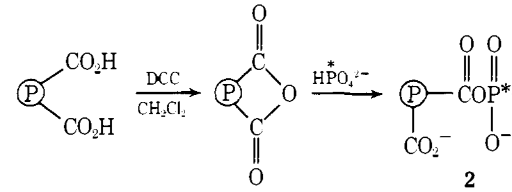
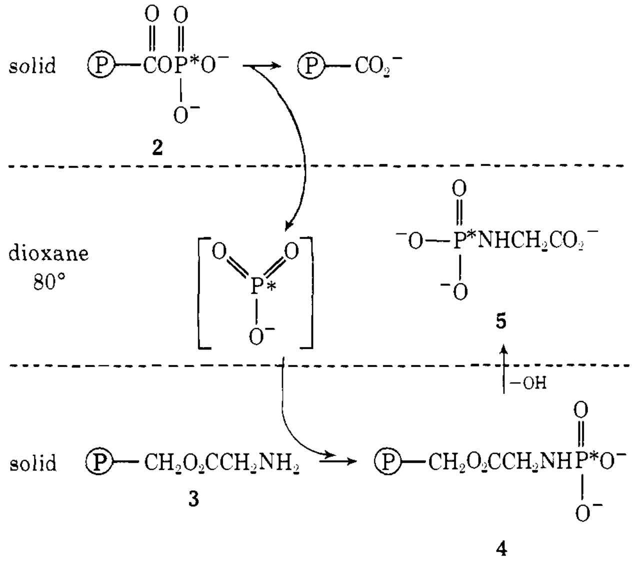
Scheme I



Scheme II



An acyl phosphate was selected as a suitable polymer-bound metaphosphate precursor. This choice was based on the work of Jencks,[3] who showed that the decomposition of acyl phosphates in media of low water or high salt concentrations produces pyrophosphate (i.e., trapping of metaphosphate by phosphate). A polymer-bound acyl phosphate linkage was therefore likely to generate metaphosphate cleanly in the aprotic medium of the polystyrene matrix. The precursor was easily prepared, although in low (10–20%) overall yield, by the reactions of Scheme I.

The polymer-bound benzoic acid[4] (ir 1720, 1670 cm^{-1}) was converted in large part to the anhydride (ir 1785, 1725 cm^{-1}) with carbodiimide, then to the radioactive acyl phosphate **2** (ir 1725, 1230 cm^{-1}) with tetramethylammonium [^{32}P] phosphate in aqueous dioxane. That the phosphate of **2** was covalently bound to rather than adsorbed on the resin was demonstrated by its failure to exchange with unlabeled phosphate in solution. The trapping agent used was the polymer-bound glycine **3** (Scheme II), prepared by established procedures of Merrifield peptide synthesis.[5]

When the polymers **2** and **3** were suspended in dioxane at 80°, phosphate transfer between the two polymers was detected generating **4** (ir 1380 cm^{-1}). Radioactivity assays indicated that the half-life of **2** is approximately 27 hr under these conditions and 70% of the released phosphate appeared on **4** while the remaining activity appeared in solution as phosphate. Saponification of **4** gave glycine *N*-phosphate, **5**, identical with an authentic sample, and isotope dilution established that 90% of the radioactivity of **4** appeared as **5**. Since direct reactions between the two resin bead surfaces have been shown to be negligible in related cases,[6] the presence of a free monophosphorylating agent in the solution between the two solid phases is established.

These results are consistent with the postulation of monomeric metaphosphate as the intermediate, but its higher oligomers, formed by disproportionation reactions within **2**, remain viable alternative possibilities as the actual phosphorylating agents. The dimer (pyrophosphate) was excluded as the intermediate in question by its inability to phosphorylate **3** under these conditions.

Acknowledgments. We are pleased to thank Professors J. M. Jordan and L. T. Scott of UCLA for some of the materials used in this study. Financial support was provided by the Fulbright Commission's Program of Cultural Cooperation between the USA and Spain and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorous", Elsevier, Amsterdam, 1967, Chapter 10, and references cited therein.
(2) J. Rebek and F. Gavina, *J. Am. Chem. Soc.*, **97**, 1591 (1975).
(3) G. DiSabato and W. P. Jencks, *J. Am. Chem. Soc.*, **83**, 5500 (1961).
(4) Lithiated, 1% cross-linked polystyrene (F. Camps, J. Castells, M. J. Ferrando, and J. Font, *Tetrahedron Lett.* 1713 (1971)) was carboxylated with CO_2 at −78° in THF. Acid prepared in this manner showed 1 mequiv of titratable acid functions per gram of resin: L. T. Scott and C. S. Sims, private communication.
(5) J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis", W. H. Freeman, San Francisco, Calif., 1969.
(6) J. Rebek, D. Brown, and S. Zimmerman, *J. Am. Chem. Soc.*, **97**, 454 (1975). Detection of intermediates in these cases was possible even when the two resins were physically separated by wire screens or sintered glass barriers.
(7) Visiting Fulbright Scholar on leave from the University of Valencia, Valencia, Spain.

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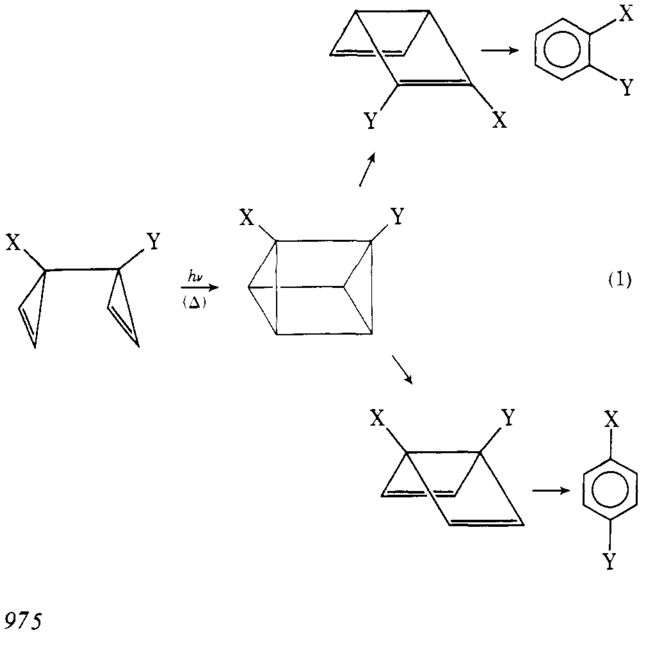
Does the Photochemical Bicyclopropenyl Rearrangement Involve a Prismane Intermediate?[1]

Sir:

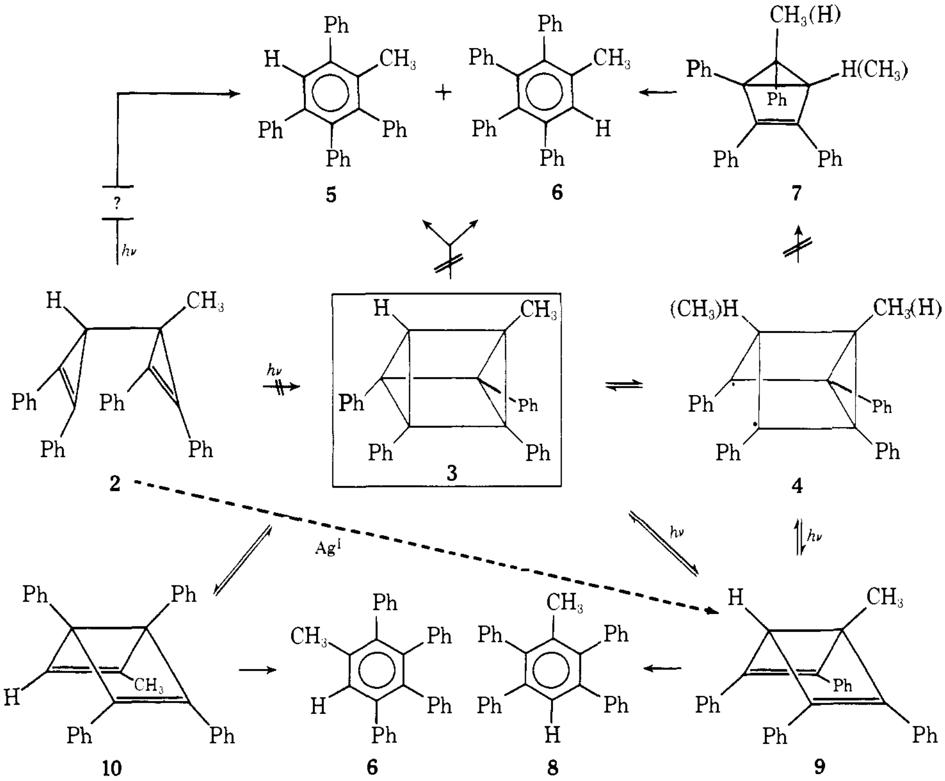
In his pioneering work on both thermal and photochemical versions of the bicyclopropenyl → benzene rearrangement, Breslow suggested mechanism 1 with a prismane as the key intermediate to account for the observed ortho-para scrambling of x,y-substituents in the process of aromatization.[2] While we have dealt with the thermal (and transition metal catalyzed) case in recent papers[3-5] we have now turned to an investigation of the photochemical rearrangement whose mechanism has remained unchallenged so far.[6]

In order to facilitate product analysis by NMR, we modi-

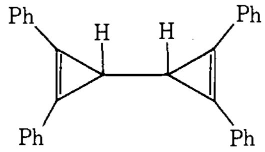


(1)

Scheme I



fied Breslow's original compound 1[2] by introducing a methyl group at one of the bridgehead carbon atoms.[7]



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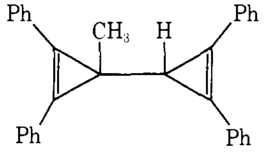

2

Our recent[3-5] discovery of the Ag^I-catalyzed bicyclopropenyl → Dewar benzene rearrangement now provides the basis for a crucial test of mechanism 1 (see Scheme I); the supposed prismane intermediate **3** in the photolysis of **2** can also be independently reached via the conventional $[\pi_s^2 + \pi_s^2]$ photocyclization of **9**.[4] As the further fate of **3** should be independent of its mode of generation, one expects the same product distribution in the photolysis of both **2** and **9**. This, however, proved to be not even qualitatively so.

Direct irradiation of **2** at 254 nm in benzene (Graentzel reactor 400, 600 W, substrate concentration 10^{-3} mol/l., irradiation time 5 hr) cleanly yielded benzene derivatives **5** and **6** in a 1:2 ratio. No **8** could be detected. Product composition was established by VPC separation[8] and identification of the individual components by comparison with authentic samples.[9] We thus observe ortho-meta scrambling of bicyclopropenyl bridgehead substituents in the process of aromatization![12] This result strongly contrasts with Breslow's observation of ortho-para scrambling in photolysis of **1**[13] and is clearly inconsistent with (eq 1) as there is no set of prismane ⇌ Dewar benzene interconversions capable of this scrambling pattern. However, a prismane intermediate, **3**, can still not be ruled out in this process as there is the possibility of vibrationally excited **3** rearranging to **5** and **6** via the sequence **3** → **4** → **7**. This di-π-methane-like rearrangement is well documented for hexamethylprismane.[14] If this explanation holds, then generation of **3** via **9** should also yield **5** and **6**.

However, when the experimental test was made, *only* **6** *and* **8** *were formed but significantly no* **5**! (Reaction conditions and product analysis as above.) That is: prismane **3**[15] does indeed behave according to eq 1 (ortho-para scrambling involving **9** and **10**, see Scheme I) *but it cannot be an intermediate in the photolysis of* **2**. Obviously there must exist a hitherto unrecognized pathway for photochemical bicyclopropenyl → benzene rearrangements. In the accompanying paper[16] we report on observations which may be relevant in this context.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References and Notes

(1) Reactions of coupled three-membered rings, part VII. For part VI of this series see R. Weiss, and H. P. Kempcke, *Tetrahedron Lett.* 155 (1974).

(2) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).

(3) R. Weiss and C. Schlierf, *Angew. Chem., Int. Ed. Engl.*, **10**, 811 (1971).

(4) R. Weiss and S. Andrae, *Angew. Chem., Int. Ed. Engl.*, **12**, 150 (1973).

(5) R. Weiss and S. Andrae, *Angew. Chem., Int. Ed. Engl.*, **12**, 152 (1973).

(6) G. Maier, "Valenzisomerisierungen", Verlag Chemie, Weinheim, 1972, p 157.

(7) This was achieved by a conventional route, which, starting from **1**, involved hydride abstraction, quenching of the resulting cyclopropenium ion[2] with CH$_3$OH–CH$_3$O$^-$ and subsequent Grignard reaction with CH$_3$MgJ.

(8) We thank Professor R. Breslow for experimental details concerning his VPC analysis of mixtures of isomeric tetraphenylbenzenes.[2]

(9) **6**[10] and **8**[4] are known compounds and can easily be distinguished by their NMR spectra and melting points (**6**, CH$_3$ (s) τ 7.79, mp 186°; **8** CH$_3$ (s) τ 8.04, mp 270°). The nonidentity of **5** with either of these two isomers also follows from NMR and mp (**5**, CH$_3$ (s) τ 7.94, mp 226°) while all three compounds have very similar uv and ir spectra as well as virtually identical fragmentation patterns in MS, which establishes their close structural relationship. The obvious suspicion that **5** should be assigned the structure of the hitherto unknown meta isomer in the series is confirmed by our observation that **5** is also formed—in addition to **8**—in *Ag^I-catalyzed* aromatization of **9**. We have found that this Ag^I-induced meta-para scrambling of Dewar benzene bridgehead substituents in the process of aromatization is quite a general phenomenon for a variety of substituents.[11] Our structural assignment is further confirmed by a close 1:1 correspondence of melting points of the three isomeric benzene derivatives which can be derived from **1** and **2**:

	(H, H)	(H, CH$_3$)
ortho	193°	186°
meta	220°	226°
para	270°	269–270°

(10) D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organomet. Chem.*, **2**, 417 (1964).
(11) R. Weiss and S. Andrae, *in preparation.*
(12) Benzene derivatives **5**, **6**, and **8** are photostable under our irradiation conditions.
(13) Professor R. Breslow has kindly informed us that prompted by our results he reinvestigated his earlier work[2] and was indeed able to confirm his original results. At present the reasons for the discrepancy between his and our results are not fully understood.
(14) D. M. Lemal and J. P. Lokensgard, *J. Am. Chem. Soc.*, **88**, 5934 (1966).
(15) Attempts to observe **3** directly in the photolysis of **9** were unsuccessful.
(16) R. Weiss and H. Kölbl, following paper in this issue.

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Received October 25, 1974

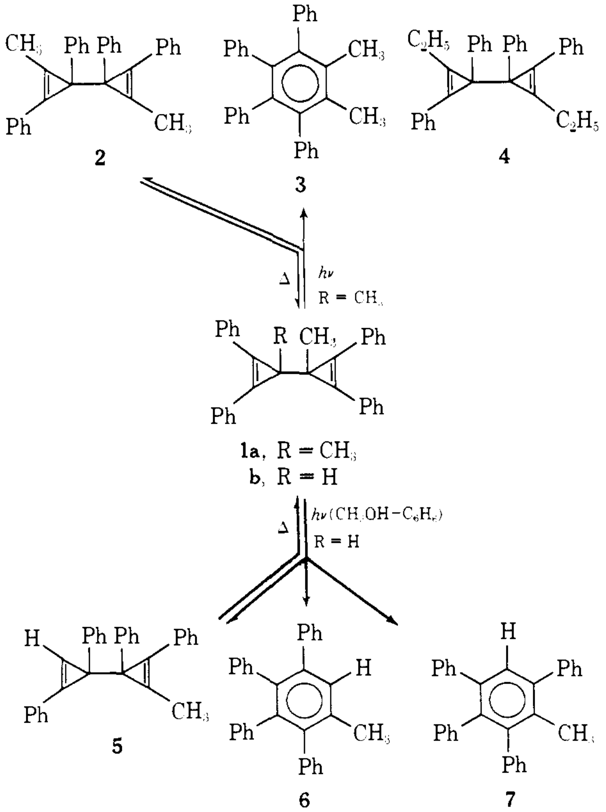
The Bicyclopropenyl Cope Rearrangement[1,2]

Sir:

So far there have been no reports of Cope rearrangements involving cyclopropene moieties. In this communication we wish to report the first examples, both photochemical and thermal, of bicyclopropenyl → bicyclopropenyl rearrangements which, apart from adding new mechanistic and structural facets to the Cope rearrangement, also allow some insight into bicyclopropenyl → benzene rearrangement pathways.

Direct 320-nm irradiation of **1a**[3] (see Scheme I) in 3:1 CH_3OH-C_6H_6 (Graentzel reactor 400, 600 W, substrate concentration $\sim 10^{-3}$ mol/l., irradiation time 7 hr) gave two new products, **2** (95%) and **3** (5%), which after total conversion of **1a** could be separated by fractional crystallization. The structure of **3** (mp 230°) follows from spectral comparison with an authentic sample.[4] The structural assignment of **2** (mp 173°) as a bicyclopropenyl isomeric with **1a** is based on the following data: ir (KBr) 1845 cm^{-1} (ν >C=C<); uv (CH_2Cl_2) λ_{max} 270 nm (ϵ 23,600); NMR ($CDCl_3$) τ 7.58 (6 H, s); MS 410 (M^+), 205.

Scheme I



Ir and UV characteristics of **2** are completely analogous to the spectra of bicyclopropenyl **4** synthesized by Breslow via reductive coupling of the ethyldiphenylcyclopropenium ion.[5]

2 is photostable under 320-nm irradiation because the transformation **1a** → **2** is connected with a pronounced blue shift in the longest wavelength absorption (331 → 270 nm).

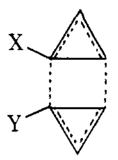
Similarly, under the same irradiation conditions, photolysis of **1b** gave a mixture of **5** (65%), **6** (30%), and **7** (5%).[2] **5** was isolated by low-temperature fractional crystallization from ether and had the following: mp 128–130°; ir (KBr) 1845, 1755 cm^{-1} (ν >C=C<); uv (CH_2Cl_2) λ_{max} 269 nm (ϵ 21,400); NMR ($CDCl_3$) τ 7.58 (3 H, s); MS 396 (M^+), 205, 191. Typically, the two cylopropene >C=C< absorptions in the ir spectrum of **5** reflect the different substitution patterns of the two double bonds. Like **2**, **5** is fairly photostable at 320 nm (and for the same reasons).

While the interconversions **1a** → **2** and **1b** → **5** constitute the first examples of photochemically induced Cope rearrangements in the bicyclopropenyl series, the thermal counterpiece was discovered in the thermolysis of **2** and **5** (see Scheme I).

It was found that both **2** and **5** under rather mild conditions were reconverted exclusively[6] to the starting bicyclopropenyl systems, this reaction being accompanied by formation of benzene derivatives (**2** $\tau_{1/2}^{150°}$ (*o*-dichlorobenzene) 15 min with product composition, **1a** (50%), **3** (50%); **5** $\tau_{1/2}^{80°}$ (benzene) 30 min with product composition, **1** (85%), **6** (10%), **7** (5%).

The driving force of these thermal Cope rearrangements is probably provided by restoration of conjugation between the phenyl substituents. Evidently the photo-Cope rearrangements furnish the more endothermic of the two equilibrium partners—a feature which it shares with some of the few known photo-Cope rearrangements in the open-chain series.[7] This fact allows the conclusion[8] that in all probability **2** and **5** are formed in a true photoreaction and not in a hot ground state reaction.

Our observations immediately provoke some mechanistic comments. (1) As concerns stereochemistry our results strongly suggest that both **2** and **5** arise via a *chair* transition state (and hence in the case of **2** should possess *d,l* rather than mesoconfiguration). This follows from the observed *mutually stereospecific* **1a** ⇌ **2** (**1b** ⇌ **5**) interrelationships which imply *that either both thermal and photochemical Cope rearrangements proceed via a boat or both via a chair transition state.*[9] As it is totally unreasonable in view of the rotational flexibility and the mild reaction conditions that the *thermal* Cope rearrangement should exclusively proceed via a boat transition state, the above conclusion concerning the photochemical case follows. (2) Pericyclic vs. two-step process. In view of the continuing discussion of whether open-chain Cope rearrangements proceed as a pericyclic or as a two-step process,[10] we wish to point out that a two-step process in the case of **9** should be inherently more favorable. This arises because the introduction of a single bond between the two cyclopropene moieties to yield the *anti*-1,4-tricyclohexylene (biradicaloid[10]) intermediate **10** is connected with some 25 kcal relief of total strain



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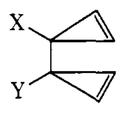

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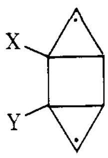

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