Photochemistry of Mono- and Diacetylenic Systems. Exploratory and Mechanistic Organic Photochemistry. LXXVII[1]

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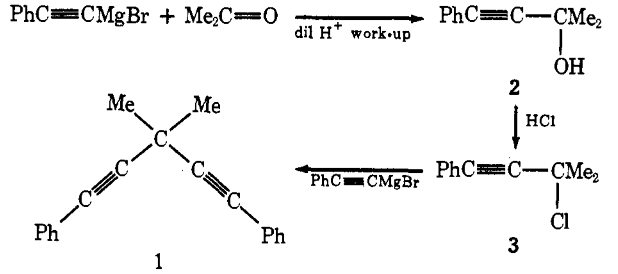
Abstract: The photochemistry of phenyl-*tert*-butylacetylene and 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne was studied. Although the latter compound is formally a di-π-methane system, it did not undergo the di-π-methane rearrangement. Rather, it afforded 5,5-dimethyl-2,3-diphenylcyclopentadiene and 3,3-dimethyl-1,5-diphenyl-1-penten-4-yne when the photolysis was run in isopropyl alcohol. In *tert*-butyl alcohol photolysis afforded only the cyclopentadiene. Sensitization with acetophenone in *tert*-butyl alcohol again gave the cyclopentadiene. Using xanthone in isopropyl alcohol both products were observed. This difference was interpreted as deriving from excited state ethynyl–ethynyl bridging to give an energetic hydrogen abstractor. From the photochemistry of phenyl-*tert*-butylacetylene information was obtained about the mechanisms of the reduction processes. Photolysis in isopropyl alcohol gave phenyl-*tert*-butylethylene with the cis product being kinetically preferred. The same product could be obtained by xanthone sensitization. In *tert*-butyl alcohol no reaction was observed. Labeling experiments demonstrated that both hydrogens transferred come from the carbinol carbon of the isopropyl alcohol.

In view of the considerable number of examples of the di-π-methane rearrangement involving two ethylenic groups,[2] a problem of some interest was the study of a diethynylmethane. For this study 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne (1) was selected.

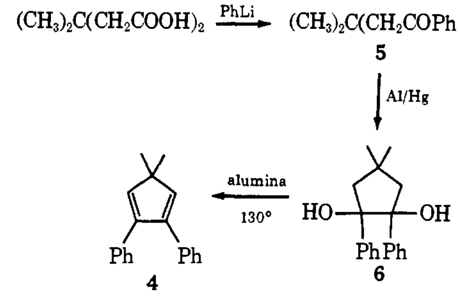
Synthesis of Reactants. The required 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne (1) was prepared as delineated in Chart I. This involved the reaction of phenylethynylmagnesium bromide with acetone, conversion of the resulting carbinol (2) to the corresponding tertiary chloride (3) with hydrogen chloride, and finally reaction of tertiary chloride 3 with phenylethynylmagnesium bromide to give the desired diyne 1. Phenyl-*tert*-butylacetylene, required for comparative study, was available as a known compound.[3]

Chart I. Synthesis of 3,3-Dimethyl-1,5-diphenyl-1,4-pentadiyne



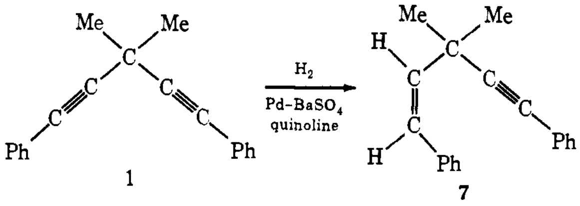
Photochemical Studies. Irradiation of the diyne 1 in isopropyl alcohol gave two products, both analyzing as dihydro derivatives of reactant 1. The first of the two products revealed two equivalent methyl groups as a sharp singlet and two equivalent vinyl hydrogens, again as a singlet. This suggested a 5,5-dimethyl-2,3-diphenylcyclopentadiene structure (*i.e.*, 4). Confirmation was obtained by independent synthesis (note Chart II).

Chart II. Synthesis of 5,5-Dimethyl-2,3-diphenylcyclopentadiene



Thus, reaction of phenyllithium with 3,3-dimethylglutaric acid afforded 1,5-diphenyl-3,3-dimethylpentane-1,5-dione (5). This compound, on treatment with aluminum amalgam, gave 4,4-dimethyl-1,2-diphenyl-1,2-cyclopentanediol (6). The diol was dehydrated over alumina at 130° to give 5,5-dimethyl-2,3-diphenylcyclopentadiene (4) which proved identical with the first photochemical product.

The second photochemical product, 7, revealed a six hydrogen singlet due to two equivalent methyl groups and a vinyl AB quartet suggestive of a *cis*-styryl moiety. With a *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne structure indicated by this evidence, the compound was independently prepared by catalytic hydrogenation of diyne 1 using the Cram–Lindlar catalyst[4] (note eq 1). The synthetic material proved identical with the second photochemical product.



(1)

In contrast to the behavior in isopropyl alcohol, irradiation of diyne 1 in *tert*-butyl alcohol gave only the cyclopentadiene 4.

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(1) For paper LXXVI of the series, note H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **95**, 2957 (1973).

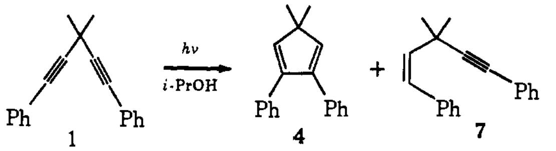
(2) (a) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970); (c) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(3) B. S. Krispin and A. A. Petrov, *J. Gen. Chem. USSR*, **31**, 2758 (1961).

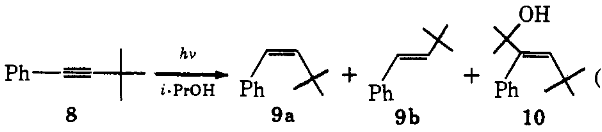
(4) D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

It was felt that a better understanding of the reactions of the diyne **1** would be possible if a model were available with just one acetylenic unit. This then would define what portion of the diyne photochemistry depended on the presence of two triple bonds. For this study, phenyl-*tert*-butylacetylene (**8**) was selected.

In *tert*-butyl alcohol, irradiation of this monoyne (*i.e.*, **8**) gave no reaction. However, in isopropyl alcohol direct irradiation gave 3,3-dimethyl-1-phenyl-1-butene (**9**) as the major product. Both stereoisomers were obtained with the cis isomer being heavily kinetically preferred. Additionally, 2-hydroxy-2,5,5-trimethyl-3-phenyl-3-hexene (**10**) was formed in lesser amounts. This photochemistry, along with that for diyne **1**, is summarized in eq 2 and 3.



(2)



(3)

Sensitization of diyne **1** in *tert*-butyl alcohol with acetophenone was found to give only cyclopentadiene **4** as a product. In isopropyl alcohol xanthone sensitization led to both enyne **7** and to cyclopentadiene **4**. Table I summarizes this and other diyne reaction efficiencies.

Table I. Quantum Yields for the Reaction of 3,3-Dimethyl-1,5-diphenylpentadiyne

Conditions	Quantum yields Cyclopentadiene **4**	Enyne **7**
Direct, *t*-BuOH	0.130	
Direct, *t*-BuOH	0.145	
Sens, acetophenone, *t*-BuOH	0.244	
Sens, acetophenone, *t*-BuOH	0.252	
Sens, xanthone (4.3 × 10^{-3} *M*), *t*-BuOH	0.060	
Sens, xanthone (5.9 × 10^{-3} *M*), *t*-BuOH	0.054	
Direct, *i*-PrOH	0.108	0.129
Sens, xanthone (7.5 × 10^{-3} *M*), *i*-PrOH	0.045	0.043
Sens, xanthone (1.6 × 10^{-2} *M*), *i*-PrOH	0.020	0.016

In the case of phenyl-*tert*-butylacetylene (**8**), xanthone sensitization in isopropyl alcohol afforded the same mixture of *cis*- and *trans*-*tert*-butylstyrenes **9a** and **9b** with the former being kinetically preferred again. The various monoyne (*i.e.*, **8**) quantum yields are given in Table II.

Since the sensitized runs were designed to avoid singlet energy transfer while generating the triplets of reactants, the observation of the usual reaction products in sensitization runs of the monoyne and diyne provides strongly suggestive evidence favoring triplet excited states as responsible for the observed reactions.

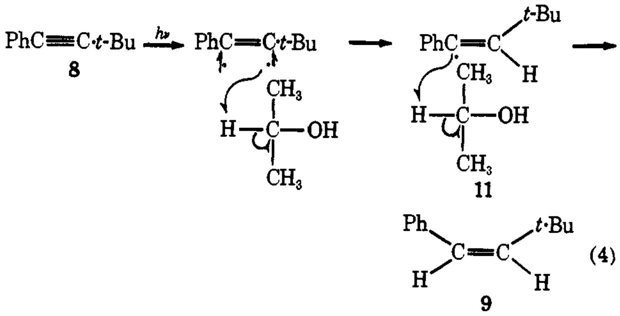
The direct quantum yields are also summarized in Tables I and II. These results are discussed below in connection with the reaction mechanism. For the present, however, it is of interest that the efficiencies are quite appreciable (*i.e.*, above 0.1). Previously the empirical rule was advanced[5] that quantum yields above *ca.* 0.05 generally prove synthetically useful.

Table II. Quantum Yields for the Reaction of 3,3-Dimethyl-1-phenyl-1-butyne (Phenyl-*tert*-butylacetylene)

Conditions	Quantum yields *cis*-**9**	*trans*-**9**	Alcohol **10**
Direct, *i*-PrOH	0.184	0.028	0.021
Direct, *i*-PrOH	0.164	0.029	0.018
Sens, xanthone (3.5 × 10^{-3} *M*), *i*-PrOH	0.028	0.0050	
Sens, xanthone (2.1 × 10^{-3} *M*), *i*-PrOH	0.029	0.0055	

In order to ascertain the molecular details of the mechanisms involved, experiments were devised using deuterium labeled isopropyl alcohol. In one approach O-deuterated isopropyl alcohol was used, while in a second test methyl deuterated alcohol was employed. It was found that irradiation of phenyl-*tert*-butylacetylene (**8**) in isopropyl alcohol-*O-d* led to *tert*-butylstyrene (**9**) with no deuterium incorporation. Photolysis in isopropyl alcohol deuterated at the methyl carbons produced *tert*-butylstyrene (**9**) in which hydrogen had been abstracted by the β position and, to the extent of 80%, hydrogen also was picked up by the α carbon.

This evidence clearly demonstrates that the β carbon of electronically excited phenyl-*tert*-butylacetylene (**8**) abstracts the carbinol hydrogen atom of isopropyl alcohol solvent. This is pictured in eq 4. With this initial abstraction in mind, and with the availability of the hydroxyisopropyl radical engendered, one might have expected the hydroxyl hydrogen to be delivered to the α carbon of intermediate radical **11**. The labeling studies show this not to be the case. The fate of the hydroxyisopropyl radical proved to be disproportionation to give acetone and isopropyl alcohol as was demonstrated by the vpc assay showing the formation of acetone in close to the expected amount. Delivery of the second hydrogen is seen from the results to be primarily from the carbinol carbon of a second isopropyl alcohol solvent molecule and to a lesser extent from the methyl carbon. Equation 4 summarizes the situation.



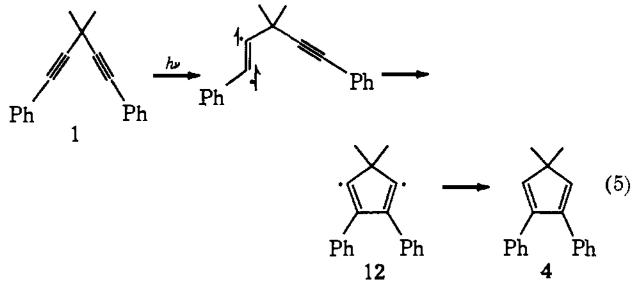
The rather interesting preferred geometry can be construed to signify approach of the bulky isopropyl alcohol molecule to the less hindered side of vinyl radical **11**. This preferred stereochemistry is found again in the photochemistry of diyne **1** and thus appears to be general. Accordingly, the formation of enyne **7** seems likely to follow the same reaction course. This is emphasized by the similarity of the quantum

[5] H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3662 (1971). Perhaps a more realistic value would be 0.005.

yields (*i.e.*, $\phi = 0.17$ for the monoyne **8** and $\phi = 0.13$ for the diyne **1**).[6]

Remaining for discussion is the intriguing formation of the cyclopentadiene from irradiation of diyne **1**. In *tert*-butyl alcohol this was the exclusive product, suggesting that facile hydrogen abstraction is not a requisite for the reaction. In fact, the similar quantum yields in isopropyl alcohol and in *tert*-butyl alcohol (a very poor hydrogen donor) strongly indicate that hydrogen abstraction does not occur prior to the rate-limiting stage of the reaction. Furthermore, the abstraction of two hydrogens from *tert*-butyl alcohol solvent suggests that some reactive hydrogen abstracting species is a reaction intermediate.

To accommodate these facts a mechanism beginning with bridging between the two ethynyl groups seems most reasonable. This leads to biradical **12** which then is the energetic hydrogen abstractor. This mechanism is pictured in eq 5.



1

12

4

(5)

Finally, it is to be noted that the present reaction occurs by a different type of π–π bridging than the di-π-methane rearrangement. In one instance of an acetylenic system, the ordinary di-π-methane rearrangement does occur; however, in this example by Griffin,[7] bridging between an acetylenic group and phenyl ring occurs and no five ring is available for formation. Indeed there are a few examples of photochemical ethynyl–ethynyl bridging although the literature cases follow different overall reaction courses.[8] That the reaction begins with ordinary di-π-methane bridging and then affords a cyclobutadiene valence tautomer of **12** is an intriguing possibility for which, however, no evidence is available.

Experimental Section[9]

3-Hydroxy-3-methyl-1-phenyl-1-butyne. A solution of 102 g (1.00 mol) of phenylacetylene in 150 ml of ether was added over 1 hr to a stirred solution of 1.00 mol of ethylmagnesium bromide in 400 ml of ether, and the reaction was refluxed for an additional hour. A solution of 58.1 g (1.00 mol) of acetone in 150 ml of ether was then added and the mixture refluxed 1 hr more. The mixture was then poured into 1 *N* HCl and ice; the ether layer was washed with water, dried over $MgSO_4$, and concentrated *in vacuo* to give 160 g of dark viscous oil that crystallized on standing. Two crystallizations from hexane gave 110 g (73%) of 3-hydroxy-3-methyl-1-phenyl-1-butyne: mp 53.5–54.5°; ir (CCl_4) 2.74, 2.90 (br), 3.32, 3.37, 6.25, 6.71, 8.00, 8.59, 10.42, 11.05, 11.60, 14.50 μ; nmr (CCl_4) τ 8.40 (s, 6 H, CH_3), 7.49 (s, 1 H, OH), 2.9–2.5 (m, 5 H, arom).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.45; H, 7.75. Found: C, 82.55; H, 7.53.

3-Chloro-3-methyl-1-phenyl-1-butyne. A solution of 15 g (0.10 mol) of 3-hydroxy-3-methyl-1-phenyl-1-butyne in 300 ml of hexane was injected in 40-ml portions into a Brown hydrochlorinator[10] with the reaction flask cooled to 0°. In 45 min the reaction had stopped after consuming 11.0 ml of concentrated HCl (92% of theory). The reaction mixture was then dried over $MgSO_4$, filtered, and concentrated to give 16.8 g (100%) of the desired chloride as a pale yellow liquid: ir (CCl_4) 3.25, 3.33, 3.40, 4.48, 6.25, 6.71, 6.92, 7.22, 7.31, 7.73, 8.02, 8.43, 9.00, 9.35, 9.72, 10.48, 10.95, 11.7, 14.5 μ; nmr (CCl_4) τ 8.10 (s, 6 H, CH_3), 2.9–2.4 (m, 5 H, arom).

Attempts at vacuum distillation resulted in decomposition by loss of HCl so the compound was used without further purification.

3,3-Dimethyl-1,5-diphenyl-1,4-pentadiyne. A solution of 8.97 g (0.088 mol) of phenylacetylene in 50 ml of tetrahydrofuran was added to 0.080 mol of ethylmagnesium bromide in 50 ml of tetrahydrofuran, and the reaction was refluxed for 1 hr. After adding 200 mg of cuprous chloride[11] the reaction was refluxed for 1 hr more. Finally, 8.83 g (0.053 mol) of 3-chloro-3-methyl-1-phenyl-1-butyne in 50 ml of tetrahydrofuran was added and the mixture stirred at room temperature for 16 hr. The reaction mixture was then poured into 1 *N* HCl and ice and ether extracted. The extract was washed with a 5% $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give 16.7 g of a dark brown oil which crystallized on standing. The mixture was chromatographed on a 4 × 40 cm column of silica gel plus Norit (8 cm 1:1 Norit-SiO_2 at the top), and elution with hexane gave 7.54 g of the acetylene. One crystallization from ethanol gave 6.18 g (48%) of pure 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne: mp 79–80°; ir (CCl_4) 3.25, 3.33, 3.40, 4.50 (wk), 6.25, 6.72, 6.93, 7.23, 7.35, 7.73, 8.56, 9.36, 9.72, 10.98, 14.53 μ; nmr (CCl_4) τ 8.30 (s, 6 H, CH_3), 2.9–2.4 (m, 10 H, arom); uv max (MeOH) 256 nm (ϵ 43,100), 240 (36,800).

Anal. Calcd for $C_{19}H_{16}$: C, 93.39; H, 6.61. Found: C, 93.37; H, 6.70.

The same preparation was also carried out using ether as the solvent for the Grignard coupling reaction but the yield of the diyne was only 23%. This observation is in agreement with some similar preparations previously reported.[11]

Photolysis of 3,3-Dimethyl-1,5-diphenyl-1,4-pentadiyne in *tert*-Butyl Alcohol. A solution of 597 mg (2.45 mmol) of the diyne in 50 ml of *tert*-butyl alcohol was photolyzed for 2 hr using a 450-W Hanovia medium-pressure mercury lamp with a 1-mm Corex glass filter.[12] The reaction was purged with nitrogen before and during the photolysis. Removal *in vacuo* of the *tert*-butyl alcohol gave a dark yellow crystalline mass which was subjected to reverse phase methanol–cyclohexane liquid–liquid partition chromatography on a 3 × 204 cm column of polystyrene beads as described previously.[2c] The eluent was scanned at 260 nm and collected in 40-ml fractions. Fractions 11–20 contained 79 mg of a yellow oil which by nmr and ir analysis seemed to be a complex mixture of compounds; fractions 58–68, 312 mg of starting diyne; fractions 71–86, 116 mg of 5,5-dimethyl-2,3-diphenylcyclopentadiene, mp 103–104°; fractions 86–103, 33 mg of an unknown compound. The total recovery of the diyne and the cyclopentadiene was 428 mg (70%).

The cyclopentadiene was recrystallized from ethanol and then sublimed at 40° and 1 mm to give the pure compound: mp 104.5–105.5°; ir (CCl_4) 3.26, 3.37, 3.41, 3.48, 6.25, 6.72, 6.95, 8.02, 9.00, 9.32, 9.72, 9.85, 10.6, 10.95, 11.6, 11.8, 14.4 μ; nmr (CCl_4) τ 8.69 (s, 6 H, CH_3), 3.72 (s, 2 H, vinyls), 2.90 (s, 10 H, arom); uv max (MeOH) 225 nm (ϵ 20,500), 238 (23,400); mass spectrum parent ion 246.

Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.77; H, 7.22.

3,3-Dimethyl-1,5-diphenyl-1,5-pentanedione. To a solution of 3.20 g (0.020 mol) of β,β-dimethylglutaric acid in 125 ml of tetrahydrofuran was added 75 ml of a freshly prepared 1.0 *M* solution

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[6] Note that several cases of photochemical reductions of acetylenes have been reported previously: (a) D. A. Ben-Efraim, *Tetrahedron Lett.*, 957 (1967); (b) J. W. Wilson and U. S. Stubblefield, *J. Amer. Chem. Soc.*, **90**, 3423 (1968); (c) T. D. Roberts, L. Ardemagni, and H. Shechter, *ibid.*, **91**, 6185 (1969); (d) T. D. Roberts, *Chem. Commun.*, 362 (1971).

[7] (a) B. Halton, M. Kulig, M. A. Battiste, J. Perreton, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971); (b) Professor Griffin has brought to our attention that he has been studying similar systems. Thus, note G. W. Griffin, 16th PRF Annual Reports, 1971, where mention is made that compound 1 had been synthesized and that investigation of diacetylenic di-π-methanes had been begun.

[8] B. Bossenbrock, D. C. Sanders, H. M. Curry, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 371 (1969), and references therein.

[9] All melting points were taken on a hot-stage apparatus calibrated with known compounds.

[10] H. C. Brown and N. H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

[11] H. Tanaguchi and S. I. Miller, *Tetrahedron*, **22**, 867 (1966).

[12] The Corex filter was checked and found to cut off below 260 nm. We have been informed (private communication) by H. Morrison that presently available Corex no longer is opaque at this wavelength.

of phenyllithium in ether. The mixture was left stirring for 16 hr and then poured into ice water and ether extracted. The extracts were washed with water, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give 4.00 g of yellow oil. This oil was chromatographed on a 2.5 × 90 cm column of 25% Celite and 75% silica gel (Mallinckrodt Silicar CC-7, 200–325 mesh) to give 2.50 g (45%) of the required 3,3-dimethyl-1,5-diphenyl-1,5-pentanedione as a clear oil: ir (CCl_4) 3.27, 3.38, 3.48, 5.92, 6.25, 6.32, 6.90, 7.38, 8.10, 8.50, 9.90, 11.0, 11.6, 14.5 μ; nmr (CCl_4) τ 8.82 (s, 6 H, CH_3), 6.82 (s, 4 H, CH_2), 2.8–2.4 (m, 6 H, arom), 2.2–2.0 (m, 4 H, arom).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.44. Found: C, 81.43; H, 7.44.

It is worth noting that this compound has been reported previously;[13] however, the preparation described gives instead 3,3-dimethyl-5,5-diphenyl-δ-valerolactone.[14]

4,4-Dimethyl-1,2-diphenyl-1,2-cyclopentanediol. The method of Hoffman and coworkers was used.[15] A mixture of 20 ml of ethanol, 10 ml of water, 237 mg (0.847 mmol) of 3,3-dimethyl-1,5-diphenyl-1,5-pentanedione, and 200 mg of freshly prepared aluminum amalgam was refluxed for 3 hr. Filtration and removal of the solvent *in vacuo* gave 216 mg of a viscous oil which was chromatographed on a 2.5 × 80 cm silica gel column (Matheson Coleman and Bell, Grade 62, 60–200 mesh). Elution with 15% ether–hexane gave 114 mg (50%) of the diol in the 1200–1700-ml fraction. Two crystallizations from hexane gave 91 mg of pure 4,4-dimethyl-1,2-diphenyl-1,2-cyclopentanediol: mp 135–136°; ir (CCl_4) 2.92, 3.25, 3.38, 6.72, 6.95, 7.35, 7.60, 8.50, 8.90, 9.45, 9.70, 10.05, 10.85, 14.4 μ; nmr (CCl_4) τ 8.77 (s, 3 H, CH_3), 8.63 (s, 3 H, CH_3), 8.23 (d, J = 16 cps, 2 H, CH_2), 7.63 (d, J = 16 cps, 2 H, CH_2), 6.42 (s, 2 H, OH), 3.10 (s, 10 H, arom).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.72; H, 8.12.

5,5-Dimethyl-2,3-diphenylcyclopentadiene. A sample of 41 mg (0.15 mmol) of 4,4-dimethyl-1,2-diphenyl-1,2-cyclopentanediol was slurried in hexane with 570 mg of activated alumina (Woelm, neutral, heated to 400° at 1 mm for 20 hr). The hexane was removed under vacuum and the mixture was pyrolyzed for 1 hr at 130°. The alumina was then extracted with 3 × 100-ml portions of hexane, and the filtrate was concentrated *in vacuo* to give 12.6 mg of an oil. This was chromatographed by silica gel tlc using hexane eluent to give 9.9 mg (28%) of 5,5-dimethyl-2,3-diphenylcyclopentadiene, which had the same melting point (104–105°) and spectral properties as that obtained from photolysis of 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne (*vide supra*).

Photolysis of 3,3-Dimethyl-1,5-diphenyl-1,4-pentadiyne in 2-Propanol. A solution of 1.00 g (4.1 mmol) of the diyne in 1000 ml of 2-propanol was photolyzed under nitrogen for 2.5 hr using a 450-W Hanovia medium-pressure mercury lamp with a 1-mm Corex glass filter.[12] Removal of the solvent gave a yellow oil which was chromatographed on a 2.5 × 200 cm silica gel column (Matheson Coleman and Bell, Grade 62, 60–200 mesh) using hexane eluent, uv scanning (260 nm), and collection in 40-ml fractions. Fractions 40–53 contained 121 mg of 5,5-dimethyl-2,3-diphenylcyclopentadiene; fractions 54–61, 26 mg of a mixture of the cyclopentadiene and *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne; fractions 62–71, 138 mg of a mixture of the enyne and the starting material, 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne; fractions 72–87, 434 mg of a similar mixture but richer in the diyne; fractions 88–108, 81 mg of pure diyne. The total yield of recovered hydrocarbons was 800 mg (80%). Although complete separation of the three hydrocarbons was not possible by column chromatography, vpc analysis on a 0.25 in. × 6 ft 15% Carbowax 20M on Chromosorb W column (200°, 30 ml/min) indicated that the original reaction mixture contained 15% 5,5-dimethyl-2,3-diphenylcyclopentadiene, 14% *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne, and 71% 3,3-dimethyl-1,5-dimethyl-1,5-diphenyl-1,4-pentadiyne.

A pure sample of *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne was obtained by chromatographing fractions 62–71 from above on a 2.5 × 200 cm alumina column (neutral, activity 1) using hexane eluent and 40-ml fractions; fractions 161–225 contained 42 mg of pure (by vpc analysis) enyne. Later fractions contained mixtures of the enyne and the diyne.

Spectral properties for *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne were: ir (film) 3.25, 3.38, 3.48, 6.30, 6.75, 6.98, 8.60, 8.90, 9.80, 11.0, 12.9, 13.3, 14.6 μ; nmr (CCl_4) τ 8.55 (s, 6 H, CH_3), 4.40 (d, J = 12 cps, 1 H, C-2 vinyl), 3.57 (d, J = 12 cps, 1 H, C-1 vinyl), 3.0–2.5 (m, 10 H, arom); uv max (MeOH) 240 nm (ϵ 25,000), 252 (21,100); mass spectrum parent ion 246.

Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.49; H, 7.25.

***cis*-3,3-Dimethyl-1,5-diphenyl-1-penten-4-yne.** The hydrogenation of a 104-mg (0.42 mmol) sample of 3,3-dimethyl-1,5-dipenyl-1,4-pentadiyne was effected using 408 mg (3.2 mmol) of quinoline and 106 mg of 5% palladium on barium sulfate as the catalyst.[4] The reaction was stopped after 30 sec. Filtration and concentration *in vacuo* gave a crystalline residue which by nmr analysis indicated 20% conversion to *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne. Three such runs were combined and subjected to preparative tlc to remove the quinoline. This hydrocarbon mixture was then crystallized once from ethanol to remove excess diyne, and the mother liquors (108 mg) were chromtographed on a 2.5 × 200 cm alumina column (neutral, activity 1) using hexane as eluent. Fractions 165–185 contained 15.3 mg of material which was predominantly (90%) *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne. This material had identical spectra and vpc retention time as that obtained from the photolysis of the diyne (*vide supra*). The impurity in this material was assumed, on the basis of the nmr spectra, to be 3,3-dimethyl-1,5-diphenyl-1,4-pentadiene obtained from the reduction of both acetylenic bonds of the diyne.

Quantum Yields for the Reaction of 3,3-Dimethyl-1,5-diphenyl-1,5-pentadiyne. All quantum yield irradiations were performed on the optical bench described previously.[16] Light output was monitored by ferrioxalate actinometry[17] and the light absorbed in the reaction cell was determined by the splitting ratio technique described.[16] Monochromator slits were set at 3 mm giving a band pass of 22 nm at half-peak height. The quantum yields for product formation were determined by vpc analysis using a 0.25 in. × 6 ft 15% Carbowax 20M on Chromosorb W column (200°, 30 ml/min). Retention times were: 5,5-dimethyl-2,3-diphenylcyclopentadiene, 22 min; *cis*-3,3-dimethyl-1,5-diphenyl-1-penten-4-yne, 30 min; 3,3-dimethyl-1,5-diphenyl-1,4-pentadiyne, 57 min. Anthracene was used as an internal standard, and the flame ionization detector of the Varian Aerograph Model 2100 gas chromatograph was calibrated for the relative response of the compounds in the photolysate and the standard. The estimated precision of the quantum yields is ±5% based on the total error in the actinometry and the analysis.

Summary of Quantum Yields. Data are listed as follows: wavelength of irradiation, solvent and volume, starting diyne (mmol), light absorbed, cyclopentadiene formed (mmol), quantum yield, enyne formed (mmol), quantum yield, per cent conversion.

Run I-1: 252 nm, 39 ml of *tert*-butyl alcohol, diyne (112×10^{-3} mmol), 13.8×10^{-3} mEinsteins, cyclopentadiene (1.80×10^{-3} mmol), $\phi = 0.130$, 1.6%.

Run I-2: 252 nm, 39 ml of *tert*-butyl alcohol, diyne (93.8×10^{-3} mmol), 13.6×10^{-3} mEinsteins, cyclopentadiene (2.02×10^{-3} mmol), $\phi = 0.145$, 2.2%.

Run I-3: 313 nm, 39 ml of *tert*-butyl alcohol, diyne (69.7×10^{-3} mmol), acetophenone (99.2×10^{-2} mmol), 47.9×10^{-3} mEinsteins, cyclopentadiene (11.7×10^{-3} mmol), $\phi = 0.244$, 17%.

Run I-4: 313 nm, 39 ml of *tert*-butyl alcohol, diyne (92.0×10^{-3} mmol), acetophenone (100×10^{-2} mmol), 90.7×10^{-3} mEinsteins, cyclopentadiene (22.9×10^{-3} mmol), $\phi = 0.252$, 25%.

Run I-5: 335 nm, 39 ml of *tert*-butyl alcohol, diyne (135×10^{-3} mmol), xanthone (168×10^{-3} mmol), 24.0×10^{-3} mEinsteins, cyclopentadiene (1.44×10^{-3} mmol), $\phi = 0.060$, 1.1%.

Run I-6: 335 nm, 39 ml of *tert*-butyl alcohol, diyne (135×10^{-3} mmol), xanthone (231×10^{-3} mmol), 28.4×10^{-3} mEinsteins, cyclopentadiene (1.54×10^{-3} mmol), $\phi = 0.054$, 1.1%.

Run I-7: 252 nm, 39 ml of 2-propanol, diyne (216×10^{-3} mmol), 9.93×10^{-3} mEinsteins, cyclopentadiene (1.07×10^{-3} mmol), $\phi = 0.108$, 1-penten-4-yne (1.28×10^{-3} mmol), $\phi = 0.129$, 1.1%.

Run I-8: 335 nm, 39 ml of 2-propanol, diyne (140×10^{-3} mmol), xanthone (294×10^{-3} mmol), 20.8×10^{-3} mEinsteins, cyclopentadiene (0.943×10^{-3} mmol), $\phi = 0.045$, 1-penten-4-yne (0.897×10^{-3} mmol), $\phi = 0.043$, 1.3%.

Run I-9: 335 nm, 39 ml of 2-propanol, diyne (129×10^{-3} mmol), xanthone (633×10^{-3} mmol), 20.0×10^{-3} mEinsteins.

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cyclopentadiene (0.78×10^{-3} mmol), $\phi = 0.020$, 1-penten-4-yne (0.62×10^{-3} mmol), $\phi = 0.016$, 1.1%.

3,3-Dimethyl-1-phenyl-1-butyne. This acetylene has been prepared previously but no experimental details are given.[3] A solution of 20.1 g (0.20 mol) of phenylacetylene in 100 ml of ether was added over 1 hr to a solution of 0.20 mol of ethylmagnesium bromide in 100 ml of ether. The reaction was stirred for 1 hr more and then 27.4 g (0.20 mol) of *tert*-butyl bromide in 100 ml of ether was added. After 16 hr the mixture was poured into 1 *N* HCl and ice. The ether layer was washed with water, dried over $MgSO_4$, and concentrated *in vacuo* to give 23 g of a thick dark oil. Distillation gave 10 g (31%) of 3,3-dimethyl-1-phenyl-1-butyne, bp 80–81° (8 mm) (lit.[3] 84° (10 mm)). The acetylene was further purified by preparative gas chromatography on a 1 in. × 12 ft 15% Carbowax 20M on Chromosorb W column (130°, 1000 ml/min). Spectral data were: nmr (CCl_4) τ 8.70 (s, 9 H, *t*-Bu), 3.0–2.5 (m, 5 H, arom); uv max (MeOH) 248 nm (ϵ 24,400), 238 (27,800).

Photolysis of 3,3-Dimethyl-1-phenyl-1-butyne in 2-Propanol. A solution of 517 mg (3.3 mmol) of 3,3-dimethyl-1-phenyl-1-butyne in 500 ml of 2-propanol was photolyzed (under nitrogen) for 5 hr using a 450-W Hanovia medium-pressure mercury lamp with a 1-mm Corex glass filter.[12] The photomixture was analyzed by vpc using 0.25 in. × 6 ft 15% Carbowax 20M on Chromosorb W column (110°, 30 ml/min) and contained *cis*-3,3-dimethyl-1-phenyl-1-butene (52%, based on starting material), 3,3-dimethyl-1-phenyl-1-butyne (11%), *trans*-3,3-dimethyl-1-phenyl-1-butene (3%), and 2-hydroxy-2,5,5-trimethyl-3-phenyl-3-hexene (11%). As well there were two other peaks in the vpc scan which only appeared after prolonged photolysis and accounted for approximately 10% of original acetylene. These are assumed to be secondary products resulting from the photolysis of *cis*- and *trans*-3,3-dimethyl-1-phenyl-1-butene.[18]

The photolysis mixture was then chromatographed by preparative tlc using hexane as eluent to separate the hydrocarbons from the alcohol photoproduct. Pure samples of *cis*- and *trans*-3,3-dimethyl-1-phenyl-1-butene were then isolated from the hydrocarbon fraction by preparative scale glc using a 1 in. × 12 ft 15% Carbowax 20M on Chromosorb W column (110°, 1000 ml/min). These were found identical with known samples of the compounds.[19] Isolation of the alcohol product gave 75 mg of 2-hydroxy-2,5,5-trimethyl-3-phenyl-3-hexene, mp 85–86°. A pure sample, mp 86.5–87.5°, was obtained by vacuum sublimation at 1 mm at room temperature: ir (CCl_4) 2.90, 3.35, 3.42, 3.47, 6.80, 7.32, 7.55, 8.50, 9.00, 9.35, 9.75, 10.3, 10.7, 10.9, 12.0, 13.9, 14.2, μ; nmr (CCl_4) τ 9.20 (s, 9 H, *t*-Bu), 8.77 (s, 6 H, CH_3), 7.5 (s, 1 H, OH), 4.20 (s, 1 H, vinyl), 3.1–2.7 (m, 5 H, arom).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.29; H, 10.22.

Quantum Yields for the Reaction of 3,3-Dimethyl-1-phenyl-1-butene. Quantum yield irradiations were performed on the optical bench as described above.

The quantum yields for product formation were determined by vpc analysis using a 0.25 in. × 6 ft 15% Carbowax 20M on Chromosorb W column (30 ml/min). Two temperatures were used: 110° to analyze for the hydrocarbons and 140° for the alcohol. Retention times were: at 110°: *cis*-3,3-dimethyl-1-phenyl-1-butene, 11 min; 3,3-dimethyl-1-phenyl-1-butyne, 18 min; *trans*-3,3-dimethyl-1-phenyl-1-butene, 22 min; at 140°: 2-hydroxy-2,5,5-trimethyl-3-phenyl-3-hexene, 34 min. Naphthalene was used as an internal standard, and the flame ionization detector of the Varian Aerograph Model 2100 gas chromatograph was calibrated for the relative response of the compounds in the photolysate and the standard. The estimated precision of the quantum yields is 5% based on the total error in the actinometry and the analysis.

Summary of Quantum Yields. Data are listed as follows: wavelength, solvent and volume, starting acetylene (mmol), light absorbed, products formed (mmol), followed by quantum yield, percent conversion.

Run II-1: 252 nm, 39 ml of 2-propanol, acetylene (131×10^{-3} mmol), 16.4×10^{-3} mEinsteins, cis olefin (3.02×10^{-3} mmol), $\phi = 0.184$, trans olefin (0.46×10^{-3} mmol), $\phi = 0.028$, alcohol (0.34×10^{-3} mmol), $\phi = 0.021$, 3%.

Run II-2: 252 nm, 39 ml of 2-propanol, acetylene (163×10^{-3} mmol), 10.1×10^{-3} mEinsteins, cis olefin (1.69×10^{-3} mmol), $\phi = 0.164$, trans olefin (0.29×10^{-3} mmol), $\phi = 0.029$, alcohol (0.18×10^{-3} mmol), $\phi = 0.018$, 1.3%.

Run II-3: 335 nm, 39 ml of 2-propanol, acetylene (150×10^{-3} mmol), xanthone (101×10^{-3} mmol), 25.2×10^{-3} mEinsteins, cis olefin (0.70×10^{-3} mmol), $\phi = 0.028$, trans olefin (0.12×10^{-3} mmol), $\phi = 0.0050$, 0.5%.

Run II-4: 335 nm, 39 ml of 2-propanol, acetylene (135×10^{-3} mmol), xanthone (82×10^{-3} mmol), 52.5×10^{-3} m Einsteins, cis olefin (1.52×10^{-3} mmol), $\phi = 0.029$, trans olefin ($0.29\ 10^{-3}$ mmol), $\phi = 0.0055$, 1.3%.

Preparation of Deuterated 2-Propanols. *O*-Deuterio-2-propanol was synthesized according to the method of Cohen[20] by the deuterium oxide hydrolysis of diisopropyl sulfite. 1,1,1,3,3,3-Hexadeuterio-2-propanol was prepared as described previously[21] by lithium hydride reduction of acetone-d_6.

Photolysis of 3,3-Dimethyl-1-phenyl-1-butyne in Deuterated 2-Propanol. In a typical run, 50 mg (0.32 mmol) of 3,3-dimethyl-1-phenyl-1-butyne in 3 ml of deuterated 2-propanol was irradiated for 6 hr at 254 nm (Rayonet-like apparatus containing 32 GE G15T8 15-W germicidal lamps). The solution was purged with nitrogen before and during the photolysis. Analysis by vpc indicated approximately 60% conversion of starting acetylene to photoproducts. The solvent was removed *in vacuo*, and the resulting mixture was examined by nmr in order to determine the deuterium incorporation in *cis*-3,3-dimethyl-1-phenyl-1-butene.

O-Deuterio-2-propanol: nmr (CCl_4) τ 4.43 (d, J = 13 cps, C-2 vinyl, rel area 1), 3.60 (d, J = 13 cps, C-1 vinyl, rel area 1).

Hexadeuterio-2-propanol: nmr (CCl_4) τ 4.43 (two doublets; J = 13 cps, J = 2 cps, C-2 vinyl, rel area 1), 3.60 (doublet, J = 13 cps, C-1 vinyl, rel area 0.8).

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