Note Added in Proof. 7-*cis*-Retinal is formed upon photolysis of **1** in polar solvents.[25]

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(15) The failure to detect these isomers in our previous study[5] may be the result of a number of factors. In that study the photoconversions of **1** were 1–2%. Quantum yields were obtained from the peak areas of these chromatograms. Since the peak corresponding to **1** was kept on scale, it is likely that a small amount of 9-*cis*-retinal could have gone unnoticed in the hexane solutions (or 11-*cis*-retinal in the methanol solutions). We specifically sought to observe the presence of these isomers in the present experiments and were aided by the increased sensitivity of the Model 440 absorbance detector, compared to the Model 100 absorbance detector used earlier. The increased sensitivity is approximately two orders of magnitude. One nanogram of **1** can be observed ($S/N = 3$) using the Model 440 absorbance detector, 365-nm detection. Since the conversions of **1** were >5% in this study and only one-bond isomerizations were observed (Table I), we do not feel that the observation of 9-*cis*- or 11-*cis*-retinal is due to the method of irradiation. We did notice, however, when solutions of **1** in ethanol (or methanol) were irradiated and stored in aerated vials in the freezer for several days, that the amount of detectable 11-*cis*-retinal had diminished considerably. The presence of water in these alcoholic solvents also appears to diminish the amount of 11-*cis*-retinal observed upon irradiation of **1**.
(16) A peak with a retention time shorter than that of 13-*cis*-retinal is present in the photoequilibrium mixture.
(17) Prolonged photolysis of the photoequilibrium mixtures reported in Table II results in the loss of absorption above ~300 nm.
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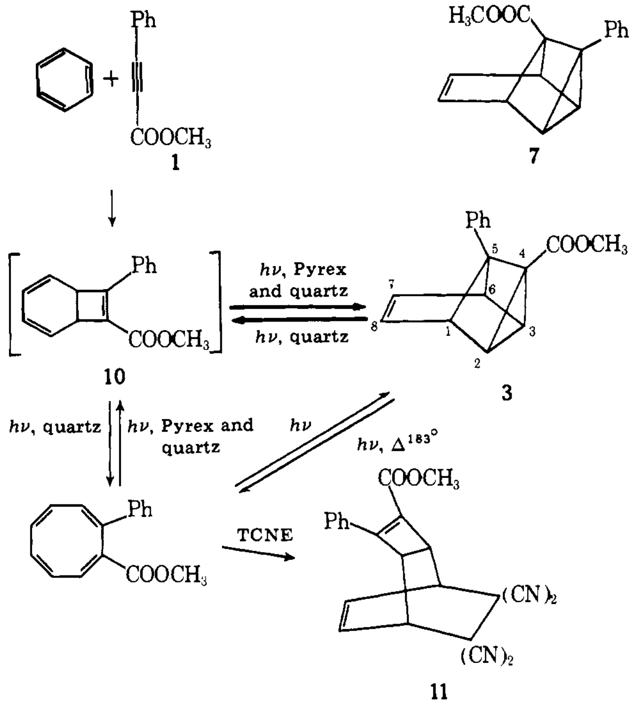
Photoaddition of Methyl Phenylpropiolate to Benzene.[1] Formation of a Tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octa-7-ene

Sir:

Few photocycloaddition reactions are as well studied as those of acetylenes to aromatic compounds.[2-4] It is unanticipated therefore that one should discover new behavior in the photochemical system—alkyne and benzene. We have made such a discovery, however, and report a new ring system from the photochemical addition of methyl phenylpropiolate to benzene.

Scheme I



Methyl phenylpropiolate (**1**) and benzene is reported[3] to give 1-carboxymethyl-8-phenylcyclooctatetraene (**2**) when irradiated at 253.7 nm or at wavelengths >290 nm, where only the acetylene absorbs light to a significant degree. The English workers reported no perceptible difference in the amount of cyclooctatetraene formed under different conditions.

Unable to confirm Bryce-Smith's results, we obtained instead a previously unknown compound when a 5×10^{-3} M solution of **1** in benzene was irradiated. We identified the new product as 4-carboxymethyl-5-phenyltetracyclo[3.3.0.0^{2,4}.0^{3,6}]octa-7-ene (**3**). (Irradiations were carried out under a N_2 atmosphere for 3 days with a Hanovia 450-W medium-pressure mercury lamp through a Pyrex filter. Compound **3** separated from residual **1** by column chromatography over silica gel and was isolated in 85% yield.)

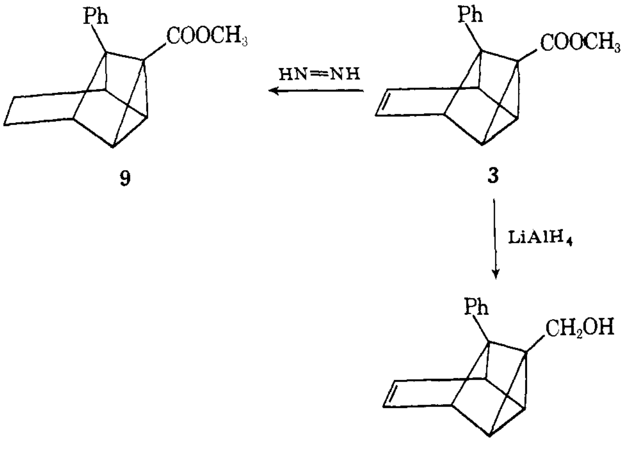
Photoproduct **3** was found to be isomeric with cyclooctatetraene **2** by elemental analysis[5] and the parent ion (*m/e* 238) confirmed its molecular weight. Apart from McLafferty-type cleavage reactions induced by the ester group, the most important mode of mass spectral fragmentation was formation of the ion at *m/e* M − 78. The infrared absorption of the carbonyl group at relatively low wavenumber proves cyclopropyl conjugation:[6a] IR (CCl_4, cm^{-1}) 3050, 1715, 1440, 1395, 1260, 1235, 1195, 1160, 1150, 1120, 1108, 1087, 975, 952, 870, 738, 714, 703, 675. The ^1H NMR spectrum of **3** in $CDCl_3$ consisted of two triplets, vinyl protons at δ 6.12 (2 H, $J = 2$ Hz, H_7 and H_8) and another at 3.02 (2 H, $J = 2$ Hz, H_2 and H_3), a multiplet centered at 3.93 (2 H, H_1 and H_6), and two singlets at 3.65 (3 H, $COOCH_3$) and 7.29 (5 H, Ar). This spectrum suggests a high degree of symmetry. That **3** is symmetrical is further revealed by its ^{13}C NMR spectrum in $CDCl_3$, consisting of the following absorptions:[7] 33.61 (d, $C_{2,3}$), 35.31 (s, C_4), 51.08 (q, C_{methyl}), 54.59 (d, $C_{1,6}$), 73.71 (s, C_5), 127.08 (d, C_{Ar}), 127.81 (d, C_{Ar}), 134.63 (d, $C_{7,8}$), 136.06 (s, C_{Ar}), and 171.09 (s, C_{ester}).

In view of the known photoreaction of tolane with naphthalene,[4] and Klumpp's reports[6] regarding $(CH)_8$ valence isomers, **3** or **7** appear to be most like alternative structures for our newly formed photoproduct, Scheme I.

Structure proof follows from spectral data as well as from the following experiments.

The position of the ester group in the unknown was conclusively established by reducing the unknown ester with $LiAlH_4$ to give corresponding alcohol **8**, a colorless oil:[5] ^1H NMR ($CDCl_3$) δ 1.62 (s, OH), 2.23 (t, 2 H, J = 2 Hz, H_2 and H_3), 3.76 (m, 2 H, H_1 and H_6), 3.97 (s, 2 H, CH_2O), 6.12 (t, 2 H, H_7 and H_8), and 7.23 (br s, 5 H, Ar). In the presence of the shift reagent $Eu(fod)_3$, the chemical shift of the cyclopropyl protons at δ 2.23 and bridgehead protons at δ 3.76 in the alcohol **8** shifted ~2.6 and 2.2 times as much downfield as the vinylic protons. From this, structure **7** is definitely ruled out since one would expect the opposite.

More evidence for the proposed structure **3** derived when the ester was subjected to a selective reduction of the double bond. With diimide in ethanolic solution,[8] **3** gave 95% of **9**, a colorless oil:[5] ^1H NMR ($CDCl_3$) δ 1.70 (m, 4 H, H_7 and H_8), 2.62 (m, 2 H, H_2 and H_3), 3.26 (m, 2 H, H_1 and H_6), 3.55 (s, 3 H, $COOCH_3$), and 7.25 (br s, 5 H, Ar). Furthermore, heating a solution of **3** in decalin at 183 °C for 4 h gave **2** as the only product in 80% yield.[9]



9 **3** **8**

The formation of **3** can be shown to be a wavelength dependent phenomenon. Under conditions where only methyl phenylpropiolate is absorbing the light, i.e., through Pyrex, **3** is exclusively obtained. There is no **2**. Through quartz, however, the reaction mixture contains **2** in minor quantities and, after 56% conversion, both **2** and **3** are present in a 35:65 ratio. Control experiments established that **2** could be converted into **3** and vice versa, on irradiation through quartz. Through Pyrex, however, **3** was shown to be photostable, though **2** was converted cleanly into **3** in excellent yield under these conditions.

We interpret our results as follows. The photoaddition of methyl phenylpropiolate to benzene likely proceeds as suggested for other alkynes,[3] by way of a bicyclo[4.2.0]octatriene. In fact, such an intermediate has been isolated in the photoaddition of acetylenes to hexafluorobenzene.[2c] Formation of our product **3**, at longer wavelengths, as well as **2**, at shorter wavelengths, requires the same intermediate, 7-carboxymethyl-8-phenylbicyclo[4.2.0]octa-2,4,7-triene (**10**). The excited species leading to the formation of **10** in our experiments must be that of methyl phenylpropiolate rather than of benzene.[10]

Unless **10** rearranges to **3** by energy-transfer process, **10** must live long enough[11,12] to absorb a second photon in competition with residual **1**. This photochemical reaction of **10** must also compete with the thermal and/or photochemical ring opening leading to **2**. Therefore, **3** is the kinetically controlled photoproduct and cannot be reconverted into **2** (via **10**), in Pyrex.[13] The formation of **2** at shorter wavelengths comes from a photoreversion of **3** likely but not necessarily via **10** at these wavelengths. The formation of **2** from **3** when the latter is irradiated through quartz experimentally confirms the reverse reaction. This contention is also supported by the observation that the ratio of **2**/**3** obtained from **1** and benzene through quartz increases at higher conversions.

New product **3** is the first example of photochemical trapping of a bicyclo[4.2.0]octatriene like **10**. Whether it is occurring via a concerted symmetry allowed process, or via the most stable biradical is still unclear. We are presently pursuing the mechanistic ramifications of this unusual new reaction.

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(9) Compound 2 was characterized by its ^1H NMR spectrum in $CDCl_3$: δ 3.55 (s, 3 H, $COOCH_3$), 6.55–5.72 (m, 5 H, H_{4-8}), 7.30 (s, 5 H, Ar), 7.35 (br s, 1 H, H_3) (cf. D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Angew. Chem., Int. Ed. Engl.*, **10**, 746 (1971)). Reaction of **2** with tetracyanoethylene in EtOAc gave 3-carboxymethyl-4-phenyl-9,9,10,10-tetracyanotricyclo-[4.2.2.0^{2,5}]deca-3,7-diene (**11**) in 72% yield[5] mp 246–247 °C dec; NMR (Me_2SO) δ 3.36 (t, 1 H, H_5 or H_2, J = 5 Hz), 3.62 (t, 1 H, H_2 *or* H_5, J = 5 Hz), 3.73 (2, 3 H, $COOCH_3$), 4.10–4.24 (m, 1 H, H_6 or H_1), 4.52–4.66 (m, 1 H, H_1 or H_6), 6.17–6.57 (ddd, 2 H, H_7 and H_8), 7.40–7.65 (m, 3 H, Ar) and 7.85–8.15 (m, 2 H, Ar).

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(11) In the present study no direct evidence was obtained for an appreciable concentration of **10**. Its half-life, however, is supposed to be comparable with that of the unsubstituted bicyclo[4.2.0]triene ($t_{1/2}$ = 14 min at 0 °C): E. Vogel, H. Keifer, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964).

(12) The ultraviolet spectrum of the intermediate is expected to have a considerable absorption above 280 nm. Cf. bicyclo[4.2.0]octa-2,4-diene, λ_{max} 274 nm (ϵ 3340): A. C. Cope, A. C. Haven, Jr., F. I. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

(13) Under these conditions **3** is nonabsorbing. Its UV spectrum consists $\pi-\pi^*$ λ_{max} 228 nm (ϵ 6370). There is essentially no absorption above 280 nm.

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Use of Copper(I) Phosphine Compounds to Photosensitize the Valence Isomerization of Norbornadiene

Sir:

Several studies dealing with the photoassisted reactions of olefins in the presence of Cu(I) compounds have been re-