, 3 H), 1.32 (s, 3 H), 1.53 (s, 3 H), 3.40 (d, J = 6.5 Hz, 1 H), 4.16 (d, J = 6.5 Hz, 1 H), 7.02–8.10 (m, 10 H)].[8] The adducts XIII[8] [mp 313–313.5°; nmr ($CDCl_3$), δ 0.56 (s, 6 H), 1.14 (s, 6 H), 4.24 (s, 2 H), 7.3–8.1 (m, 10 H)] and XIV[8] [mp 219.5–222°; nmr ($CDCl_3$), δ 0.65 (s, 6 H), 1.64 (s, 6 H), 3.49 (s, 2 H), 7.1–8.0 (m, 10 H)] from reaction with maleonitrile were formed in the ratio 2:1. The structural assignments for XIII and XIV rest on the observation that XIV (the minor product) has a low-field pair of methyl groups deshielded by the *endo*-cyano groups.[16]



These reactions are interpreted as involving the cycloaddition of the carbonyl ylide VI to the dipolarophile.[17] The instability of VIIa and b and IX at 120° is not unexpected where decomposition can give the observed products *via* retro Diels–Alder reactions.

In summary, the central bond of II is cleaved heterolytically both thermally and upon irradiation, to give the colored carbonyl ylide VI which is surprisingly stable

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(11) J. M. Dunston and P. Yates, *Tetrahedron Lett.*, 505 (1964); E. F. Ullman and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **88**, 4942 (1966).

(12) F. R. Japp, *J. Chem. Soc.*, **63**, 469 (1893).

(13) The infrared spectrum of VIIIb is different in many respects from that of 4,5-diphenyl-2-*p*-toluoloxazole prepared by the reported procedure [A. E. Siegrist, *Helv. Chim. Acta*, **50** (3), 906 (1967)].

(14) R. Pfleger and F. Rheinhardt, *Chem. Ber.*, **90**, 2404 (1957).

(15) S. Adjangba, D. Billet, and C. Mentzer, *Bull. Soc. Chim. Fr.*, 132 (1962).

(16) A. D. Cross and I. T. Harrison, *J. Amer. Chem. Soc.*, **85**, 3223 (1963).

(17) For other examples of cycloaddition involving carbonylylides see: (a) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); (b) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3651 (1965); (c) W. J. Linn and R. E. Benson, *ibid.*, **87**, 3657 (1965); (d) W. J. Linn, *ibid.*, **87**, 3665 (1965); (e) R. W. Hoffmann and H. J. Luthardt, *Chem. Ber.*, **101**, 3861 (1968).

toward return to II but reacts as a typical 1,3 dipole. Colored intermediates have been observed upon irradiation of monocyclic aryloxiranes only at low temperatures (77°K). The proposed structures in these cases result from carbon–oxygen bond cleavage.[5b,18] Similarly, irradiation of monocyclic aryloxiranes in alcoholic solution affords products from carbon–oxygen bond cleavage.[19,20] Dark reactions involving central bond cleavage of oxiranes have been reported previously.[6e–j,17b–d]

Acknowledgment. We are grateful to Dr. E. B. Whipple and M. Ruta for assistance with the nmr experiments and to Dr. P. Kasai for carrying out the esr measurements.

[18] It has now been shown that the carbon–carbon bond is cleaved in these intermediates (T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970)).

[19] R. C. Petterson, C. S. Irving, A. M. Khan, G. W. Griffin, and I. M. Sarkar, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, No. ORGN 10; K. Tokumaru, *Bull. Chem. Soc., Jap.*, **40**, 242 (1967).

[20] Dr. Paul Kropp has shown that these additions are acid-catalyzed dark reactions following the formation of acid upon irradiation (Hanovia Photochemical Symposium, Chicago, Ill., Oct 1969).

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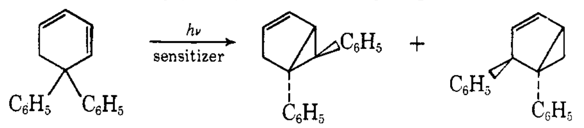
Geometric Factors in Multiplicity-Dependent Photochemistry. Intramolecular Triplet-State Rearrangement of 5,5-Diphenyl-1,3-cyclohexadiene

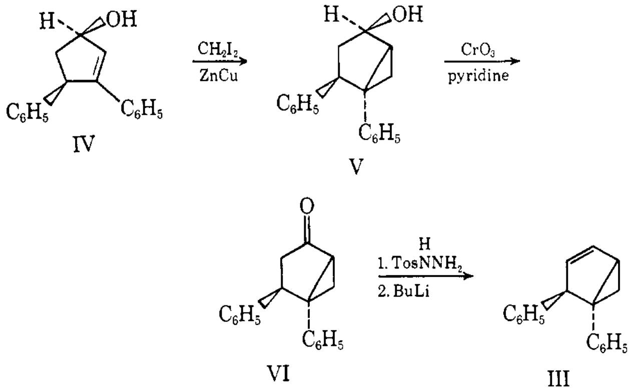
Sir:

An interesting mechanistic aspect of the di-π-methane–vinylcyclopropane rearrangement is the dependence of the multiplicity of the process on the structural character of the substrate.[1] Molecules having the possibility of rotational freedom in the excited state (*i.e.*, acyclic dienes and dienes having exocyclic methylene groups) undergo rearrangement most efficiently in the excited singlet state,[2] whereas systems possessing geometric constraints to rotation prefer to undergo reaction in the triplet state.[3,4] Our interest in the importance of excited-state geometry in modifying the photochemical and photophysical processes of the excited state[5] led us to surmise that the generalizations noted above resulted from conformational effects in the excited state.[6] To test this idea we chose for study 5,5-diphenylcyclohexa-1,3-diene (I). The cyclohexadiene skeleton can accommodate limited twisting about the carbon–carbon linkages, yet free rotation about any of the ring bonds appears unlikely.

Sensitized irradiation of I in benzene using fluorenone (E_T = 53.3 kcal/mol), 2-acetonaphthone (E_T = 59.6 kcal/mol), or Michler's ketone (E_T = 61 kcal/mol) as sensitizer[7] yielded two monomeric products in a ratio of 91:9 (80–90% yield).[8] The major product was isolated by chromatography and identified as *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (II) by comparison with authentic material.[9] The minor product was isolated by a combination of column and vapor phase chromatography and its identity was established as *trans*-4,5-diphenylbicyclo[3.1.0]hex-2-ene (III) by comparison with synthetic material (*vide infra*).[11] To add credibility to the marked stereoselectivity observed in the photoprocess, the *cis* isomers VII and VIII were prepared.[12] Vapor-phase analysis of the reaction mixture



I II III



IV V VI III

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[1] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

[2] (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); (b) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969); (d) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967); (e) E. C. Sanford and G. S. Hammond, Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 6, 1969, Paper 63.

[3] (a) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966); (b) J. R. Edman, *ibid.*, **88**, 3454 (1966); (c) H. E. R. Zimmerman, W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (d) J. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (e) P. Rabideau, J. B. Hamilton, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968); (f) R. S. H. Liu, *ibid.*, **90**, 215 (1968); (g) H. Hart and R. K. Murray, *ibid.*, **91**, 2183 (1969).

[4] Two recent examples not in complete accord with these generalizations are: (a) R. C. Hahn and L. J. Rothman, *ibid.*, **91**, 2409 (1969); (b) S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

[5] A discussion on the importance of geometric change in the photochemistry of biaryls has been presented: J. S. Swenton, B. H. Williams, and T. Ikeler, Symposium on Excited State Chemistry, Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 7, 1969, Paper 104.

[6] The low reactivity of the acyclic and exocyclic olefins would result from rotation about bonds of low π-bond order in the excited state affording a facile pathway for loss of electronic energy. In the more rigid systems this mode of energy dissipation would not be available; thus these molecules would have maximum opportunity for rearrangement.

[7] Photolyses were carried out on 0.3 g of diene and 0.3 g of sensitizer in 150 ml of benzene using Pyrex-filtered light from a 450-W medium-pressure source. The starting material was completely converted in 0.5 hr. Yields were determined by vpc using fluorenone or 2-acetonaphthone as internal standards. The ratios of II and III from vpc and nmr determination were within ±1%. Preliminary results using acetone as sensitizer resulted in formation of three major products: II (75%), III (7%), and VII (18%).

[8] Preliminary preparative irradiations of I in cyclohexane at 2537 Å yielded no detectable amounts of II or III. One of the singlet products has been identified as 1,1-diphenyl-1,3,5-hexatriene on the basis of its hydrogenation to 1,1-diphenylhexane.

[9] The authentic material was synthesized using the Shapiro–Shechter–Dauben[10] method from the known *trans* ketone [H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964)]. The olefin II, mp 56–57°, had the expected ir and nmr spectra.

[10] (a) R. H. Shapiro and M. J. Heath, *ibid.*, **89**, 5734 (1967); (b) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967); (c) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *ibid.*, **90**, 4762 (1968).

[11] The alcohol IV was prepared by reduction of 3,4-diphenylcyclopent-2-en-1-one using either sodium borohydride or the Meerwein–Ponndorf–Verley reduction. The ratio of IV and its epimer obtained from sodium borohydride reduction was 75:25 while MPV reduction yielded a ratio of 33:67. Note that the MPV results are in disagreement with those obtained by P. Bladon, S. McVey, P. L. Pauson, G. D. Broadhead, and W. M. Horspool, *J. Chem. Soc., C*, 306 (1966). The *trans* olefin III was obtained as a clear oil showing the expected ir and nmr absorptions.

[12] The *cis*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (VII) was prepared from the corresponding ketone[9] and had mp 69–70°. The *cis*-4,5-diphenyl[3.1.0]hex-2-ene, mp 58–59° (VIII), was prepared by the same