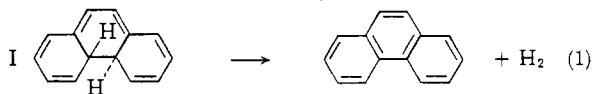


(i) Addition of 10 to 24 mm. of oxygen gas has no observable effect on the formation of phenanthrene in the vapor phase. At the same time evidence for attack by oxygen on stilbene itself was obtained, but the results were not reproducible. No distillable product of such reaction was detected.

(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).

THOMAS J. WATSON  
RESEARCH CENTER  
IBM CORPORATION  
YORKTOWN HEIGHTS, N. Y.

R. SRINIVASAN  
J. C. POWERS, JR.

RECEIVED JANUARY 7, 1963

#### 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. Weldes, *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).

The mechanism of the reaction is not known at present, but the following observations have been made. (1) The order of reactivity of the alkyllithium reagents for alkylation is tertiary > secondary > primary. This corresponds to presently accepted ideas concerning the reactivity of alkyl carbanions and also to the observations of Bartlett and co-workers<sup>7</sup> on the addition of alkyllithium reagents to simple olefins. (2) Monoalkylation of naphthalene by *t*-butyllithium occurs at least 95% in the 1-position. Further alkylation appears to occur at the 3, 6 or 7 position. (3) Hydrogen is present in significant amounts in the gases evolved during hydrolysis of the reaction mixture.

A representative reaction was conducted as follows. The pentane in a commercial<sup>8</sup> solution of *t*-butyllithium (0.11 mole) was replaced by decalin. To this was added naphthalene (0.11 mole), and the homogeneous mixture was heated at 165° for 41 hr.<sup>9</sup> After hydrolysis, the organic products were separated by fractional distillation to give 5.69 g. of *t*-butylnaphthalene and 6.81 g. of a mixture of di-*t*-butylnaphthalenes. These represent 30 and 50% yields, respectively, based on *t*-butyllithium.

The n.m.r. spectrum of the presumed *t*-butylnaphthalene showed an aliphatic hydrogen singlet at 8.60  $\tau$  and an aromatic hydrogen multiplet at 1.70 to 3.15  $\tau$ . The ratio of the areas was 1.3 to 1.0. The calculated ratio for *t*-butylnaphthalene is 1.3 to 1.0.

The infrared spectrum had strong absorptions at 1395  $\text{cm}^{-1}$ , 795  $\text{cm}^{-1}$  and 767  $\text{cm}^{-1}$  characteristic of alpha-substituted naphthalenes.<sup>10</sup>

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}$ : C, 91.25; H, 8.75. Found: C, 91.02; H, 8.99.

The n.m.r. spectrum of the mixture of presumed di-*t*-butylnaphthalene isomers exhibited three- $\text{CH}_3$  singlets at 8.13, 8.44 and 8.67  $\tau$  and an aromatic multiplet at 1.80 to 3.05  $\tau$ . The areas under the aliphatic and aromatic peaks were in the ratio 3.0 to 1.0; calculated for dibutylnaphthalene: 3.0 to 1.0.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{24}$ : C, 89.94; H, 10.06. Found: C, 90.10; H, 10.15.

Research on the scope and limitations, optimum reaction conditions and mechanism of this reaction is being continued actively.

**Acknowledgment.**—The generous support of the American Petroleum Institute is gratefully acknowledged.

(8) Lithium Corporation of America.

(9) Later experiments indicate that the reaction probably is completed in a much shorter time.

(10) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 78.

WHITMORE LABORATORY  
COLLEGE OF CHEMISTRY AND PHYSICS  
THE PENNSYLVANIA STATE UNIVERSITY  
UNIVERSITY PARK, PENNSYLVANIA

JOSEPH A. DIXON  
DAVID H. FISHMAN

RECEIVED FEBRUARY 18, 1963

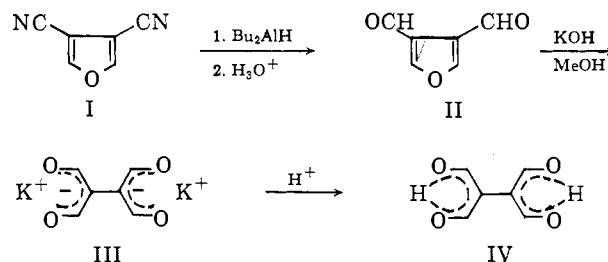
1,1,2,2-ETHANETETRACARBOXALDEHYDE  
BY THE OPENING OF A FURAN RING WITH  
HYDROXIDE ION

Sir:

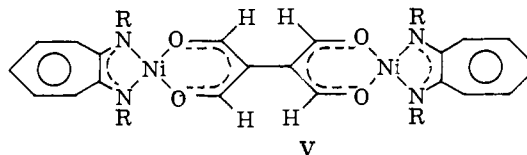
The furan ring system is normally stable toward base and labile to acid.<sup>1</sup> A dramatic reversal of this generalization was found in the case of 3,4-furandicarboxaldehyde (II). This compound (which may be regarded as the anhydride of 1,1,2,2-ethanetetracarboxaldehyde

(1) Under drastic conditions 2-phenyl-4-benzoylfuran was reported to be cleaved by KOH: R. C. Fuson, C. L. Fleming and R. Johnson, *J. Am. Chem. Soc.*, **60**, 1994 (1938). On the other hand, diethyl 3,4-furandicarboxylate was rapidly saponified by alcoholic KOH, the furan ring remaining intact: T. Reichstein, A. Grüssner, K. Schindler and E. Hardmeier, *Helv. Chim. Acta*, **16**, 276 (1933).

(IV)) reacted exothermally with hydroxide ion yielding the salt of IV, of interest as the simplest bifunctional 1,3-dicarbonyl chelating system suitable for the preparation of chelate polymers,<sup>2</sup> and as the only compound of this type where coplanarity with resultant electronic interaction between the quasiaromatic<sup>3</sup> ring systems is feasible. The synthesis of IV by another route has been reported recently.<sup>4</sup>



Reduction of 3,4-furandicarbonitrile<sup>5</sup> (I) with diisobutylaluminum hydride, followed by hydrolysis, afforded 3,4-furandicarboxaldehyde (II), m.p. 77–78° in about 50% yield ( $\text{C}_6\text{H}_4\text{O}_3$ : C, 58.1; H, 3.25; mol. wt. 124. Found: C, 58.5; H, 3.52; mol. wt. 129); its n.m.r. spectrum has two equal singlets at 1.88 ( $\alpha$ -H) and  $-0.15$   $\tau$  ( $-\text{CHO}$ ). Treatment of II with freshly prepared methanolic KOH gave the salt III (ultraviolet:  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  270  $\text{m}\mu$ ,  $\epsilon$  39,800) which on acidification yielded IV, ( $\text{C}_6\text{H}_6\text{O}_4$ : C, 50.7; H, 4.26. Found: C, 50.8; H, 4.08). Its infrared shows broad absorption in the 1800–2800- $\text{cm}^{-1}$  region, along with the expected broad band at 1560  $\text{cm}^{-1}$ . The compound is sublimable and melts around 190°, being dehydrated,<sup>6</sup> mainly to II and to polymeric products. Its saturated solution has a pH of 2.35. Salts of IV undergo a two-electron oxidation by bromine, iodine, ferric and mercuric ions, and readily form polymeric chelates with most transition metal ions. Mixed chelates of the type V were also prepared. For instance V ( $\text{R} = \text{C}_6\text{H}_5$ ) was obtained as bronze-colored plates, m.p. 236–237° ( $\text{C}_{32}\text{H}_{42}\text{N}_4\text{O}_4\text{Ni}_2$ : C, 57.9; H, 6.33; N, 8.44; mol. wt. 663. Found: C, 57.2; H, 6.17; N, 8.35; mol. wt. 650).



The facile opening of a furan ring by alkali appears to be general (additional examples thereof will be reported later), and of synthetic utility for furans substituted in the 3 and 4 positions with electron-delocalizing, yet base-resistant groups. The driving force for this reaction is provided by the formation of a resonance-stabilized dianion, such as III.

CONTRIBUTION NO. 849 FROM  
CENTRAL RESEARCH DEPARTMENT  
EXPERIMENTAL STATION  
E. I. DU PONT DE NEMOURS AND COMPANY  
WILMINGTON 98, DELAWARE

S. TROFIMENKO

RECEIVED MARCH 11, 1963

(2) (a) J. C. Bailar, *et al.*, WADC, Technical Report 57-391, Part II, May, 1958; (b) V. V. Korshak, E. S. Kronganz, A. M. Sladkov, V. E. Sheina and L. K. Luneva, *Vysokomolekul. Soedin.*, **1**, 1765 (1959); (c) V. V. Korshak and S. V. Vinogradova, *Dokl. Akad. Nauk USSR*, **138**, 1353 (1961); (d) T. Moeller and J. C. Bailar, ASD-TDR-62-209.

(3) (a) J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961); (b) J. P. Collman and E. T. Kittleman, *ibid.*, **83**, 3529 (1961); (c) R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958); (d) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(4) Z. Arnold, *Collection Czech. Chem. Commun.*, **27**, 2993 (1962).

(5) C. D. Weiss, *J. Org. Chem.*, **27**, 3514 (1962).

(6) Surprisingly, Arnold<sup>4</sup> reports IV not to melt up to 250°.