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1,3-Bis(1-phenylvinyl)benzene and Its Reactions with Electron Transfer Reagents

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SUMMARY:

The investigation of electron transfer and subsequent reactions of divinylidene compounds not capable of anionic homopolymerization was extended to 1,3-bis(1-phenylvinyl)benzene (2). A new method for the preparation of this compound is described. Its reaction with Li, Na, and K as electron transfer reagents in THF as solvent results in an increasing yield in polymeric combination products of the radical anions formed primarily with increasing reducing power of the alkali metal.

The main product, however, in any case is the cyclic dimeric tetra-anion of **2**, which upon protonation yields 1,4,11,14 -tetraphenyl[4.4]metacyclophane (**3**).

Introduction

The investigations of subsequent reactions of an electron transfer to divinylidene compounds incapable of anionic homopolymerization have shown¹⁻⁴⁾ that the compounds formed are dependent on whether the group R in the general formula 1 allows conjugation of the two double bonds or not.



If R, e.g., is 1,4-phenylene the two double bonds are conjugated and the transfer of an electron to one of the double bonds increases the electron density at the other one by both, an inductive and a mesomeric effect. The negative excess charge is more or less distributed over the whole molecular system which may be considered as an extended allyl anion^{1,2)}. That is why the electron transfer to the second double bond of a molecule of this type is severely hindered. With Li such an electron transfer does not occur at all. With Na it takes place exclusively and with K predominantly after dimerization of the monoradical mono-anions.

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If, however, the conjugation between both double bonds is interrupted by a group R designed in a proper way, a negative excess charge in the one half of the molecule only provides some inductive influence on the double bond in the other half^{3,4)}. In this case, the electron transfer to the second double bond is hardly affected. Thus, not only the formation of linear polymers by intermolecular combination reactions is to be expected but also the formation of cyclic oligomers by intramolecular reaction. The exclusive formation of a cyclic dimer with four carbanionic centers would be of special interest since this compound might act as a tetrafunctional initiator for the anionic polymerization of suitable monomers. In this respect the two compounds **1a** and **1b** proved to be less promising¹⁻⁴):

1a after electron transfer yields besides the cyclic dimer the cyclic monomer with two carbanionic centers³⁾. Electron transfer reactions to **1b** on the other hand are accompanied by side reactions resulting from the internal methylene group.

It should be possible to avoid these difficulties using 1,3-bis-(1-phenylvinyl)benzene (2).



This paper is concerned with the reactions of 2 with different electron transfer reagents and the analysis of the reaction products.

Reaction of 1,3-bis(1-phenylvinyl)benzene with different electron transfer reagents

Electron transfer reagents used were Li, Na, and K applied as dispersions in THF. The concentration of **2** was $2 \cdot 10^{-2} \text{ mol dm}^{-3}$, the mole ratio alkali metal/**2** was 20:1, and the temperature was $-75 \,^{\circ}\text{C}$.

Fig. 1 shows the GPC curves of the protonated reaction products. As the alkali metal is changed from Li over Na to K the portion of higher oligomeric and polymeric combination products clearly increases while the portion of the main product (Fig. 1, $V_E = 68 \text{ ml}$) decreases. The main product was isolated by a two step fractionation.

The IR spectrum is in agreement with the structure of the expected 1,4,11,14-tetraphenyl[4.4]-metacyclophane (3)*).



^{*)} Systematic name: 4,7,11,14-tetraphenylhexahydro-4H,7H-dibenzo[ab,hi]cyclotetradecene.



m|e

Fig. 1. GPC curve of the protonated products of the reaction of 1,3-bis(1-phenylvinyl)benzene with Li (a), Na (b), and K (c), as electron transfer reagents



The 60 MHz ¹H NMR spectrum (in CCl₄) yields: $\delta = 7,2$ (m; 28 aromatic H), 3,9 (m; 4 tert-H), and 2,2 (m; 8 sec-H). No further signals can be detected. Thus, there is no evidence for an open-chain structure.

Both, the signal of the secondary and even more that of the tert. aliphatic hydrogens are very broad. This is due to the strongly hindered flexibility of the ring members, which results in a direct spin-spin coupling between different protons.

A full prove of the structure is given by the mass spectrum shown in Fig. 2.

The molecular ion peak (m/e=568) corresponding to the cyclic dimer 3 shows up with a relatively high intensity (70%) as to be expected for a cyclic molecular structure. The most significant fragments can be explained as well on the basis of the structure of 3.

Discussion of the results

On the basis of the results observed the following general reaction scheme can be deduced:



In the first step an electron is transferred to the divinylidene molecule 2 yielding the monoradical-monoanion 4. This may attack an unreacted double bond of another 2 to yield a dimeric monoradical-monoanion, which by a second electron transfer reaction is converted to the dimeric dianion with two terminal double bonds. In addition, the same species may be formed by direct combination of two 4. Further transfer of electrons to the unreacted double bonds

yields mono- and diradicals which can react intermolecularly to form higher oligomers and polymers. In addition, however, the formation of cyclic oligomers by intramolecular reaction may occur.

In principle these reactions as well may proceed by combination of two radical sites or by radical attack of a CC-double bond. Although the rate constant of the latter reaction is supposed to be smaller than that of the first one, the radical attack may be favored over the combination reaction because the concentration of radicals usually is much lower than that of unreacted double bonds. In this particular case the resulting distribution of oligomers, i.e. the ratio of the inter- and the intramolecular reaction, is governed by the relative reactivities of the different kinds of double bonds but not by the stationary concentration of radicals, because there is always only one radical site participating in the reaction. Although a final decision between the two reaction mechanisms seems to be impossible from the present results, the observed influence of the reducing power of the alkali metal is better explained by the assumption that the direct combination of two radical sites is the main reaction.

Thus, with Li as a weak electron transfer reagent the intramolecular combination is favored since the concentration of radicals is small.

As shown in Fig. 1 the portion of higher oligomers and polymers in the reaction products increases with increasing reactivity of the electron transfer reagent.

The more reactive an electron transfer reagent the faster is the formation of radical anions, i.e., the higher is the concentration of radical anions in solution. Consequently the probability of an intermolecular reaction is increased yielding a higher amount of higher oligomers and polymers.

Experimental Part

1,3-Bis(1-phenylvinyl)benzene (2): It was prepared by the Wittig olefination of 3-benzoylbenzophenone since the method reported earlier⁵⁾ only gave relatively poor yields.

3-Benzoylbenzophenone was synthesized by Friedel Crafts reaction of benzene (p. a.) with isophthaloyl dichloride in the presence of AlCl₃ (both from Merck-Schuchardt) according to a procedure described by $Ador^{6}$, however, modified by using 1,2-dichloroethane as solvent (purified by distillation after treatment with conc. H₂SO₄ and water and drying over Na₂SO₄ and P₄O₁₀).

51 g (0,25 mol) of isophthaloyl dichloride in 50 ml of 1,2-dichloroethane were added to a suspension of 80 g (0,6 mol) of AlCl₃ in 150 ml of 1,2-dichloroethane with stirring and cooling in an ice bath. Then 54 ml (46,8 g, 0,6 mol) of benzene were added keeping the temperature of the reaction mixture at 20 °C. After 2 h of stirring the mixture was kept overnight and then decomposed by addition of 250 ml of ice. The organic phase was separated and the aqueous phase was extracted twice with 1,2-dichloroethane. The combined organic phases were washed with 2% aqueous NaOH solution and water, and then dried over Na₂SO₄. After evaporation of the solvent the product was recrystallized from ethanol/ligroin (1:1 by vol.). Yield: 58,6 g (82%); mp 106 °C (Lit.⁶): mp 99,5–101 °C).

Triphenylmethylphosphonium bromide was prepared by the method described by $Wittig^{7}$. Phenyllithium was synthesized according to the procedure of $Gilman^{8}$ directly before use from 3.7 g (0,525 mol) of lithium and 26,3 ml (39,25 g, 0,25 mol) of bromobenzene in 190 ml of ether. The product was forced through a sintered glass disk by nitrogen into the reaction vessel containing 71,5 g (0,2 mol) of triphenylmethylphosphonium bromide and 210 ml well dried ether, cooled by means of an ice bath. Upon addition the color of the mixture immediately turned orange-red due to the formation of the methylene phosphorane. After stirring for 3 h at room temperature the temperature again was lowered to 0°C and 22,9 g (0,08 mol) of 3-benzoylbenzophenone (well dried and degassed) were added. The mixture was stirred for some hours and kept overnight. Then, it was decomposed by addition of ca. 300 ml of water. The phosphine oxide precipitated as a mud, and was separated from the liquid by decantation and/or filtration, and washed with ether. The organic phases were combined, dried over Na₂SO₄, and the solvent was evaporated i. vac. After distillation (bp 163° C (at 0,01 Torr)) the product was recrystallised from methanol/acetone (2:1 by vol.). Needles, mp 46° C^{*}). Yield: 18 g (80%).

¹H NMR (CCl₄): $\delta = 7,35$ and 7,25 (m; 14 phenyl-H), and 5,47 (s; 4 vinyl-H).

C ₂₂ H ₁₈ (282,4)	Calc.	C 93,58	H 6,42
	Found	C 93,45	H 6,56

Reactions of 2 with electron transfer reagents: They were carried out in an inert atmosphere¹). In the case of Li argon was used, otherwise nitrogen. The solvent, THF, was purified by methods described earlier¹).

Li was used as a powder with an average particle size of 0,05 mm (Metallgesellschaft, Frankfurt). Na and K (15% by weight) were supported on Al₂O₃.

The reaction vessel was a Schlenk tube equipped with a dropping funnel. After drying the apparatus by heating, 20 mmol of the alkali metal was filled into the Schlenk tube cooled by means of a mixture of dry ice and methanol. The funnel contained 282 mg (1 mmol) of **2** and 50 ml of THF. The solution was added to the alkali metal and stirred for 2 h (Li) or 1 h (Na, K). Then the deep red solution was forced into a flask containing a small amount of methanol, becoming colorless immediately. The solvent was evaporated until the volume of the solution was 5 ml and the products precipitated upon pouring the solution into a stirred mixture of methanol/water (1:1 by vol.). The products were filtered off and dried at 50°C.

In order to isolate the main product 3 1 g of the product mixture was suspended in 100 ml methanol/acetone (3:2 by vol.) and stirred for 2 h at room temperature. The insoluble fraction (II) was filtered off, dissolved in THF and precipitated in methanol/water (1:1 by vol.); Yield: 225 mg II. The filtrate was concentrated up to 20 ml and, with stirring, mixed with 20 ml of water. Thus, fraction I precipitated, amounting to 643 mg after drying. The product was dissolved in 80 ml of boiling ethanol to 95% and then the solution was filtered. Upon cooling to -20° C fraction Ia (154,3 mg) precipitated. The solution was mixed with 10 ml of water, yielding 369,3 mg of fraction Ib, i.e. 3 with a purity of >95% as determined by GPC. Mp 105–110°C.

C44H40 (568,8)	Calc.	C 92,91	H 7,09
	Found	C 93,36	H 6,93

Spectra: The 60 MHz ¹H NMR spectra were taken with a JEOL apparatus model JNM-MH-60 III. The mass spectrum was taken with a Varian CH 7 a.

Chromatography: GPC was performed with a Waters ALC 200 high pressure liquid chromatograph. The columns were filled with μ -styragel with pore sizes of 100, 500, 1000, and 10000 Å, two columns of each (1 ft. long, 7 mm diameter). As a detector a Waters differential refractometer Type R 401 was used.

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^{*)} This compound has been described earlier as a liquid⁵⁾.