

with a 2 *N* solution of sodium hydrogen carbonate and with water and dried over sodium sulfate. Removal of solvent yielded 93 mg. of a crude product, which, after chromatography on a silica gel column and recrystallization from methylene chloride-ether, gave 37 mg. of 7.

D. With Lithium Aluminum Hydride, Followed by Chromic Acid Oxidation.—A solution of 200 mg. of the tosylate (6) in 20 ml. of absolute tetrahydrofuran was added at once to a solution of 500 mg. of lithium aluminum hydride in 50 ml. of tetrahydrofuran and the mixture refluxed for 20 hr. After cooling, the excess reagent was decomposed with ethyl acetate, a saturated solution of sodium sulfate and then anhydrous sodium sulfate was added and the precipitated inorganic material filtered off. After thoroughly washing the residue with ethyl acetate, the combined solutions were dried over sodium sulfate and evaporated *in vacuo* to yield 195 mg. of a crystalline alcohol, m.p. 131–145°, which showed in the infrared absorption spectrum a large hydroxyl band and no bands for aromatic C=C or carbonyl groups. The crude product was oxidized with chromic acid under the same conditions as described. Chromatographic separation of the mixture on a column of silica gel furnished 23 mg. of 7, identical in all respects with authentic material. No androst-4-ene-3,17-dione (8) could be isolated.

E. With Sodium Borohydride Followed by Lithium Aluminum Hydride.—To a solution of 200 mg. of 8 in 50 ml. of ethanol was added a solution of 200 mg. of sodium borohydride in 50 ml. of ethanol; it was allowed to stand for 18 hr. at 25°. After pouring the solution on crushed ice and letting the mixture warm up to room temperature, the solids were filtered off and dried. The crude tosylate showed infrared absorption maxima at 3500 (—OH), 1580, and 1615 (aromatic C=C) cm^{-1} .

The crude sodium borohydride reduction product was now reduced with lithium aluminum hydride and the reaction product oxidized with chromic acid as indicated above, whereby 19 mg. of 7 and 17 mg. of 8 could be isolated.

5 β ,19-Cycloandrostan-3,17-dione-4-*d* and Androst-4-ene-3,17-dione-19-*d* from 6.—19-Tosyloxyandrost-4-ene-3,17-dione was first reduced with lithium aluminum deuteride and then the crude mixture was oxidized with chromic acid using the same conditions as those employed before. Separation on a thin layer chromatographic plate, using silica gel as adsorbent and 30% ethyl acetate in benzene as eluent, furnished a 1:1 mixture of androst-4-ene-3,17-dione-19-*d* and 5 β ,19-cycloandrostan-3,17-dione-4-*d*, $\nu_{\text{max}}^{\text{C}=\text{C}}$ 2142 (*C-d* axial) and 2167 cm^{-1} (*C-d* equatorial). The mass spectral analysis of the latter gave

<i>m/e</i>	286	25%	<i>d</i> ₀
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<i>m/e</i>	287	64%	<i>d</i> ₁
<i>m/e</i>	288	54%	<i>d</i> ₂
<i>m/e</i>	289	51%	<i>d</i> ₃

Equilibration with a 2.5% methanolic sodium hydroxide solution followed by isolation of androst-4-ene-3,17-dione gave a product which did not contain any deuterium.

Androst-4-ene-3,17-dione-19-*H*³ from 7.—To the solution of 27 mg. of 7 in 0.5 ml. of dioxane was added by distillation 4 mg. of tritiated water (13 c.) and 0.05 ml. of concentrated hydrochloric acid. After sealing the flask, the solution was heated on a steam bath for 24 hr. and then kept an additional 24 hr. at 25°. The break seal of the flask was then opened, the solvents distilled off, and the residue equilibrated with 2.5% potassium hydroxide in methanol-water (1:2 v./v.).

After addition of water the mixture was extracted with methylene chloride, the extract dried over anhydrous sodium sulfate, and evaporated. The crude mixture was finally chromatographed on a Celite partition column using the Bush A system, which yielded 11 mg. of androst-4-ene-3,17-dione-19-*H*³ with a specific activity of 20 $\mu\text{c.}/\mu\text{g.}$ The radiochemical purity was tested by chromatographing about 1 $\mu\text{c.}$ of the material with 5 $\mu\text{g.}$ of authentic androst-4-ene-3,17-dione on paper on the Bush A system. Scanning in a Vanguard automatic windowless flow chromatogram scanner (Model 800 autoscanner) gave a single sharp peak corresponding to the marked spot due to the carrier and found by inspection with the ultraviolet lamp.

In a second experiment, 20 mg. of 7 was dissolved in a flask containing 1 ml. of dioxane and 0.1 mg. of sodium hydroxide. The flask was connected to the vacuum line, degassed, and evacuated, and 4 mg. of tritiated water (13 c.) was distilled into it. Then the flask was sealed off, removed from the line, heated on a steam bath for 6 hr., and left at room temperature for 18 hr. After opening the break seal, the solvents were distilled off on the vacuum line, and water was added to the residue and worked up exactly as described above. After chromatography, 12 mg. of androst-4-ene-3,17-dione-19-*H*³ with a specific activity of 30 $\text{mc.}/\text{mg.}$ was isolated.

Acknowledgment.—The authors thank Dr. Karl Heusler of Ciba Ltd., Basel, Switzerland, for a generous gift of 19-hydroxyandrost-4-ene-3,17-dione and Mr. Thomas Wittstruck for the recording, calculation, and interpretation of the n.m.r. spectra. The methyl 17 β -acetoxy-3,5-seco-4,19-bisnorandrostan-5-one-3-oate was first prepared in this laboratory by Dr. H. J. Brodie.

COMMUNICATIONS TO THE EDITOR

The Chemistry of Barrelene. II.¹ A Remarkable Transformation to Naphthalene Derivatives

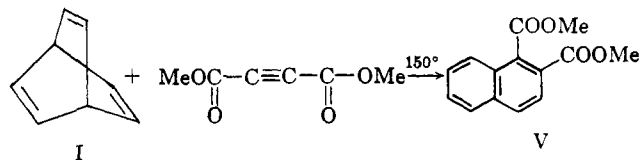
Sir:

Following our reported synthesis of barrelene^{1,2} (I), we have pursued investigations of the chemistry of this unusual compound. In one of these investiga-

(1) For Part I, cf. H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

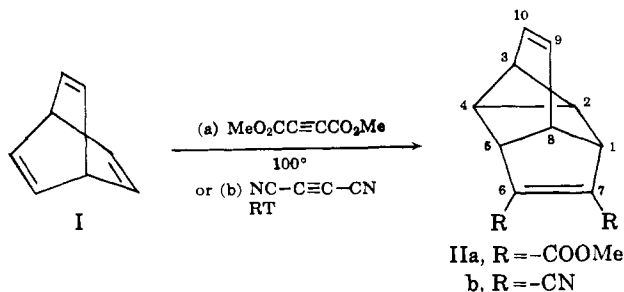
(2) The trivial name of "barrelene" was suggested for bicyclo[2.2.2]-octa-2,5,7-triene (I) because of the barrel shaped array of molecular orbitals possessed by this six electron π -system. However, electronic interaction and electron delocalization enforced by orbitals held within distance for appreciable overlap does not imply whether this interaction is stabilizing, destabilizing, or neither [e.g., bringing the terminal *p*-orbitals of hexatriene within overlap distance leads to stabilizing interaction (benzenoid electronics), bringing the terminal *p*-orbitals of butadiene within overlap distance leads to loss of delocalization energy (cyclobutadiene electronics), bringing three ethylenic moieties together with barrelene geometry leads to no change in delocalization energy]. The point that barrelene has no delocalization energy was clearly stated (ref. 1) but clarification of this seem-

ingly obvious distinction between interaction and stabilizing interaction appears necessary because we have been misquoted [J. M. Tedder, *Ann. Rept. Prog. Chem.*, **62**, 232 (1960)] as suggesting barrelene to be stabilized and then criticized for this opinion opposite to our published statement. Still another criticism seemed to be voiced by Tedder. But since we do not know how to interpret the comment "They even go so far as to suggest that the compound should be called barrelene," we are unable to reply to this. In contrast, one should note the more perceptive review of our work by M. F. Ansell in the same volume [*ibid.*, **62**, 246 (1960)]; unfortunately, Ansell's accurate report was not indexed.



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In order to elucidate the mechanistic nature of the transformation, we turned to lower temperature reaction conditions. At 100°, dimethyl acetylenedicarboxylate was observed to react with barrelene to form a monoadduct, m.p. 56.5–57.5°, in 29% yield. A similar adduct, m.p. 116–118.5°, resulted in 95% yield from reaction of dicyanoacetylene³ with barrelene at room temperature. These adducts are assigned structures IIa and IIb. The assignments are supported



by elemental analysis,⁴ n.m.r. (note Table I), analogy with the reaction of norbornadiene with dicyanoacetylene,^{5,6} and are consonant with the observed ultraviolet spectra (*cf.* Table II).

TABLE I
NUCLEAR MAGNETIC RESONANCE DATA

	Peak, τ	No. of H's	Positional assignment	Corresponding norbornadiene adduct peak (ref. 6)
Adduct IIa	3.47 triplet ^a	1	9	
	4.14 triplet ^a	1	10	
	6.20 singlet	6	Methoxyls	
	7.2–7.6 multiplet	2	3, 8	
	7.67 singlet	2	1, 5	
	8.19 doublet	2	2, 4	
Adduct IIb	3.37 triplet ^a	1	9	
	4.10 triplet ^a	1	10	
	7.0–7.5 multiplet	2	3, 8	7.93, 7.55
	7.59 singlet	2	1, 5	6.96
	8.13 doublet	2	2, 4	8.22

^a Minor further splitting was observed.

TABLE II
ULTRAVIOLET DATA

Compound ^a	Absorption $\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ), $\text{m}\mu$	Reference
Adduct IIa	245 (3.84)	Present work
Norbornadiene—dicyanoacetylene adduct	255 (3.90)	5
Adduct IIb	251 (3.94), 285 (3.58)	Present work
2,3-Dicarbomethoxybicyclo[2.2.1]-hept-2-ene-7-spiro-1'-cyclopentane	242 (3.77)	b
Dimethyl norbornene-2,3-dicarboxylic ester	238 (3.67)	b

^a The comparison compounds in Table I were selected because of structural similarity and/or molecular strain. It is to be noted that unstrained maleonitriles and maleic esters absorb at considerably shorter wave length. ^b C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 4258 (1961).

(3) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

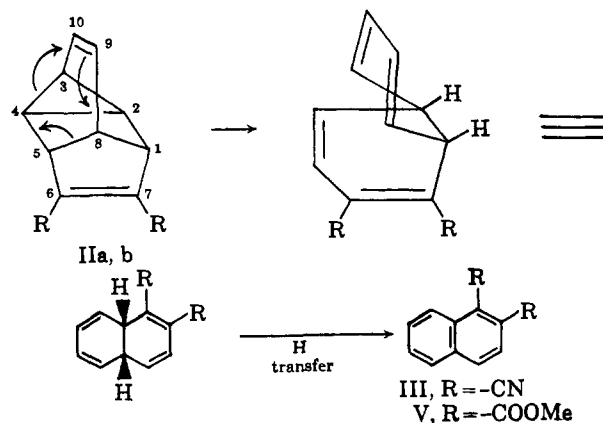
(4) Satisfactory analyses were obtained for all new compounds reported.

(5) R. C. Cookson and J. Dance, *Tetrahedron Letters*, 879 (1962).

(6) C. D. Weis, *J. Org. Chem.*, **28**, 74 (1963).

Interestingly, heating these adducts was found to convert them to 1,2-disubstituted naphthalene derivatives as major products. The reaction of IIb was studied in greater detail. In this case pyrolysis of the dicyanoacetylene-barrelene adduct (IIb) at 100° for 3.5 hr. was found to afford⁷ 63% of 1,2-dicyanonaphthalene^{8a} based on 32% of nonrecovered IIb. In a 6.5-hr. run IIb gave 63% of 1,2-dicyanonaphthalene (III) and 4% of 2,3-dicyanonaphthalene^{8b} based on 56% nonrecovered reactant IIb. After pyrolysis of the dimethyl acetylenedicarboxylate-barrelene adduct (IIa) at 150° for 4 hr., 33% of dimethyl naphthalene-1,2-dicarboxylate^{8c} (V) was isolated.

While the over-all transformation of barrelene and acetylenic dienophiles to naphthalene derivatives is indeed striking, once the intermediacy of adducts IIa and IIb is recognized the over-all transformation is readily understood. Thus adducts IIa and IIb have available to them a low energy transformation in which bonds 3–4 and 5–8 (or 1–8 and 2–3) break in a concerted process affording a 4,5 π -bond and a diene moiety comprising atoms 3, 10, 9, and 8. The result is seen to be a 9,10-dihydro-1,2-disubstituted naphthalene, the progenitor of the observed 1,2-disubstituted naphthalenes III and V.^{9,10}



We plan to report further on the chemistry of barrelene.¹¹

(7) Products were separated by chromatography on ethyl acetate-washed alumina. Known mixtures of IIb, III, and IV were recoverable unchanged on such chromatography.

(8) (a) Authentic 1,2-dicyanonaphthalene [E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936)] was synthesized for comparison; (b) authentic 2,3-dicyanonaphthalene for comparison purposes was prepared by a modification of the procedure of J. A. Mitchell and E. E. Reid [*J. Am. Chem. Soc.*, **53**, 321 (1931)]; (c) authentic material was prepared as described in ref. 8a.

(9) No molecular hydrogen was detectable by mass spectrometry of the gas in the pyrolysis tubes. However, the balance of the material isolated from chromatography seemed from infrared to be sp^3 C-H bond rich and intermolecular hydrogen transfer probably accounts for formation of naphthalenes from 9,10-dihydronaphthalenes. The formation of small quantities of 2,3-disubstituted naphthalenes could arise from fission of the 9,10-bond of the dihydronaphthalene followed by reclosure and dehydrogenation.

(10) Our observation of conversion of adducts of type II to 1,2-disubstituted naphthalenes is pertinent to the intriguing chemistry reported by C. G. Krespan, B. C. McKusick, and T. L. Cairns [*J. Am. Chem. Soc.*, **83**, 3428 (1961)]. An intermediate of type II (with R = trifluoromethyl and trifluoromethyl groups at C-9 and C-10) was considered as a possible intermediate leading mainly to 2,3,6,7-tetrakis(trifluoromethyl)naphthalene. In view of the behavior of intermediates of type II as delineated presently it seems likely that one of the alternative mechanisms entertained by these researchers is more likely.

(11) The n.m.r. data reported (ref. 1) by us earlier are in error. While the pattern reported is correct, the peak positions are shifted. The vinyl hydrogen quartet actually centers at 3.36 τ and the bridgehead multiplet at 5.31 τ . Comparing these with 4.06, 7.22 τ for norbornene and 3.35, 6.53 τ for norbornadiene, one finds no evidence for marked ring current "around the barrel." It is of interest to consider whether this derives from

Acknowledgment.—G. L. G. gratefully acknowledges a Wisconsin Alumni Research Foundation Fellowship (1960–1961) and a National Institutes of Health Pre-doctoral Fellowship (1961–1963). Thanks are due to Mr. Gary A. Zimmerman for the n.m.r. spectra.

the absence of any single molecular orbital having a continuous electron density around the barrel, or is due to the nodes present at each carbon nucleus so that electron density is necessarily discontinuous, or results from the relatively poor overlap noted in ref. 1.

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Mechanistic Organic Photochemistry. VIII. Identification of the $n-\pi^*$ Triplet Excited State in the Rearrangement of 4,4-Diphenylcyclohexadienone¹

Sir:

We proposed a mechanistic approach to organic photochemistry and noted that this treatment is applicable to transformations of both $n-\pi^*$ singlets and triplets.^{2a,c} Despite our choice of investigating molecular and gross electronic details first, the singlet *vs.* triplet question in the reactions we studied is an intriguing problem. As noted^{2c} we have been investigating this point in the 4,4-diphenylcyclohexadienone (I) to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (VII) reaction.^{2b,c} In the interim Richards³ has studied the problem in the related santonin rearrangement.

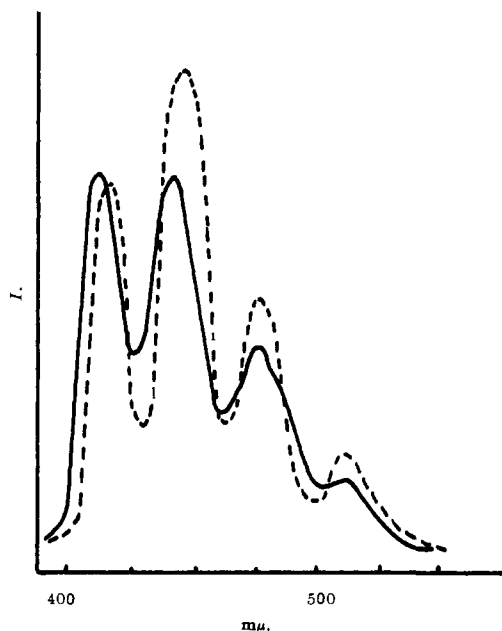


Fig. 1.—Triplet emission spectra: —, dienone; ---, benzophenone.

We now report that: (1) This reaction proceeds *via* a triplet state (III). (2) This triplet state undergoes molecular rearrangement at a rate rapid enough to

(1) Presented in preliminary form at the Gordon Research Conference in Organic Reactions, July, 1963, Tilton, N. H.

(2) (a) H. E. Zimmerman, Abstracts of the 17th National Organic Chemistry Symposium of the American Chemical Society, p. 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962); (d) H. E. Zimmerman, *et al.*, *ibid.*, **86**, 947 (1964) (paper VII).

(3) M. H. Fisch and J. H. Richards, *ibid.*, **86**, 3029 (1963).

invalidate one of the usual criteria for detecting triplets. (3) The triplet is of the $n-\pi^*$ variety, more electron rich at the β -carbon than is the ground state.^{2b} Our conclusions 1 and 2 are compatible with the findings of Richards.³

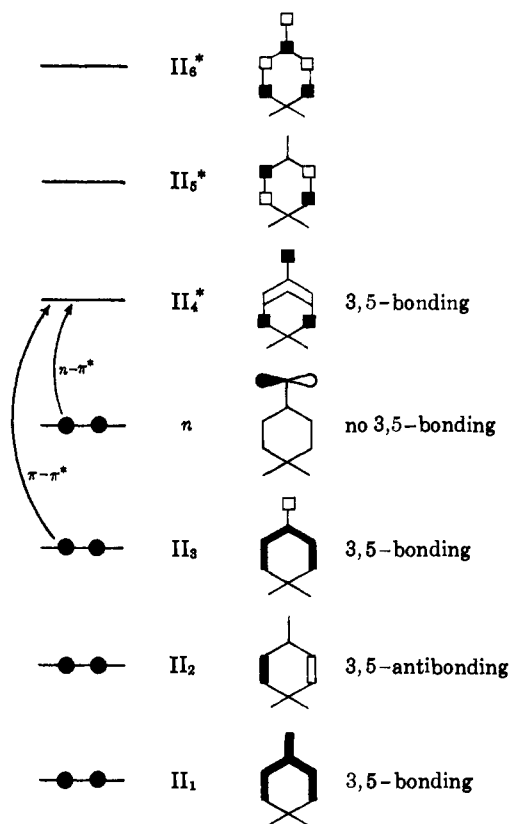


Fig. 2.—Cyclohexadienone molecular orbitals: ■, wave function positive; □, wave function negative.

Regarding the first point, we determined the 4,4-diphenylcyclohexadienone (I) to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (VII) conversion (Table I) to

TABLE I
RELATIVE CONVERSIONS

Conditions ^{a,d,h}	Dienone disappearance	VII formation
Dienone alone ^e	11	8.3
Dienone alone ^f	11	7.7
Dienone + acetophenone ^{c,e,g}	50	38
Dienone + naphthalene ^{b,f,g}	11	8.4

^a Dienone, 0.005 *M.* ^b Naphthalene, 0.1 *M.* ^c Acetophenone, 0.09 *M.* ^d All runs in benzene. ^e 310–360-m μ filter. ^f 335–420-m μ filter. ^g Beers' law adherence assured no ground state complexation. ^h Standardized for constant light.

be independent of minor wave length changes. With acetophenone present in concentration to absorb 98% of the light (Table I, entry 3) a fourfold increase resulted despite the negligible direct excitation of dienone, providing strong evidence for photosensitization by acetophenone forming 4,4-diphenylcyclohexadienone triplet (III). Since the same product (VII) resulted as in the ordinary irradiation, it is reasonably assumed that the dienone triplet (III) is also an intermediate in the unsensitized reaction (see Chart I).