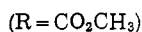
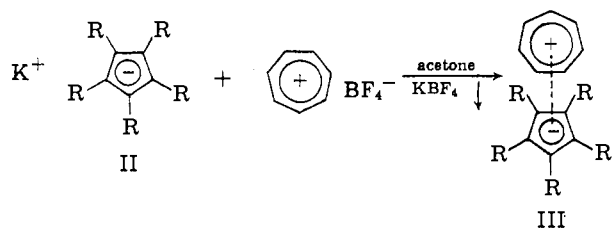


sion of potassium 1,2,3,4,5-pentacarbomethoxycyclopentadienyliide, II,<sup>6</sup> with an "ylium" salt in an appropriate solvent (*e.g.*, II and tropylium tetrafluoroborate in acetone), separating the inorganic potassium salt (quantitative in all cases), then isolating and recrystallizing the organic salt. Physical properties of



each salt are shown in Table I.

TABLE I  
PHYSICAL PROPERTIES OF THE SALTS OF 1,2,3,4,5-PENTACARBOMETHOXYCYCLOPENTADIENE

Cation (m.p. of salt) <sup>a</sup>	Charge-transfer absorptions $\lambda_{\text{max}}$ m $\mu$ ( $\epsilon$ ) <sup>b</sup> [color]	N.m.r. spectra $\tau$ (multiplicity) <sup>c</sup> assignment <sup>d</sup>
 157-159°(vac) III	470 (1870) [orange]	1.76 (S) C <sub>7</sub> <sup>+</sup> protons 6.41 (S) O—CH <sub>3</sub>
 154-155° IV	418 (758) [yellow]	3.05 (S) =C—H 6.37 (S) O—CH <sub>3</sub> 7.51 (S) 2,6-CH <sub>3</sub> 7.72 (S) 4-CH <sub>3</sub>
 250-251° V	420 (17,000) [yellow]	2.25-3.10 (M) =C—H 6.41 (S) O—CH <sub>3</sub>
 104-105° VI	350 (768) [pale yellow]	1.9-2.8 (M) =C—H 6.06 (S) N—CH <sub>3</sub> 6.34 (S) O—CH <sub>3</sub>
 106-107° VII	402 (1020) [yellow]	1.3-2.8 (M) =C—H 5.82 (S) N—CH <sub>3</sub> 6.41 (S) O—CH <sub>3</sub>

<sup>a</sup> Melting points are corrected. <sup>b</sup>  $\epsilon$  values were found to be somewhat concentration dependent. <sup>c</sup> S = singlet, M = complex multiplet. <sup>d</sup> Integrations consistent with assignments.

The structure of each salt is established by its analysis, infrared and proton magnetic resonance spectrum.<sup>7</sup> The ultraviolet-visible spectra appear to be

(4) K. Hafner, *Angew. Chem.*, **69**, 393 (1957).

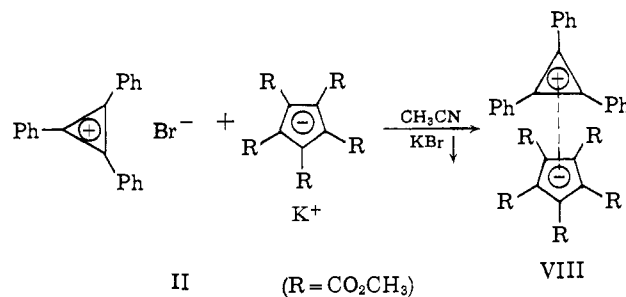
(5) K. Hafner, *Ann.*, **606**, 79 (1957).

(6) The preparation and properties of this compound are described in a paper submitted to *J. Org. Chem.* by the authors.

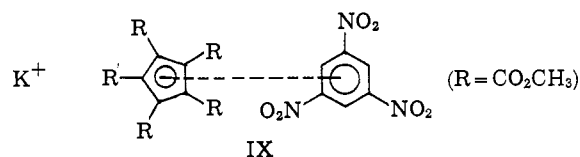
(7) Satisfactory analyses were obtained from various commercial laboratories; infrared spectra were taken in solution (HCCl<sub>3</sub>); n.m.r. spectra were recorded with a Varian A-60 spectrometer using chloroform-*d* as solvent and tetramethylsilane as internal standard; ultraviolet-visible spectra were taken with dichloromethane solutions.

composed of the absorptions of the individual ions plus a new long wave length absorption. That this long wave length arises from a charge-transfer transition is shown by a plot of the long wave length absorption frequencies of the cyclopentadienyliide salts III, IV, V, VI and VII against the charge-transfer absorptions of the corresponding iodides.<sup>8</sup> A nearly linear plot is obtained with a slope of approximately unity.

Yellow acetonitrile solutions of triphenylcyclopropenyl salt, VIII, (identified by n.m.r. and ultraviolet-visible spectra) are readily obtained; however, this salt could not be induced to crystallize. VIII also appears to be of the charge-transfer type (long tailing of broad absorptions from 300 m $\mu$  to 500 m $\mu$ ).<sup>9</sup>



The potassium salt II also forms charge-transfer salts with neutral acceptors. Thus, II and 1,3,5-trinitrobenzene afford the yellow crystalline salt, IX, m.p. 200-201°, II and trinitrofluorenone give a red crystalline salt, m.p. 199-200°, while II and tetracyanoethylene yield an unstable (in solution) blue complex ( $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$  590 m $\mu$ ).



(8) M. Feldman and S. Winstein, *Tetrahedron Letters*, 853 (1962).

(9) We have found that triphenylcyclopropenyl iodide, a yellow salt, has an absorption band at 361 m $\mu$  (CH<sub>3</sub>CN), an absorption not found in the bromide. We believe this absorption is caused by a charge-transfer transition. This would place the charge-transfer absorption of VIII in the vicinity of 300 m $\mu$ , a portion of the spectrum where both triphenylcyclopropenyl cation (307, 320 m $\mu$ )<sup>10</sup> and pentacarbomethoxycyclopentadienyliide anion (294 m $\mu$ )<sup>11</sup> absorb strongly.

(10) R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958).

(11) R. C. Cookson, J. Hudc and B. Whitear, *Proc. Chem. Soc.*, 117 (1961).

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#### MECHANISM OF THE PHOTOCHEMICAL FORMATION OF PHENANTHRENE FROM *cis*-STILBENE IN THE VAPOR PHASE

Sir:

In an attempt to study the mechanism of the formation of phenanthrene from the photolysis of *cis*-stilbene, we have investigated this system in the vapor phase at 170° at a pressure of about 5 mm. Under these conditions, at both 3130 Å. and shorter wave lengths, photolysis of *cis*-stilbene led to the formation of phenanthrene and hydrogen in equivalent amounts (within experimental error) and *trans*-stilbene. This is in sharp contrast to the recent report<sup>1</sup> that in cyclohexane solution photolysis of *cis*-stilbene leads to phenanthrene only in the presence of oxygen. To reconcile the data in the two phases we have carried out a number of control experiments with the following results.

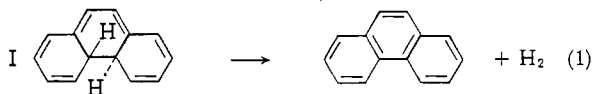
(1) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4361 (1962).

(i) Addition of 10 to 24 mm. of oxygen gas has no observable effect on the formation of phenanthrene in the vapor phase. At the same time evidence for attack by oxygen on stilbene itself was obtained, but the results were not reproducible. No distillable product of such reaction was detected.

(ii) In the absence of light, oxidation of *cis*-stilbene vapor ( $p = 4.7$  mm.) by oxygen ( $p = 0.95$  mm.) at  $170^\circ$  was not observed. In a separate experiment under similar conditions the oxidation of phenanthrene also was not observed.

(iii) Addition of 250 mm. of diethyl ether vapor to 5 mm. of *cis*-stilbene during photolysis did not cause a change in the rate of formation of phenanthrene which was greater than the experimental error.

It has been suggested<sup>1</sup> that the formation of phenanthrene from *cis*-stilbene in solution involves *trans*-dihydrophenanthrene of structure I as the intermediate which can react with oxygen. It also has been indicated that this intermediate can dehydrogenate spontaneously in the gas phase according to (1) by virtue of the excess vibrational energy it would possess at the moment of its formation; that in solution it will



lose this vibrational energy rapidly in collisions with molecules, so that an oxidant will be required to form phenanthrene.

It appears more reasonable to assume that the precursor for the formation of phenanthrene and hydrogen in the *vapor phase* is *cis*-dihydrophenanthrene rather than the *trans*-compound.<sup>2a</sup> The net reaction would then be analogous to the photochemical isomerization and dehydrogenation of 1,3,5-hexatriene.<sup>2b,3</sup> If the initially formed species in the *vapor phase* is a vibrationally excited *trans*-dihydrophenanthrene, it is difficult to understand what magnitude the rate constant for its isomerization to *cis*-dihydrophenanthrene can be. On the one hand this rate constant must be so large that the reaction is not substantially affected by the addition of even 250 mm. of ether vapor. Since ether has been found to be quite efficient in the removal of vibrational energy,<sup>4</sup> this would require that the rate constant for the *trans*→*cis* conversion be larger than the collision rate between I and ether molecules which is about  $10^9$  sec.<sup>-1</sup>. On the other hand, a rate constant of  $10^{10}$  sec.<sup>-1</sup> for such a drastic change in stereochemistry seems extraordinary.<sup>5</sup>

We have obtained quantum yields for the formation of phenanthrene in the *vapor phase* at  $170^\circ$  and in cyclohexane solution at room temperature in the presence of oxygen with the 3130 Å. mercury lines as the radiation. In the calculation of the quantum yields, we have used the extinction coefficient of *cis*-stilbene at this wave length in solution to calculate the absorbed

(2) (a) The torsional movement that is necessary to bring the hydrogens together in *trans*-dihydrophenanthrene for molecular elimination seems to us to be highly unlikely. Although the molecule may have 57 kcal./mole of excess energy (at 3130 Å.), even elimination of *cis*-hydrogens may have an activation energy of 59 kcal./mole as in cyclopentene: D. W. Vanas and W. D. Walters, *J. Am. Chem. Soc.*, **70**, 4035 (1948); (b) R. Srinivasan, *ibid.*, **83**, 2806 (1961).

(3) It has been observed (R. Srinivasan and J. C. Powers, unpublished work) that pyrolysis of *cis*-stilbene at  $550^\circ$  in a clean Pyrex vessel led to a 40% conversion to phenanthrene and hydrogen. N. D. Zelinskii and I. N. Titz, *Ber.*, **62B**, 2869 (1929), have shown that stilbene vapor can be converted quantitatively to phenanthrene when passed in a current of carbon dioxide over platinized charcoal at  $300^\circ$ .

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432 (1962).

(5) (a) The formation of a molecular entity such as *cis*-dihydrophenanthrene in the *gas phase* is unnecessary if the elimination of hydrogen and the formation of a carbon to carbon bond occur simultaneously; (b) The stepwise loss of hydrogen from I or *cis*-stilbene in the *vapor phase* is unlikely since the formation of phenanthrene is unaffected by the addition of oxygen.

intensity in the *vapor phase* at  $170^\circ$ . Since absorption of the useful radiation was nearly complete, we do not believe that this has introduced a significant error in our results. The quantum yields we found were 0.02 in solution in cyclohexane at a concentration of  $4 \times 10^{-3}$  M and 0.002 in the *vapor phase*. The former value is lower than that reported by Stegemeyer<sup>6</sup> although of the same order of magnitude. Our results indicate that there is a concentration dependence attached to this quantity.

The fact that the quantum yield in solution is an order of magnitude greater than the quantum yield in the *gas phase* is interesting. It is possible to explain this<sup>1</sup> by attributing certain chemical properties to a hypothetical intermediate such as *trans*-dihydrophenanthrene. On the other hand, such an oversimplification of the picture seems to be unwarranted at present. More work with similar photochemical systems would demonstrate the importance (or lack of it) of the stereochemistry of the hydrogen atoms at the new bond that is formed on the dehydrogenation reaction.

**Acknowledgment.**—The authors wish to thank Dr. Frank Mallory of Bryn Mawr College for making his results available to them prior to publication.

(6) H. Stegemeyer, *Z. Naturforsch.*, **17b**, 153 (1962).

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#### ALKYLATION OF AROMATIC HYDROCARBONS BY ALKYL LITHIUM REAGENTS

Sir:

It is well known<sup>1-3</sup> that the reactions of alkyl-lithium, -sodium and -potassium compounds with aromatic hydrocarbons lead to metalation of the aromatic nucleus. Regardless of the choice of alkyl groups, substrate or alkali metal, alkylation has never been reported as a significant reaction course.<sup>4</sup> Hafner and co-workers<sup>5,6</sup> have observed a reaction of methyl-lithium with azulene, but this is an addition across a bond having appreciable double-bond character<sup>7</sup> rather than an aromatic substitution, and a dehydrogenation is required to recover the aromatic nucleus.

Recently, however, we have found that when alkyl-lithium reagents are heated with aromatic hydrocarbons in a paraffin hydrocarbon solvent, alkylation is an important reaction. Under the best conditions the yields are such as to make the reaction of synthetic value.

TABLE I

RLi	Hydrocarbon	% Alkylation <sup>a</sup>	
		Mono	Di
<i>tert</i> -Butyl	Benzene	15	...
<i>n</i> -Butyl	Naphthalene	15	...
<i>sec</i> -Butyl	Naphthalene	20	...
<i>tert</i> -Butyl	Naphthalene	30-45	50-80
<i>tert</i> -Butyl	Phenanthrene	50	...

<sup>a</sup> Equal molar quantities of RLi and ArH in decalin at  $165^\circ$  for 20 hr.

(1) R. G. Jones and H. Gilman in "Organic Reactions," Vol. VI, Roger Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951.

(2) G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960.

(3) E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.*, 861 (1953).

(5) K. Hafner and H. Welde, *Ann.*, **606**, 90 (1957).

(6) K. Hafner, C. Bernhard and R. Mueller, *ibid.*, **650**, 35 (1961).

(7) P. D. Bartlett, S. Friedman and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953).