

acid with ethoxyacetylene in the presence of mercuric salt catalysts are under investigation. We have already shown that adenosine-5' phosphate (as the pyridinium or triethylammonium salts) in methanol solution, reacts with ethoxyacetylene (in the presence of  $\text{Hg}^{++}$  catalyst) on standing overnight to give the monomethyl ester of AMP. This product, obtainable in quantitative yield, was characterized by comparison with a sample prepared by Khorana's dicyclohexylcarbodiimide technique<sup>10</sup> using two chromatographic systems (2-propanol-ammonia-water, 7:1:2; butanol-acetic acid-water, 5:2:3) and two paper electrophoretic systems (0.1 M  $\text{K}_2\text{HPO}_4$ : 0.1 M  $\text{KH}_2\text{PO}_4$ ).

(10) M. Smith, J. G. Moffatt and H. G. Khorana, *THIS JOURNAL*, **80**, 6204 (1958).

(11) This work was supported by U. S. Public Health Service Grant, RG-3789(C6).

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RECEIVED JUNE 27, 1960

#### ACCELERATION OF THE DIELS-ALDER REACTION BY ALUMINUM CHLORIDE

Sir:

Although catalysis of the Diels-Alder reaction by acids<sup>1</sup> has been reported, the influence of catalysts and condensing agents on the rate of this reaction has been held to be small.<sup>2</sup> Our observation of the acceleration by aluminum chloride of the rearrangement of a dicyclopentadien-8-one derivative to a dicyclopentadien-1-one derivative,<sup>3</sup> and the proposal that this type of reaction is related to the Diels-Alder reaction,<sup>4</sup> has led us to investigate the effect of aluminum chloride on the rate of the latter reaction. We have found that in appropriate cases (*vide infra*), the presence of one or more molar equivalents of aluminum chloride can bring about remarkable acceleration of the Diels-Alder reaction. The following cases are illustrative.

(i) Equimolar amounts of anthracene, maleic anhydride and aluminum chloride were dissolved in dichloromethane at room temperature to give a solution 0.0625 M in each; the progress of the reaction was followed by infrared spectroscopy, which showed that reaction was complete in 1.5 minutes. The reaction mixture was then poured onto ice, giving a quantitative yield of the Diels-Alder adduct.<sup>5</sup> From extrapolation of the rate curve for the reaction under equivalent conditions of temperature and concentration in the absence of aluminum chloride it is estimated that 4800 hours would be required for 95% completion.<sup>6</sup>

(1) A. Wassermann, *J. Chem. Soc.*, 618, 623 (1942); W. Rubin, H. Steiner and A. Wassermann, *ibid.*, 3046 (1949); A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953); L. E. Gast, E. W. Bell and H. M. Teeter, *J. Am. Oil Chemists' Soc.*, **33**, 278 (1956).

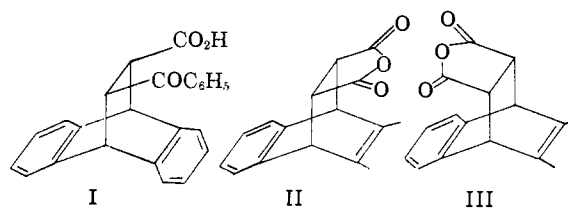
(2) K. Alder in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N.Y., 1948, p. 404; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 720.

(3) P. Yates and P. Eaton, *Tetrahedron Letters*, No. 11, 5 (1960).

(4) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(5) E. Clar, *Ber.*, **64**, 2194 (1931).

(6) The reaction of anthracene, maleic anhydride and aluminum chloride in benzene solution at 60-70° has been reported to yield  $\beta$ -(9-anthroyl)-acrylic acid.<sup>7</sup> We have found that this compound should be reformulated<sup>8</sup> as  $\text{C}_{24}\text{H}_{18}\text{O}_3$  and that it has structure I, formed



(ii) Reaction of equimolar amounts of anthracene, dimethyl fumarate and aluminum chloride dissolved in dichloromethane at room temperature was complete in less than two hours. When the relative molar concentration of aluminum chloride was increased to two, reaction was complete in less than 5 minutes. A quantitative yield of the Diels-Alder adduct<sup>9</sup> was obtained in each case. The reaction in the absence of aluminum chloride when carried out in boiling dioxane requires 2-3 days<sup>9</sup> and affords a less pure product.

(iii) Reaction of equimolar amounts of anthracene, *p*-benzoquinone and aluminum chloride dissolved in dichloromethane at room temperature was complete in less than 15 minutes, giving the 1:1 adduct<sup>10</sup> in 90% yield. When the relative molar concentration of anthracene was increased to two, there was obtained in 90% yield the previously unknown bis-adduct, m.p. 230° dec.,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  5.90  $\mu$ , identified by its oxidation to the corresponding quinone.<sup>10</sup> Formation of the bis-adduct did not occur in boiling xylene in the absence of aluminum chloride.

(iv) Reaction of equimolar amounts of 2,3-dimethylnaphthalene, maleic anhydride and aluminum chloride in dichloromethane at room temperature was complete in *ca.* 4 hours. A 1:1 adduct m.p. 175-178° dec., was obtained in 40% yield; this is assigned structure II, since on treatment with boiling methanol it was converted to an acid ester,  $\text{C}_{17}\text{H}_{15}\text{O}_4$ , m.p. 184-185°,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  5.75, 5.85  $\mu$ , which gave with bromine and aqueous sodium carbonate a bromolactonic ester,  $\text{C}_{17}\text{H}_{17}\text{O}_4\text{Br}$ , m.p. 191.5-192°,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  5.60, 5.75  $\mu$ .<sup>11</sup> The same adduct has been obtained previously by heating 2,3-dimethylnaphthalene (1 mole) and maleic anhydride (30 moles) in a sealed tube at 100° for 24 hours.<sup>12</sup> Infrared spectral examination of the crude product formed under either set of reaction conditions indicated the presence of another adduct, presumably III; this was formed to a greater extent in the absence of aluminum chloride.

In addition to the cases cited in detail above, evidence has been obtained for the acceleration by aluminum chloride of the following Diels-Alder reactions: anthracene and diethyl maleate, diethyl fumarate, citraconic anhydride, or dichloromaleic anhydride (in dichloromethane); cyclopentadiene and *p*-benzoquinone (in carbon tetrachloride) *via* an initial Diels-Alder reaction followed by a Friedel-Crafts condensation with the solvent.

(7) H. G. Oddy, *THIS JOURNAL*, **45**, 2156 (1923).

(8) Satisfactory elementary analyses for this compound and all new compounds here reported have been obtained.

(9) W. E. Bachmann and L. B. Scott, *ibid.*, **70**, 1458 (1948).

(10) E. Clar, *Ber.*, **64**, 1676 (1931).

(11) *Cf.* K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); **514**, 1 (1934).

(12) M. C. Kloetzel and H. L. Herzog, *THIS JOURNAL*, **72**, 1991 (1950).

chloride). Thus, this procedure promises to be of considerable utility for the acceleration of a wide range of Diels-Alder reactions.<sup>13</sup> Limitations are imposed by the instability of some dienes and dienophiles under the reaction conditions and by the preferential occurrence of Friedel-Crafts reactions in some cases.

We gratefully acknowledge a grant from the General Chemical Division, Allied Chemical Corporation, which defrayed the cost of this investigation.

(13) Following our suggestion, Mr. Kirby Scherer of these Laboratories has used aluminum chloride in dichloromethane to effect a facile Diels-Alder reaction between anthracene and 2-cyclopentenone at room temperature; in the absence of aluminum chloride the reaction in boiling xylene requires 5-6 days.

(14) N. S. F. Fellow, 1959-60.

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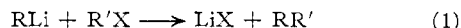
RECEIVED JULY 7, 1960

### SOLID COMPLEXES OF ALKYL LITHIUM COMPOUNDS WITH LITHIUM HALIDES<sup>1</sup>

Sir:

We wish to report the preparation of a series of relatively unreactive solid complexes of alkyl-lithium compounds with lithium halides. Materials so far obtained have apparent formulas  $RLi \cdot nLiX$ , where  $n$  is from 1.4 to 6, but these compositions appear to be mixtures of a 1:1 complex  $RLi \cdot LiX$  with excess lithium halide. In marked contrast to alkyl-lithium compounds, the complexes can safely be exposed to air, and can be handled in the laboratory with no more precautions than those used with other compounds mildly sensitive to moisture and oxygen.

The complexes are produced by carrying out the well-known coupling reaction (1) between alkyl-lithium compounds and alkyl halides. In a hydrocarbon solvent



the precipitate which forms is not simply lithium halide, but rather is a complex of lithium halide with the alkyl-lithium compound. The proportion of alkyl-lithium in the resulting solid varies with the conditions under which coupling is carried out.<sup>2</sup>

To isolate the solid complex, the precipitate from reaction (1) is filtered, washed with pentane, and dried *in vacuo*.<sup>3</sup> By this method complexes have been prepared from *n*-butyllithium and lithium bromide or iodide, from ethyllithium and lithium bromide, and from cyclohexyllithium and lithium bromide. In the *n*-butyllithium-lithium bromide system, which has been studied in the greatest detail, solids have been obtained with  $LiBr:C_4H_9Li$  ratios of 5, 3.3, 2.0, 1.5, and 1.4. Powder X-ray diffraction patterns for all of these compositions show both lithium bromide lines and new lines characteristic of the complex.<sup>4</sup> The lithium bro-

(1) This research was supported by the United States Atomic Energy Commission under contract No. AT(11-1)-64, Project No. 18.

(2) The coupling reaction may not be necessary for the synthesis of the complex, but may only provide a convenient method for slow generation of lithium halide in a solution of an alkyl-lithium compound.

(3) Preparations of both alkyl-lithium compounds and complexes were carried out in a drybox in an atmosphere of dry argon.

(4)  $d$  spacings in Å.: 16.3 (s); 8.8 (m); 5.7 (w); 4.40 (w); 4.07 (w); 3.87 (s); 3.30 (s); 2.89 (s); 2.55 (w); 2.43 (w); 2.20 (m); 1.89 (m).

mid lines decrease in relative intensity as the amount of alkyl-lithium in the solid increases, and become weaker than the "complex" lines in solids with  $LiBr:C_4H_9Li$  ratios less than 2. These X-ray data indicate that the solids are probably mixtures of lithium bromide with a 1:1 complex,  $C_4H_9Li \cdot LiBr$ .

The alkyl-lithium-lithium halide complexes appear to be quite different in their reactivity and properties from the ternary complexes of aryllithium, ether and lithium halide previously reported by Talalaeva and Kocheshkov.<sup>5</sup> The butyllithium-lithium bromide complex is rapidly hydrolyzed by water with the liberation of butane, but the rate of reaction with oxygen appears to be quite slow. Only partial decomposition was observed when the complex was exposed to laboratory air in an open beaker for three hours. The complex is also more stable thermally than is *n*-butyllithium. The latter compound undergoes rapid decomposition at temperatures above 100°, while the complex is less than 50% decomposed in one hour at 160°.

The solid complexes, when suspended in pentane or benzene, are quite unaffected by Michler's ketone (negative Gilman test<sup>7</sup> after 30 hours contact time). The addition of ether apparently destroys the complex, and an immediate Gilman test is obtained. Thus alkyl-lithium compounds can be deactivated by conversion to lithium halide complexes, and then regenerated in the form of conventional organolithium reagent solutions upon addition of ether.

No evidence has yet been obtained concerning the structure of the complexes. Two limiting ionic structures,  $Li^+[RLiX]^-$  and  $[Li_2R]^+X^-$ , could be considered, along with an intermediate electron-deficient polymeric structure. The structures of the complexes are under investigation, along with further reactions and alternate methods of preparation.

(5) T. V. Talalaeva and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, **104**, 260 (1955).

(6) D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955); K. Ziegler and H. G. Gellert, *Ann.*, **567**, 179 (1950).

(7) H. Gilman and F. Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

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RECEIVED JUNE 17, 1960

### 4-PHOSPHORINANONES

Sir:

Several recent papers attest to the lively interest in heterocyclic compounds containing only carbon and phosphorus in five-membered<sup>1</sup> and six-membered rings.<sup>2</sup>

We wish to report the preparation of a new class of six-membered carbon-phosphorus heterocyclic compounds, the 4-phosphorinanones (I), whose ring-carbonyl group affords an entry into an otherwise difficultly accessible area of organophosphorus chemistry.

(1) E. Howard and R. E. Donadio, *Dissertation Abstracts XX*, No. 2, p. 495. (1959), University Microfilms, Inc.; F. C. Leavitt, T. A. Manuel and F. Johnson, *THIS JOURNAL*, **81**, 3164 (1959); E. H. Braye and W. Hubel, *Chem. and Ind.*, 1250 (1959); I. G. M. Campbell and J. K. Way, *Proc. Chem. Soc.*, 231 (1959); F. G. Mann, I. T. Millar and H. R. Watson, *J. Chem. Soc.*, 2516 (1958).

(2) R. C. Hinton and F. G. Mann, *ibid.*, 2835 (1959).