resubjected to vpc, gave only one peak (*i.e.*, no thermal decomposition or rearrangement occurred).

General Irradiation Procedure in Solution. Irradiations in trifluoroethanol used 0.01–0.08 *M* solutions, a Hanovia 679 A-36 450-W lamp, and Pyrex or quartz as stated in the text, and were followed by vpc or uv methods. Quenching experiments were done similarly and analyzed by vpc after 0.5, 2, and 4 hr (approximately 7, 25, and 50% conversion of **1**).

Acknowledgments. We are indebted to the National Institutes of Health and the National Science Foundation for generous financial support.

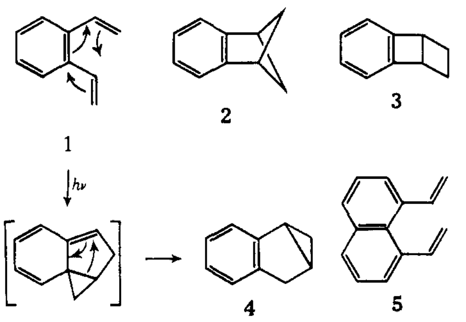
Photochemical Reactions of 1,8-Divinylnaphthalene and 1,8-Distyrylnaphthalene[1,2]

Jerrold Meinwald* and James W. Young

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850. *Received June 15, 1970*

Abstract: Ultraviolet irradiation of 1,8-divinylnaphthalene (**5**) gives *peri*-naphthobicyclo[3.1.1]heptene (**6**) and *peri*-naphthobicyclo[3.2.0]heptene (**7**) in a ratio of *ca.* 10 : 1. The high-melting photoproduct derived from 1,8-distyrylnaphthalene (**11**) is shown to be dimer **14a**, rather than the previously reported head-to-head monomer **12**. In dilute solution, three monomeric photoisomers of **11** can be characterized. The two major products, **23** and **24**, are formed *via* head-to-tail cyclizations; a minor product (**12a**) results from head-to-head cyclization. Overall, the favored products correspond to expectations based on a consideration of the preferred ground-state conformations of the starting materials.

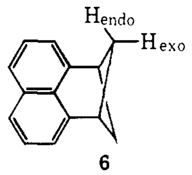
The photochemical [2 + 2] cycloaddition reaction has a long history[3] and its utility in the construction of four-membered rings has been amply demonstrated.[4] Recently, the photochemistry of *o*-divinylbenzene (**1**) was studied, in part with the thought that if it would undergo intramolecular cycloaddition of this type, it might provide entry into the then unknown benzobicyclo[2.1.1]hexene ring system (**2**).[5] The reaction in fact yielded neither **2** nor its head-to-head cycloaddition isomer **3**, but rather benzobicyclo[3.1.0]hexene (**4**). This transformation, which finds precedence in the photochemistry of 1,3,5-hexatriene,[6] requires the participation of two of the benzene π electrons. An analogous pathway is not open to 1,8-divinylnaphthalene (**5**) so that in this case $2\pi + 2\pi$ cycloadditions leading to some novel cyclobutanes might be realized. We wish to report the results of a study of the photochemistry of **5** and of the closely related diene **11**, which was carried out in pursuit of our interest in photochemical isomerizations leading to novel, small-ring compounds.



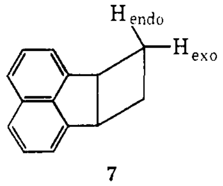
1 2 3 4 5

Discussion and Results

Photochemistry of 1,8-Divinylnaphthalene. Irradiation of **5** (0.002 *M* in cyclohexane) with a light source whose principal emission is at 254 nm gave a 40–50% yield of two products isomeric with the starting material, along with a comparable amount of polymer. The two monomeric isomers were formed in approximately equal amounts, and could be separated by careful column chromatography on alumina. They are assigned structures **6** and **7** on the basis of spectral and chemical evidence as described below. When the irradiation was carried out at the same concentration but with a medium-pressure mercury vapor lamp (Hanovia) through a Pyrex filter, very little polymer was formed, and products **6** and **7** were obtained in 80–95% yield. Under these conditions, the ratio of **6**:**7** is about 10:1. While the overall yield of monomeric products was found to be slightly dependent upon the solvent under both sets of reaction conditions, the two products were formed in the same relative amounts in each of the three



6



7

---

* Address correspondence to this author.

(1) We acknowledge with thanks the partial support of this work by the National Science Foundation (GP-13085).

(2) These results are given in part in Abstracts, 21st National Organic Chemistry Symposium, Salt Lake City, Utah, 1969, pp 62–70, and were presented in part at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, 1970.

(3) For some important early work and leading references, see G. Ciamician and P. Silber, *Ber.*, **35**, 4128 (1902).

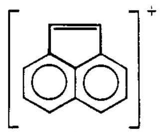
(4) There are several recent reviews. Among them are: (a) A. Schönberg, "Preparative Organic Photochemistry," 2nd ed, Springer-Verlag, Berlin, 1968, Chapters 1 and 8; (b) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (c) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966); *ibid.*, **69**, 845 (1969); (d) R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

(5) (a) M. Pomerantz, *J. Amer. Chem. Soc.*, **89**, 694 (1967); (b) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

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

solvents employed (cyclohexane, diethyl ether, and acetonitrile). The lower total yield and the relatively smaller amount of **6** produced by irradiation with the shorter wavelength light source appears to be due at least in part to the instability of **6** under the reaction conditions.

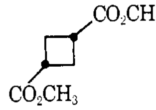
The head-to-head cyclization product **7** was identified by direct comparison with a sample of **7** prepared in these laboratories by an independent route.[7] The base peak in its mass spectrum appears at *m/e* 152 (M − 28), indicating a facile loss of ethylene to give an ion most simply formulated as **8**. The nmr spectrum of **7** consists of four very complex groupings: a six-proton multiplet at τ 2.27–2.94 (aromatic protons), and three two-proton multiplets. The benzylic protons give rise to a complex multiplet at τ 5.67–6.03. A multiplet at τ 7.07–7.53 is assigned to the exo methylene protons, by analogy with known benzobicyclo[2.1.1]-hexenes.[8] The endo protons, at τ 7.92–8.30, account for the third upfield multiplet.



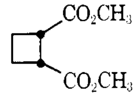
8

The mass spectrum of **6** differs significantly from that of **7**, especially in that the base peak now appears at *m/e* 165 (M − 15), and is much more intense than the peak at *m/e* 152 (M − 28). It seems reasonable that loss of ethylene should be much less facile from **6** than from **7**. The nmr spectrum of **6** shows a striking resemblance to that of **2**.[8b] The six aromatic protons are observed as a multiplet at τ 2.38–3.15. A triplet centered at τ 6.51 is attributed to the bridgehead benzylic protons. Molecular models of **6** indicate that the dihedral angle between the two bridgehead protons and the endo methylene protons is very close to 90°. Coupling between them is not observed. The splitting into a triplet is probably due to coupling with the exo methylene protons, and the measured coupling constant, $J_{\text{bridgehead,exo}}$, is 5.4 Hz. A complex multiplet (at least eight lines) between τ 7.07 and 7.43 is assigned to the exo methylene protons. Although this multiplet cannot be analyzed on the basis of first-order approximations, it is clearly the most complex of the three upfield groups, as is to be expected. The third upfield multiplet, τ 7.83–8.22, is attributable to the endo protons. Its chemical shift is in the expected range, based on analogy with **7** and the benzobicyclo[2.1.1]hexenes.[8]

To provide chemical confirmation of these structures, a sample of photoproduct (found by nmr analysis to be a 10:1 mixture of **6** and **7**, respectively) was subjected to ozonolysis. Diazomethane esterification of the resulting acids yielded diesters **9** and **10** in the expected ratio. Their identity was confirmed by comparison of each component with an authentic sample of the appropriate diester.[9] It is clear, then, that irradiation of **5** results in a pair of smooth intramolecular photocycloaddition reactions, with head-to-tail orientation predominating.

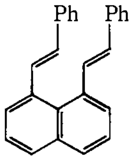


9

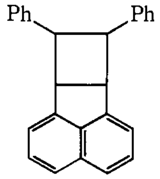


10

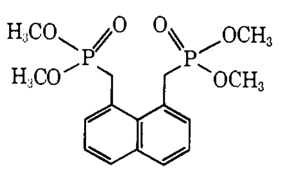
Photochemistry of 1,8-Distyrylnaphthalene. Shortly after our initial studies on 1,8-divinylnaphthalene had begun, it was reported that irradiation of 1,8-distyrylnaphthalene (**11**) produced a single product, **12**, of unspecified stereochemistry, in excellent yield.[10] This structural assignment was made on the basis of spectral data and a microanalysis which indicated that the product had the same empirical formula as **11**. Since this report contrasted somewhat with the results obtained in the case of **5**, we thought a direct comparison of the two systems would be worthwhile.



11



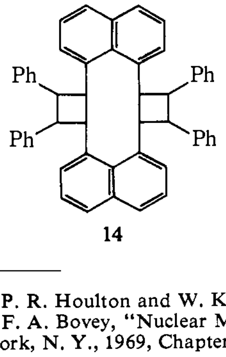
12



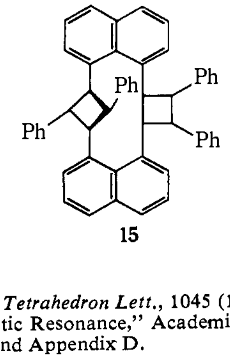
13

Preparation of 1,8-distyrylnaphthalene *via* an improved route, using the bisphosphonate ester **13**, yielded *trans,trans*-**11**, whose stereochemistry is indicated by the characteristic large (16 Hz) vinylic coupling in its nmr spectrum, as well as by an intense infrared absorption at 965 cm^{-1}. When **11** was irradiated as previously described at 254 nm in boiling cyclohexane (0.15 *M*) for 24 hr, a 53% yield of a high melting (335°) material crystallized from the reaction mixture. The melting point, nmr spectrum, and ultraviolet absorption maxima of this product are in good agreement with the literature report.[10] Its mass spectrum, however, as well as an osmometric molecular weight determination clearly indicate a *dimeric* structure.

Four interesting dimers of **11** which might be imagined to form photochemically are shown in formulas **14–17**. The dimer's nmr spectrum showed, in addition to a low-field multiplet due to the aromatic protons, a broadened pair of four-proton doublets at τ 3.55 and 5.06 with the appearance expected for a spin system of the type AA′BB′.[11] The simplicity of this spectrum excludes structure **15** from further consideration. The mass spectrum of the dimer shows, in addition to a molecular ion at *m/e* 664 (5% relative abundance), peaks at 484 (1%) and 304 (2%) corresponding to the loss of



14



15

---

(7) J. Meinwald and M. Ikeda, unpublished results.

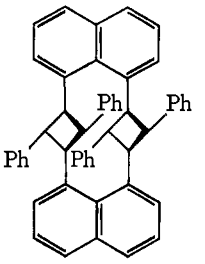
(8) (a) H. Tanida and Y. Hata, *J. Amer. Chem. Soc.*, **88**, 4289 (1966); (b) M. Pomerantz, *ibid.*, **88**, 5349 (1966).

(9) (a) N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959); (b) N. L. Allinger and L. A. Tushaus, *J. Org. Chem.*, 30, 1945 (1965). We acknowledge with thanks a gift of *cis*-1,3-cyclobutanedicarboxylic acid from Professor Allinger.

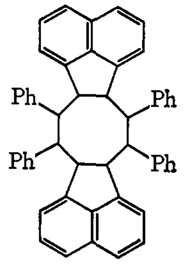
(10) P. R. Houlton and W. Kemp, *Tetrahedron Lett.*, 1045 (1968).

(11) F. A. Bovey, "Nuclear Magnetic Resonance," Academic Press, New York, N. Y., 1969, Chapter IV and Appendix D.

one and two molecules of stilbene, respectively. These fragmentations suggest that **16** and **17** can also be excluded, leaving **14** as the most likely dimer structure. This conclusion is supported by pyrolysis experiments as described below.

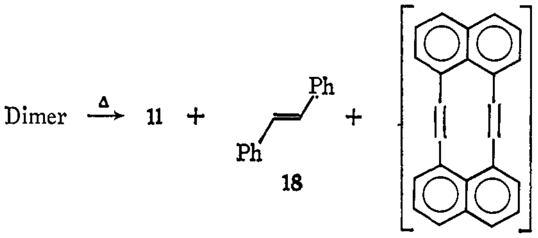


16



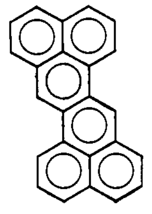
17

When a sample of the dimer was subjected to pyrolysis at 350°, the major product was shown to be *trans*-stilbene (**18**), along with a small amount of **11**. These products were trapped during the pyrolysis along with a dark red solid. Clearly, formation of **11** simply involves reversal of the original photocycloaddition, and is compatible with any of the above formulations. However, cleavage of the cyclobutane rings in the alternative sense should yield 2 equiv of stilbene plus **19** in the case of **14** only. While we were not able to isolate **19** itself from the complex pyrolysis product mixture, we did obtain a small amount of a dark red material which exhibited the highly characteristic visible absorption spectrum of zethrene (**20**): $\lambda_{\max}^{\text{benzene}}$ 405, 475, 510, and 550 nm.[12] Since it is known that zethrene is formed readily from the autoxidation of **19**,[13] this observation speaks for the assignment of structure **14** to the dimer. Ascertaining the stereochemistry of **14** was our next objective.



18

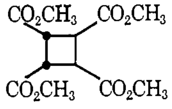
19



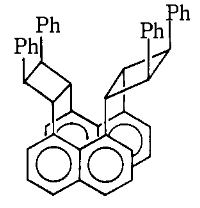
20

Toward this end, a sample of **14** was ozonized exhaustively and the resulting mixture of acids was esterified with diazomethane. Gas chromatography showed a single product with retention time longer than 8 min. This material, at t_r = 21 min, was collected and found to be identical in all respects with an independently prepared sample of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane (**21**).[14] This experiment confirms the presence of cyclobutane rings in the dimer, and indicates the stereochemistry of all substituents.

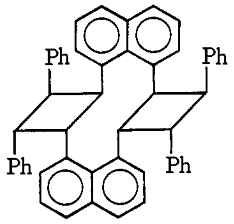
Three possible configurations for the dimer consistent with all of the data up to this point are shown in formulas **14a–c**. One of these (**14c**) appears to be sterically impossible, and can be eliminated from further consideration on that basis alone. Dimer **14b** could result, in a formal sense, from dimerization of two monomers with cis,cis stereochemistry, while **14a** corresponds to reaction from the trans,trans isomer. An experimental basis for eliminating one of these two remaining formulations was gained by examining the fluorescence spectrum of the dimer, which exhibited a broad, strong emission at long wavelengths with maximum intensity at 410 nm. Recent studies indicate that this type of emission is characteristic of naphthalene derivatives capable of forming intramolecular excimers in which the aromatic nuclei are in a sandwich arrangement.[15] Of the two possibilities, only **14a** has such a configuration. The dimer is thus formulated as arising from the head-to-head union of two molecules of **11** with retention of the stereochemistry of the original (trans,trans) monomer.[16]



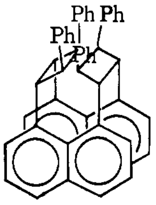
21



14a



14b



14c

Although dimerization dominates the photochemistry of **11** under the conditions previously described,[10] we find that by changing to dilute solution and shorter reaction times, the photochemistry of **11** parallels that of **5** quite closely. Thus, when a 0.001 *M* solution of **11** in diethyl ether was irradiated with the Hanovia lamp until the starting material had just disappeared, a complex mixture of chiefly monomeric photoproducts was obtained. Three isomers of **11** could be isolated from this mixture in yields of 40, 38, and 5%.

As was the case with the divinylnaphthalene photoproducts, mass spectrometry was especially useful in determining the nature of each ring system. Head-to-head photoproducts would again be expected to yield **8** readily, by loss of stilbene. Similarly, for head-to-tail products of the bicyclo[3.1.1]heptane ring system, loss of (C_6H_5-$CH_2\cdot$) to form **22** would be analogous to the prominent loss of ($CH_3\cdot$) observed in the spectrum of **6**. In fact, the mass spectra allow the recognition of the

---

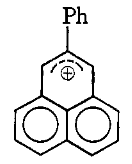
(12) E. Clar, K. F. Lang, and H. Schulz-Kiesow, *Chem. Ber.*, **88**, 1520 (1955).

(13) R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, 90, 530 (1968). We thank Professor Sondheimer for a gift of an authentic sample of 20.

(14) G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Amer. Chem. Soc.*, **83**, 2725 (1961).

(15) E. A. Chandross and C. J. Dempster, *ibid.*, **92**, 3586 (1970).

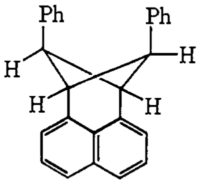
(16) Two recent accounts of similar dimerizations of *o*-divinylbenzene derivatives have appeared: D. F. Tavares and W. H. Ploder, *Tetrahedron Lett.*, 1567 (1970); E. Müller, H. Meier, and M. Sauerbier, *Chem. Ber.*, 103, 1356 (1970). See, however, W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. Nivard, *Tetrahedron*, **26**, 1069 (1970).



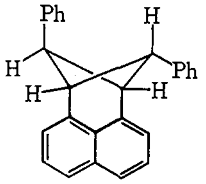
22

two major distyrylnaphthalene photoproducts as derivatives of **6**, and the minor one as a derivative of **7** on just this basis.

The nmr spectra of these three products help in determining their stereochemistry. One of the two major products (mp 158°) has, in addition to a complex multiplet (τ 2.20–3.15) for the aromatic protons, two singlets at τ 5.71 and 6.31 due to the four benzylic protons. It will be recalled from the discussion of the nmr spectrum of **6** that coupling between the bridgehead and endo protons was not observable. The absence of splitting in this spectrum allows formulation of this product as **23**.



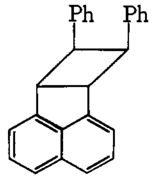
23



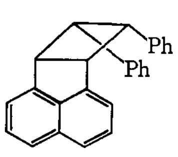
24

The second major product (mp 135°) has a more complex nmr spectrum. The region τ 5.0–6.5, characteristic of the benzylic protons, shows a one-proton singlet at τ 6.42 and an eight-line multiplet (τ 5.37–5.87) corresponding to three protons. This multiplet has the appearance of an AB_2 spin system,[11] and when analyzed as such yields the value of J_{AB} = 5.8 Hz. This isomer, then, has two magnetically equivalent protons coupled to one other proton, and a fourth proton not observably coupled to any other. If, indeed, the bridgehead-endo coupling is zero, structure **24** is in accord with the spectrum. The aromatic region of this spectrum shows a complex 11-proton multiplet between τ 2.28 and 2.93. The remaining five aromatic protons, presumably the endo phenyl protons, appear as a sharp singlet at τ 3.20.

The stereochemistry of the minor product (mp 126°) could not be deduced entirely from spectral data, although the mass spectrum, as mentioned above, establishes its structure as **12**. Its nmr spectrum (a pair of broadened doublets at τ 5.42 and 6.11 in the benzylic region) is consistent with expectations for either of the cis stereoisomers **12a** or **12b**. Ozonolysis and esterification of the acidic products, however, yielded *cis,trans,-cis*-1,2,3,4-tetracarbomethoxycyclobutane (**21**) which establishes the identity of this minor product as **12a**.

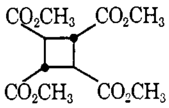


12a

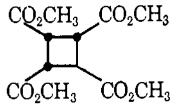


12b

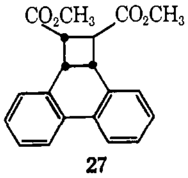
Chemical confirmation of the structures of the two head-to-tail cycloadducts was similarly obtained. Ozonolysis of **23** followed by diazomethane esterification yielded *trans,trans,trans*-1,2,3,4-tetracarbomethoxycyclobutane (**25**) whose identity was confirmed by comparison with a sample of **25** prepared by the method of Griffin, *et al.*[14] Photoproduct **24** yielded the cis,cis,-trans isomer **26**,[17] an authentic sample of which was obtained by ozonolysis of **27**.[18] The isomeric tetraesters **21**, **25**, **26**, and **28** were all clearly distinguishable on the basis of their glpc retention times, melting points, and infrared spectra.[19]



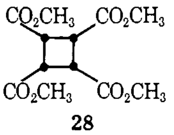
25



26

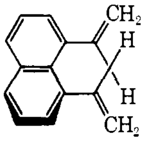


27

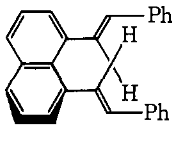


28

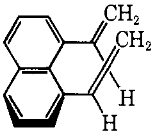
We note in conclusion that the photochemistry of **11** in dilute solution parallels closely that of **5** in that the intramolecular photocycloadditions proceed mainly in a head-to-tail fashion. Examination of molecular models suggests that this may well be related to the favored ground-state conformations of **5** and **11**, **5a** and **11a**. From these conformations, the formation of head-to-tail cyclization products involves a minimal disturbance of nuclear positions. On the other hand, formation of head-to-head products, which would be impossible from these conformations, is the most reasonable reaction from the less-favored conformations **5b** and **11b**. Especially in view of the minimal effect of the phenyl substituents of **11** on the course of its cyclization, electronic factors appear to be relatively unimportant in these reactions.



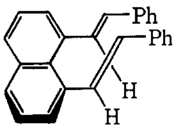
5a



11a



5b



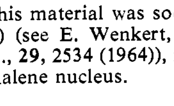
11b

---

(17) R. Criegee and H. Hover, *Chem. Ber.*, **93**, 2521 (1960).

(18) R. A. Caldwell, unpublished results. Professor Caldwell generously provided us with a sample of **27**.

(19) An initially disturbing observation during the course of this work was that glpc analysis of the reaction mixture from the ozonolysis of each of the three cycloadducts **23**, **24**, and **12a** revealed the presence of a second polyester in addition to the expected 1,2,3,4-tetracarbomethoxycyclobutanes. This material was soon identified, however, as trimethylhemimelliate (**29**) (see E. Wenkert, D. B. R. Johnston, and K. G. Dave, *J. Org. Chem.*, **29**, 2534 (1964)), resulting from incomplete degradation of the naphthalene nucleus.



29

Experimental Section

Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined using a Perkin-Elmer Model 257 spectrophotometer, and visible–ultraviolet spectra were measured on a Cary Model 14. Nmr spectra were recorded with a Varian A-60A instrument, using tetramethylsilane as internal standard. Mass spectra were determined on an A.E.I. MS-902 mass spectrometer at an ionizing voltage of 70 eV.[20] In most cases, only those ions whose relative abundance is greater than 10% are reported. Ozone was generated with a Welsbach Model T-408 laboratory ozonizer.

1,8-Divinylnaphthalene (5). This compound was prepared initially by the method of Stille and Foster.[21] In later experiments the procedure of Mitchell and Sondheimer[22] was found to be more convenient. The mass spectrum of **5** showed abundant ions at *m/e* (relative intensity) 180 (M^+, 35), 179 (40), 178 (18), 165 (100), and 152 (33). Other properties agreed well with literature reports.[21,22]

Irradiation of 1,8-Divinylnaphthalene. A solution of 100 mg of **5** in 360 ml of cyclohexane (0.002 *M*) was irradiated with a bank of eight GE Model G15T8 germicidal lamps in a quartz vessel until the starting material had been consumed (20 hr). The reaction could be monitored by following the disappearance of the strong, characteristic vinyl absorption in the infrared at 908 cm^{-1} (CS_2). The solvent was evaporated under reduced pressure, and the dark residual oil was dissolved in diethyl ether and filtered through a 2.5 cm × 1.0 cm column of alumina (Woelm activity I) to remove polymer and most of the colored impurities. The filtrate, on evaporation, yielded 40 mg (40%) of a pale yellow oil. This material was chromatographed on a column (45 cm × 1.5 cm) of basic aluminum oxide (30 g, Woelm, activity I). Elution was with pentane, and 250 2-ml fractions were collected. Fractions 68–108 were combined and yielded 14 mg of **6**: mp 52.5–53° (after recrystallization from methanol); nmr (CCl_4) τ 2.38–3.15 (multiplet, six aromatic H), 6.51 (triplet, J = 5.4 Hz, two benzylic H), 7.07–7.43 (multiplet, two exo methylene H), 7.83–8.22 (multiplet, two endo methylene H); infrared (CCl_4) 3040, 2950, 1610, and 1500 cm^{-1}; mass spectrum, *m/e* (relative intensity) 180 (M^+, 45), 179 (45), 178 (12), 166 (11), 165 ($M - CH_3$, 100), 152 ($M - C_2H_4$, 30).

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.06; H, 7.04.

Evaporation of the solvent from fractions 109–126 yielded no product. Fractions 127–233 yielded 19 mg of a second component, mp 78–78.5° (methanol), identical in all respects with an independently synthesized sample of **7**:[7] nmr (CCl_4) τ 2.27–2.94 (multiplet, six aromatic H), 5.67–6.03 (multiplet, two benzylic H), 7.07–7.53 (multiplet, two endo methylene H), 7.92–8.30 (multiplet, two exo methylene H); infrared (CCl_4) 3040, 2980, 2940, 1610, 1500, and 1370 cm^{-1}; mass spectrum, *m/e* (relative intensity) 180 (M^+, 15), 179 (8), 165 ($M - CH_3$, 12), 153 (11), 152 ($M - C_2H_4$, 100), 151 (8).

When **5** was irradiated at the same concentration (0.002 *M*) in cyclohexane with a 450-W Hanovia lamp (Pyrex filter), the product mixture was markedly different. The reaction was monitored as before and the starting material was entirely consumed after 0.5 hr. Polymer formation occurred to a much smaller extent, and the two products **6** and **7** were obtained in 90–95% total yield after initial purification by molecular distillation, thin-layer chromatography on silica gel, or filtration of an ether solution through alumina. The relative amounts of the two isomeric photoproducts in a mixture could easily be determined by integration of the nmr spectrum, since the benzylic protons of the two compounds give rise to distinctive patterns which are well resolved from one another. This measurement, and the degradation described below, indicated that the head-to-tail photoproduct **6** was the major product, and constituted about 90% of the crudely purified mixture. The head-to-head isomer **7** accounted for the remaining 10%. When this experiment was repeated in diethyl ether and in acetonitrile, the product ratio was essentially unchanged. The total yields in these solvents, after preliminary purification, were 80 and 92%, respectively.

Ozonolysis of 6 and 7. The method described here is similar to that of Criegee and Hover.[17]

A 100-mg sample of **5** was irradiated in diethyl ether with the 450-W Hanovia lamp through Pyrex for 0.5 hr, and the solvent was removed under reduced pressure. The nmr spectrum of the residue indicated the ratio of **6**:**7** to be about 9:1. The product was subjected to preliminary purification by filtration through alumina, and was dissolved in 6 ml of 85% aqueous acetic acid. The solution was stirred at room temperature, and a stream of ozonized oxygen from the ozone generator was passed through the solution for 14 hr. Six milliliters of 10% aqueous hydrogen peroxide was then added, and the solution was stirred at room temperature for 36 hr. The solution was carefully evaporated to dryness under reduced pressure. Caution was exercised to keep the bath temperature below 40°. The solid residue was dissolved in the minimum amount of methanol, and was treated with excess diazomethane. The mixture of esters was then fractionated by preparative glpc (15% SE-30 on Chromosorb W, 8 ft × 0.25 in., 145°, carrier flow rate = 125 ml/min). Several components, not fully characterized, were observed at short retention times. Two components were then eluted in a ratio of 9:1 with t_r = 24 and 20 min, respectively. The major component had a retention time identical with that of an authentic sample of **9**,[9b] and gave a single peak of the same retention time upon admixture with an equal amount of **9**. The infrared spectra and mass spectra of the collected and authentic samples were identical. The minor component was similarly shown to be identical with an authentic sample of **10**.[9a]

***cis*-1,3-Dicarbomethoxycyclobutane (9).** A sample of *cis*-1,3-cyclobutanedicarboxylic acid[9b] was esterified with diazomethane and the product was purified by preparative glpc (15% SE-30 on Chromosorb W, 8 ft × 0.25 in., 150°).

***cis*-1,2-Dicarbomethoxycyclobutane (10).** The cis 1,2 diacid was prepared from a crude mixture of *cis*- and *trans*-1,2-cyclobutanedicarboxylic acids[23] by the method of Buchman, *et al.*[24] A small portion of the recrystallized diacid was esterified with diazomethane and the ester was purified by preparative glpc (15% SE-30 on Chromosorb W, 8 ft × 0.25 in., 150°). The properties of this diester correspond well with those described.[9a]

***trans,trans*-1,8-Distyrylnaphthalene (11).** Earlier syntheses of this material have relied upon the Wittig condensation of benzaldehyde with 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide.[10,25] In our hands the purification of the product from this reaction was difficult. This difficulty was circumvented by application of the phosphonate modification of the Wittig reaction,[26] which gave **11** in comparable overall yield.

Thus 12.5 g (40 mmol) of 1,8-dibromomethylnaphthalene[22] was added to 20 g (160 mmol) of freshly distilled trimethyl phosphite, and the mixture was heated slowly, with stirring, to reflux. The bath temperature was increased to 200°, and the reaction mixture was stirred at this temperature for 15 min. The mixture was cooled, and the solid was filtered, washed several times with hexane, and dried. The yield, after recrystallization from chloroform–hexane, was 15 g (94%) of **13**, mp 171–172°: infrared ($CHCl_3$) 2950, 1250–1180 (broad), 1060–1025 (broad), and 850 cm^{-1}; nmr ($CDCl_3$) τ 2.10–2.80 (multiplet, six aromatic H), 5.92 (doublet, J = 21 Hz, four benzylic H), 6.42 (doublet, J = 11 Hz, 12 methyl H); mass spectrum, *m/e* (relative intensity) 373 (14), 372 (M^+, 100), 263 ($M - C_2H_6O_3P$, 40), 249 ($M - C_3H_8O_3P$, 26), 153 (50), 152 (60), 93 (12), and 63 (12).

Anal. Calcd for $C_{16}H_{22}O_6P_2$: C, 51.61; H, 5.96. Found: C, 51.31; H, 5.96.

A suspension of 3.1 g (57 mmol) of sodium methoxide in 150 ml of freshly distilled dimethylformamide was prepared, and was treated with 10.5 g (28 mmol) of the bisphosphonate ester **13**. The resulting red-brown mixture gradually became colorless upon dropwise addition of 6.0 g (57 mmol) of benzaldehyde. The mixture was stirred for 1.5 hr, and 150 ml of water was added. The white precipitate was filtered, washed with water, and yielded, after recrystallization from cyclohexane, 3.8 g (40%) of *trans,trans*-1,8-distyrylnaphthalene (**11**). This material, mp 145–146°, exhibited infrared and ultraviolet spectral characteristics in agreement with those previously reported:[25] nmr ($CDCl_3$) τ 2.19–2.99 (multiplet, 16 aromatic H), 2.03 and 3.16 (pair of doublets, J = 16 Hz, four vinyl H); mass spectrum, *m/e* (relative intensity) 332 (M^+, 19), 253 (10), 242 (17), 241 ($M - C_7H_7$, 100), 239 (19), 180 (26), 165 (17), and 152 (12).

Irradiation of 1,8-Distyrylnaphthalene at High Concentration (0.15 *M*). A solution of 0.76 g of **11** in 15 ml of refluxing cyclo-

---

[20] Mass spectra were determined by the Cornell High Resolution Mass Spectrometer Facility sponsored by Grant No. RR-00355 from the National Institutes of Health.

[21] J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2703 (1963).

[22] R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968).

[23] I. Wainer, Ph.D. Thesis, Cornell University, 1969.

[24] E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *J. Amer. Chem. Soc.*, **64**, 2696 (1942).

[25] E. D. Bergmann and I. Agranat, *J. Org. Chem.*, **31**, 2407 (1966).

[26] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

hexane was irradiated in a quartz vessel for 24 hr with a bank of 10 GE Model G15T8 germicidal lamps (principal emission at 254 nm). (These conditions duplicate as nearly as possible those described in an earlier report on the photochemistry of **11**.[10]) A white crystalline solid (**14a**, 0.40 g) which crystallized from the hot solution during the irradiation was removed by filtration and washed with chloroform. This product, mp 333–334° (lit.[10] mp 335°) after recrystallization from ethyl acetate, was shown to be a dimer of **11** on the basis of its mass spectrum and osmometric molecular weight.

Anal. Calcd for $(C_{26}H_{20})_n$: C, 93.98; H, 6.02. Found: C, 93.86; H, 6.14. Mol wt (osmometric) Calcd for $C_{52}H_{40}$: 664. Found: 684.

The spectral characteristics of **14a** are as follows: infrared (KBr) 3040, 2940, 1615, 1505, 1465, and 692 cm^{-1}; nmr (benzene-d_6) τ 2.11–2.78 (multiplet, 32 aromatic H), 3.55 and 5.06 (pair of doublets, slightly broadened, J = 5.5 Hz, eight benzylic H); mass spectrum, *m/e* (relative intensity) 664 (M^+, 5), 484 ($M - C_{14}H_{12}$, 1), 333 (7), 332 (M/2, 28), 304 ($M - C_{28}H_{24}$, 2), 242 (18), 241 ($(M/2) - C_7H_7$, 100), 181 (5), 180 (39), 165 (17), and 152 (7).

Ozonolysis of 14a. Ozone was bubbled through a suspension of 100 mg of **14a** in 40 ml of 80% aqueous acetic acid at room temperature for 24 hr. The resulting clear, colorless solution was treated with 5 ml of 30% aqueous hydrogen peroxide and was stirred at room temperature for 48 hr. The solution was evaporated to dryness under reduced pressure. (The bath temperature was carefully maintained below 40°.) The resulting mixture of white, crystalline solids was dissolved in methanol and treated with excess diazomethane. Glpc analysis (20% SE-30 on 60–80 firebrick, 3 ft × 0.25 in., 145°) showed a single peak with retention time longer than 8 min. This peak (t_r = 21 min) showed the same retention time as a sample of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane (**21**) prepared by the method of Griffin, *et al.*[14] The material was collected by preparative glpc on the same column. It exhibited infrared and nmr spectra identical in every respect with those of the independently synthesized sample of **21**. It was compared with authentic samples of the three other isomers of 1,2,3,4-tetracarbomethoxycyclobutane (see below), and its identity with the cis,trans,cis isomer is unambiguous.

Thermal Degradation of 14a. A sample of 50 mg of **14a** was heated from room temperature to 400° over a 0.5-hr period in a Wood's metal bath, with a slow stream of nitrogen passing through the reaction vessel. The effluent gas passed first through a trap at 0° and then through another at −78°. A red amorphous condensate was collected in the first trap. Examination of this material by tlc revealed a complex mixture of products. The major one among these (10 mg) was isolated by preparative tlc (silica gel, eluted with 8:2:1 cyclohexane–chloroform–benzene) and was shown by comparison of its infrared and nmr spectra, melting point, and tlc r_f value to be identical with an authentic sample of *trans*-stilbene (**18**). Tlc also revealed the presence of small amounts of 1,8-distyrylnaphthalene.

In an effort to isolate and identify other thermal degradation products of **14a**, a 100-mg sample was heated for 15 min under reduced pressure (60 mm) at 350° in a sublimation apparatus. The pressure was then lowered to 0.2 mm, and a dark red solid condensed on the cold finger of the apparatus. This solid was fractionated by sublimation first at 70° (0.1 mm) to remove stilbene and 1,8-distyrylnaphthalene, and then at 115° (0.1 mm) yielding a small amount of a red substance. This material was not unambiguously identified. It displayed, however, the highly characteristic visible absorption spectrum of zethrene (**20**): λ_{max} (benzene) 405, 475, 510, and 550 nm.[12]

Synthesis of the 1,2,3,4-Tetracarbomethoxycyclobutanes. The cis,-trans,cis (**21**) and trans,trans,trans (**25**) isomers were prepared by the method of Griffin and coworkers.[14] The cis,cis,cis isomer (**28**) was synthesized according to the procedure of Griffin and Veber.[27] The fourth isomer, *cis,cis,trans*-1,2,3,4-tetracarbomethoxycyclobutane (**26**) is also a well-characterized compound.[17] The synthesis reported in the literature is a lengthy one, however, and an alternative pathway seemed attractive.

A 50-mg sample of **27**[18] was dissolved in 40 ml of 80% aqueous acetic acid. Ozone was passed through the solution at room temperature for 12 hr. The solution was treated with 3 ml of 30% aqueous hydrogen peroxide, and stirred at room temperature for 48 hr. The solvents were removed under reduced pressure at 30–40°. The residue was dissolved in methanol, and treated with diazomethane. Glpc analysis (8 ft × 0.25 in., 5% Carbowax 20M, 210°) showed a single peak (t_r = 8.5 min) with retention time longer than 2 min. Preparative glpc (8 ft × 0.25 in., 15% Carbowax 20M, 210°) yielded 11 mg of **26** as an oil which could be crystallized from acetone, mp 71–73° (lit.[17] mp 73–74°).

Irradiation of 1,8-Distyrylnaphthalene in Dilute Solution (0.001 *M*). A solution of 100 mg of **11** in 300 ml of diethyl ether was irradiated with a 450-W Hanovia lamp (Pyrex filter) for 35 min, after which the characteristic ultraviolet absorption of **11** at 350 nm could no longer be detected. The solvent was removed under reduced pressure, leaving a yellow oil which was purified by tlc on silica gel (two elutions with 3:1 cyclohexane–benzene) yielding two major components in nearly equal amounts, and one minor component. One of the major components, **23**, had a slightly higher r_f on tlc and was isolated in 40% yield (40 mg) after the chromatography. It crystallized as long needles, mp 158.5–159°, from chloroform–hexane: nmr ($CDCl_3$) τ 2.20–3.15 (multiplet, 16 aromatic H), 5.71 (singlet, two bridgehead H), and 6.31 (singlet, two endo H); infrared (CCl_4) 3060, 3020, 2950, 1610, 1500, 1450, 1260, 1100, 1030, and 685 cm^{-1}; mass spectrum, *m/e* (relative intensity) 332 (M^+, 32), 253 (9), 252 (8), 242 (18), 241 ($M - C_7H_7$, 100), 239 (16), 180 (20), 165 (10), and 152 (5).

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.79; H, 5.96.

Tlc yielded 38 mg (38%) of the second major component, **24**: mp 135° (chloroform–hexane); nmr ($CDCl_3$) τ 2.28–2.93 (multiplet, 11 H, naphthalene plus exo phenyl protons), 3.20 (singlet, five endo phenyl H), 5.37–5.87 (AB_2 multiplet, eight lines, J = 5.8 Hz, two bridgehead H plus one exo H), 6.42 (singlet, one endo H); infrared (CCl_4) 3060, 3025, 2940, 1610, 1500, 1450, 1175, 1115, 1073, 1030, and 685 cm^{-1}; mass spectrum, *m/e* (relative intensity) 332 (M^+, 28), 253 (10), 252 (9), 242 (17), 241 ($M - C_7H_7$, 100), 239 (19), 180 (23), 165 (16), and 152 (10).

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.24; H, 6.02.

A third component, **12a**, could be isolated from the reaction mixture. This material had the same r_f value as **23**, and was estimated (by integration of the nmr spectrum) to be present in about 5% yield. When the reaction was repeated on a larger scale this minor product could be separated from **23** by a second tlc (silica gel, elution with CCl_4), followed by fractional recrystallization with chloroform–hexane. The first compound to crystallize was **23**. The mother liquors were evaporated and the residue was recrystallized twice from ethanol, yielding **12a**: mp 126–127°; nmr ($CDCl_3$) τ 2.19–3.08 (multiplet, 16 aromatic H), 5.42 and 6.11 (pair of doublets, broadened, J = 4 Hz, four benzylic H); infrared (CCl_4) 3030, 2930, 1612, 1505, 1240, 690, and 665 cm^{-1}; mass spectrum (*m/e*, relative intensity) 332 (M^+, 7), 242 (11), 241 ($M - C_7H_7$, 70), 239 (14), 181 (12), 180 ($M - C_{12}H_8$, 100), 179 (11), 165 (18), 152 (50).

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.97; H, 6.27

Ozonolysis of 23. A sample of 8 mg of **23** was slurried in 6 ml of 80% aqueous acetic acid and was treated with ozone for 12 hr at room temperature. Aqueous hydrogen peroxide (30%, 0.5 ml) was added, and the solution was stirred for 48 hr. The solvents were removed at 30–40° under reduced pressure, and the residue was dissolved in methanol and treated with diazomethane. Analysis by glpc (8 ft × 0.25 in., 5% Carbowax 20M, 210°) showed, in addition to minor peaks at very short retention times, two peaks at 5.7 and 9.5 min. The shorter retention time corresponds exactly to that of an authentic sample of **25**. It is also clearly different from the retention times of the other three isomeric 1,2,3,4-tetracarbomethoxycyclobutanes: **21**, t_r = 6.6 min; **26**, t_r = 8.5 min; and **28**, t_r = 18 min. The collected material (8 ft × 0.25 in., 15% Carbowax 20M, 210°) has mp 123.5–126° (lit.[14] mp 126–127°). The second component, mp 101–103.5°, was shown by comparison of infrared spectra to be identical with an authentic sample of trimethyl hemimellitate (**29**) (lit.[19] mp 99–101°) prepared by diazomethane esterification of the commercially available hemimellitic acid.

Ozonolysis of 24. A 10-mg sample of **24** was ozonized according to the above procedure. The glpc analysis of the esters indicated the presence of **29** and a second component at t_r = 8.5 min. This material was collected by preparative glpc and its infrared spectrum was shown to be identical with that of the synthesized sample of **26**.

Ozonolysis of 12a. The above procedure was carried out with a 5-mg sample of **12a**. Glpc analysis showed the presence of **21**

---

(27) G. W. Griffin and D. F. Veber, *J. Amer. Chem. Soc.*, **82**, 6417 (1960).

(t_r = 6.6 min) and, again, **29** (t_r = 9.5 min). The identity of **21** from this reaction with an authentic sample was confirmed by comparison of the infrared spectra and melting points.

Fluorescence Spectrum of 14a. The emission from a diethyl ether solution, 1.5×10^{-5} *M* in **14a**, was measured with a Cary Model 15 spectrophotometer equipped with a high-powered mercury–Xenon arc lamp and a monochromator adjusted to provide excitation light at 302 nm. A quartz cell was employed, and excitation was perpendicular to the path of the visible light detector of the spectrophotometer.

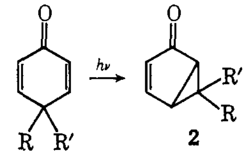
Synthesis and Photochemistry of Δ^1-4-Alkyltestosterones[1,2]

David I. Schuster*[3] and William C. Barringer[4]

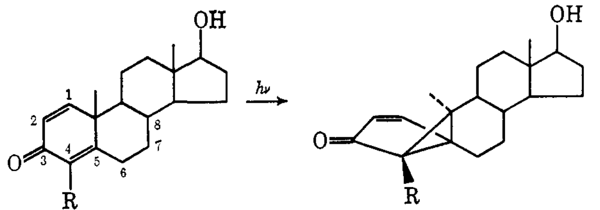
Contribution from the Department of Chemistry,
New York University, University Heights, New York, New York 10453.
Received June 23, 1970

Abstract: The synthesis of several 4-alkylated dehydrotestosterones is described, involving alkylation of testosterone and dehydrogenation using DDQ of the corresponding 17-tetrahydropyranyl ethers. Spectral data for all materials are consistent with the proposed structures. Photolysis of these steroidal dienones at 2537 Å in dioxane gives the corresponding lumiketones, with variable quantum efficiency. Quenching of the reaction is observed with 1,3-cyclohexadiene and *trans*-piperylene, with the efficiency of quenching much greater in all cases with cyclohexadiene. No orderly dependence of the quantum yields or derived rate constants on the size of the alkyl group was observed. Low-temperature absorption and emission studies indicate the lowest triplet in such systems is the π,π^* triplet. It is suggested that the two lowest triplet states, $T_{n,\pi}$ and $T_{\pi,\pi}$, may be in thermal equilibrium at room temperature. It is also postulated that the differential quenching observed with dienes may be due to relaxation of the spectroscopic triplet (E_T = ~70 kcal/mol) to a triplet (E_T = ~60 kcal/mol) whose geometry may approximate that of the previously postulated 3,5-bonded intermediate. It is also suggested that inefficiency in these reactions is not due to radiationless decay from the triplet, but rather to return to starting material from some intermediate along the reaction pathway to product.

The photochemical transformation of 2,5-cyclohexadienones **1** into bicyclo[3.1.0]hexenones (lumiketones) **2** has received much attention during the last decade, and the scope and mechanism of the photochemical rearrangement have been elucidated to a considerable extent,[5–9] although some basic questions concerning the nature and lifetime of the reactive excited state are unresolved.[10] One feature of the rearrangement which has not received attention is the role of steric effects on the reaction, as manifested in the quantum yield of the rearrangement and the rate constants for reaction and deactivation of the reactive triplet excited state.



1 **2**



3 **4**

Examination of molecular models indicated that in the course of rearrangement of 4-substituted dehydrotestosterones **3** to the corresponding lumiketones **4**, the R group experiences fairly severe steric interactions with the axial protons at C-6 and C-8. This interference could reduce the rate of product formation from the triplet, relative to the rate of radiationless decay, and might in an extreme situation lead to formation of a new type of product by a reaction path which is usually energetically unfavorable in comparison with the lumirearrangement. Accordingly, a series of compounds of type **3**, with R = H, methyl, ethyl, *n*-butyl, isobutyl, and isoamyl, was synthesized, most of them for the first time, and the details of their photochemistry were investigated.

Results

A. Synthesis of 4-Alkyldehydrotestosterones. Three basic routes to the synthesis of compounds **3** were investigated. The first, based on reactions extensively studied by Stork and his coworkers,[11] involved reductive alkylation of testosterone **5** to 4-substituted di-

---

(1) Part XXVII of a series on the photochemistry of unsaturated ketones in solution. XXVI: D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

(2) Supported in part by grants from the U. S. Army Research Office.

(3) Alfred P. Sloan Research Fellow, 1967–1969.

(4) (a) American Cyanamid Junior Educational Award, 1966–1968; (b) this paper is based on the Ph.D. Dissertation of W. C. B., New York University, 1968.

(5) For reviews, see (a) P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967); (b) K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966); H. E. Zimmerman, *ibid.*, **1**, 183 (1963).

(6) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(7) H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967).

(8) D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968).

(9) J. Frei, C. Ganter, D. Kagi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

(10) D. I. Schuster and N. K. Lau, *Mol. Photochem.*, **1**, 415 (1969).

(11) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Amer. Chem. Soc.*, **87**, 275 (1965).