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THE REACTION OF DIPHENYLLITHIOARSINE WITH QUINONES AND AROMATIC KETONES: A CONVENIENT SYNTHESIS OF TETRAPHENYLDIARSINE

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Summary

Diphenyllithioarsine is oxidized by aromatic ketones and quinones to tetraphenyldiarsine. These reactions were studied by means of EPR spectroscopy in order to ascertain the course of the reaction. Tetraphenyldiarsine was characterized by its mass spectrum, PMR spectrum, and conversion to diphenyldimethyl arsonium iodide.

Alkali metal derivatives of organylarsines of the general formula R_nAsM_{3-n} (n = 1, 2; M = Li, Na, K) have been found to be convenient starting materials for the synthesis of organic arsenic compounds in reactions with organic halides, organic dihalides, organometallic halides, epoxides, isocyanates, isothiocyanates, and carbodiimides [1]. Only three compounds containing carbonyl groups have been found to react with alkali metal derivatives of organylarsines Diphenylpotassioarsine and trifluoroacetyl chloride or pentafluoropropionyl chloride produced in low yields diphenylperfluoroacylarsines [2]. Issleib and Tzschach [3] mentioned that benzophenone and alkaliarsenides gave blue, extremely air sensitive solutions. In order to elucidate the reactive behavior of alkaliarsenides towards carbonyl compounds, reactions of diphenyllithioarsine with benzophenone, benzil, 9,10-anthraquinone, 9,10-phenanthraquinone and *p*-benzoquinone have been carried out.

Experimental

Materials and instrumentation

Triphenylarsine was prepared from arsenic trichloride and chlorobenzene

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[4]. Tetrahydrofuran was dried over sodium/benzophenone and distilled before use. Diphenyllithioarsine was synthesized from triphenylarsine and lithium in tetrahydrofuran [5]. To remove excess lithium, the solutions were filtered through glass wool in an inert atmosphere. Addition of t-butyl chloride destroyed the phenyllithium formed in the reaction. Benzophenone, benzil and *p*-benzoquinone were obtained commercially. 9,10-Anthraquinone and 9,10-phenanthraquinone were prepared according to literature procedures [6] The quinones were recrystallized before use. Benzophenone and benzil were employed without purification. All experiments were performed under dry nitrogen. NMR spectra were measured in carbon tetrachloride with TMS as internal standard using a Varian Associates Model T-60 spectrometer. The mass spectrum of tetraphenyldiarsine was obtained with a CEC 21-110B mass spectrometer employing an accelerating voltage of 8000 V. The molecules were bombarded with 70 eV electrons at a source and probe temperature of 250 and 110°, respectively.

Tetraphenyldiarsine

Into a 250 ml three-necked, round-bottomed flask was added freshly pressed lithium wire (0 42 g, 0.06 moles) and a magnetic stirring bar One neck was equipped with a nitrogen inlet tube, one was closed with a stopper and through the third neck the flask was evacuated by means of a vacuum pump. The flask was then filled with nitrogen A solution of triphenylarsine (9 2 g. 0 03 moles) in dry tetrahydrofuran (50 ml) was then added to the lithium wire. The magnetically stirred mixture developed a red coloration after approximately 15 min After 4 h stirring at room temperature the solution was filtered under nitrogen through glass wool to remove any unreacted lithium. Then t-butyl chloride (2.8 g, 0 03 moles) in dry tetrahydrofuran (10 ml) was slowly dropped into the filtered solution and the resulting mixture stirred for an hour. Benzophenone (5.5 g, 0.03 moles) in dry tetrahydrofuran (50 ml) was then added dropwise The color changed from red to dark blue. After all the benzophenone had been added the mixture was hydrolyzed with 2 *M* hydrochloric acid (15 ml, prepared with deoxygenated water) The organic layer was separated under a nitrogen atmosphere and most of the solvent removed by distillation The residue was dried at room temperature in vacuo The solid residue was recrystallized from ethanol/tetrahydrofuran (4/1 v/v). Tetraphenyldiarsine melting at 125-127° was obtained in 64% yield Similarly, benzil (6 3 g, 0 03 moles) and diphenyllithioarsine (0.03 moles) produced a 46% yield of tetraphenyldiarsine after hydrolysis of the dark brown reaction mixture

Reactions with quinones

The respective quinones (0 015 moles) dissolved in dry tetrahydrofuran (20 ml) were added to a tetrahydrofuran solution of diphenyllithioarsine (0 03 moles). The yield of purified tetraphenyldiarsine from the anthraquinone, phenanthraquinone and *p*-benzoquinone were 55, 51 and 63%, respectively.

EPR experiments

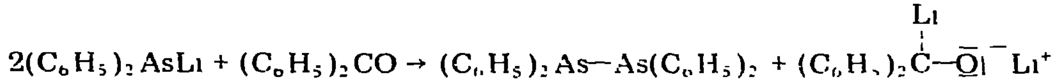
The solution required for the EPR spectra were prepared as described earlier. After diphenyllithioarsine and the appropriate carbonyl compound were combined in the desired molar ratio, small samples were transferred to 2 mm diameter EPR-quartz tubes fitted with a Schlenk-type adapter permitting the tubes to be filled under an atmosphere of dry nitrogen. The EPR spectra were obtained on a Varian Associates Model-E6A spectrometer.

Results and discussion

Addition of benzophenone to dark red solutions of diphenyllithioarsine in tetrahydrofuran causes a color change to an intense dark blue. The resulting solution is extremely air and moisture sensitive and gives an EPR signal in contrast to the lithioarsine solution. Similar observations were made when the lithioarsine was treated with benzil or the quinones. Hydrolysis and work-up of these reaction mixtures resulted in the isolation of tetraphenyldiarsine as the arsenic containing product. The experimental facts can be explained on the basis of an oxidation—reduction reaction described by eqn 1. Each of the

$$2(C_6H_5)_2AsLi + 2(C_6H_5)_2CO \rightarrow (C_6H_5)_2As{-}As(C_6H_5)_2 + 2(C_6H_5)_2\dot{C}{-}\underline{\bar{O}}|^{-}Li^{+} \qquad (1)$$

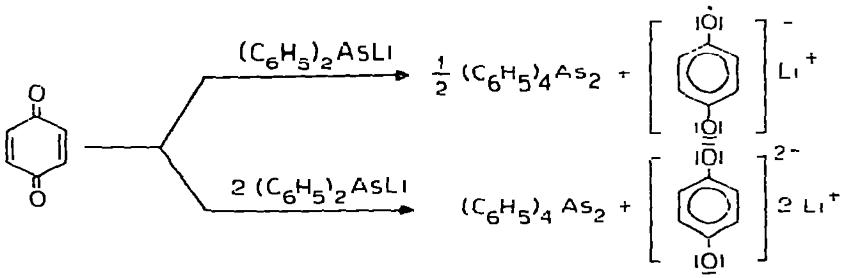
carbonyl compounds may undergo a reduction by accepting from the lithioarsine either a single electron or two electrons. Experiments were run to ascertain the course of these reactions. For benzophenone, reactions 1 and 2 depict the two possible reduction processes. If one electron each were transferred from two



$$2(C_6H_5)_2AsLi + (C_6H_5)_2CO \rightarrow (C_6H_5)_2As{-}As(C_6H_5)_2 + (C_6H_5)_2\overset{Li}{\underset{|}{C}}{-}\underline{\bar{O}}|^{-}Li^{+} \qquad (2)$$

dilithioarsine molecules to the benzophenone molecule the dilithio derivative of benzhydrol (eqn. 2) should not generate an EPR signal However, in reactions of benzophenone with a ten-fold molar excess of diphenyllithioarsine an EPR signal was observed indicating that radical anions were present

Two distinct reaction paths are possible in the interaction of quinones with the diphenyllithioarsine. Equation 3 depicts the two possibilities The first case



(3)

indicates reaction in a 1/1 molar ratio resulting in formation of a semiquinone. The second case results in the formation of the dilithio salt of the corresponding dihydroxy compound. By adjusting the stoichiometry we were able to establish that both reactions can occur. Equimolar amounts of reagents produced solutions that exhibit an EPR signal indicative of semiquinone formation. However the reaction mixture obtained from phenanthraquinone and a ten-fold molar excess of arsine did not produce an EPR signal indicating that in this case the quinone was reduced to the hydroquinone derivative 9,10-Dihydroxyanthracene was isolated as a product of the reaction between diphenyllithioarsine and 9,10-anthraquinone (2/1 molar ratio). No evidence for the formation of diphenylhydroxymethyldiphenylarsine, the product expected by reaction 4, was found when benzophenone was one of the reactants In order to most efficiently syn-

$$(C_6H_5)_2AsLi + (C_6H_5)_2CO \rightarrow (C_6H_5)_2As{-}C(OLi)(C_6H_5)_2 \qquad (4)$$

thesize tetraphenyldiarsine, a compound not easily available otherwise, equimolar amounts of the lithioarsine and benzophenone or benzil should be employed. Each mole of quinone, on the other hand, can transform two moles of lithioarsine to the diarsine. Several recrystallizations, all carried out under an atmosphere of nitrogen, were necessary in some cases to provide a product with the proper melting point Employing benzophenone, the yield of purified tetraphenyldiarsine based on triphenylarsine was 64% Earlier methods for the preparation of this diarsine were rather involved requiring in most cases two different arsenic compounds, each having two phenyl groups bonded to the arsenic atom [7]. Tetraphenyldiarsine was characterized by its melting point [7], by conversion to dimethyldiphenylarsonium iodide through a reaction with excess methyl iodide [8], by its ^1H NMR spectrum (structured resonance from δ 7 02 to 7.60 ppm) and by its mass spectrum. The following mass spectral peaks were observed (species, *m/e*, relative intensity based on R_2As = 100) R_4As_2, 458, 55, R_3As, 306, 0.9; R_2As, 229, 100; $C_6H_5AsC_6H_4$, 228, 8; $(C_6H_4)_2As$, 227, 55, R_2, 154, 19, $C_6H_5C_6H_4$, 153, 8, RAsH, 153, 1; $(C_6H_4)_2$, 152, 12, RAs, 152, 15, $C_{12}H_7$, 151, 2, C_6H_4As, 151, 12, As_2, 150, 0.3, C_4H_nAs (n = 2, 3, 4), 123 + n, 1-2; C_3H_2As, 113, 0 4; C_2H_2As, 101, 2, AsC, 87, 0.1, R, 77, 6; As, 75, 0.3; (R = C_6H_5) The base peak corresponds to $(C_6H_5)_2As$ formed by cleavage of the weak arsenic—arsenic bond in the diarsine As expected, cleavage of phenyl groups with the arsenic—arsenic bond remaining intact is only a minor fragmentation path with R_3As_2 being the only fragment formed in this manner Triphenylarsine is the major arsenic containing recombination ion The mass spectrum showed that the purified samples of tetraphenyldiarsine were free of bis(diphenylarsine) oxide.

Acknowledgements

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References

1 K J Irgolic in E I Becker and M Tsutsui (Eds), Reactions of Organometallic compounds Wiley Interscience, in preparation

2 E. Lindner and H Kranz, Chem Ber , 101 (1968) 3438

3 K Issleib and A Tzschach, Angew Chem , 73 (1961) 26

4 R L. Shriner and C N Wolf, Org. Synthesis, Coll Vol , 4 (1963) 910

5 A M. Aguiar and T G Archibald, J Org. Chem , 32 (1967) 2627.

6 R Wendland and J LaLonde, Org Synthesis, Coll. Vol , 4 (1963) 757

7 M. Dub (Ed), Organometallic Compounds, Vol III, Compounds of Arsenic, Antimony and Bismuth, 2nd ed , Springer Verlag, New York, 1968, p 125, First Suppl , 1972, p 148,
G.O Doak and L.D Freedman, Organometallic Compounds of Arsenic, Antimony and Bismuth, Wiley-Interscience, 1970, p. 268

8 G P Bergstrom and M M Dewar J Amer Chem Soc , 44 (1922) 2915