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SYNTHESIS AND PROPERTIES OF TETRAKIS(PHENYLETHYNYL)ETHYLENE

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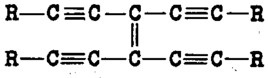
It is well known that tetrasubstituted ethylenes show various reactivities by the nature of their substituents. For example, tetracyanoethylene reacts as strong electrophile. On the contrary, tetraalkoxy- and tetraamino-ethylenes behave as electron-rich olefines (1). One unique type, tetraethynylethylenes have not received significant attention by organic chemist perhaps because of the synthetic difficulties. Nevertheless their chemical and physical properties are of interest, because they may show both the above reactivities by the nature of R.



$$\begin{array}{c} R-C\equiv C-C-C\equiv C-R \\ \| \\ R-C\equiv C-C-C\equiv C-R \end{array}$$

Further interest can be expected for cross-conjugation because they have planar cross-conjugated configuration.

We should like to report the synthesis and some properties of tetrakis-(phenylethynyl)ethylene and its isomers.

The reaction of 1,5-diphenyl-3-bromo-1,4-pentadiyne <u>I</u> with potassium tert-butoxide in 4:1 mixture of tetrahydrofuran and N-methyl-2-pyrrolidone gave three yellow crystalline compounds, <u>II</u> mp. 210°, <u>III</u> mp. 163° and <u>IV</u> mp. 147°. These were separated by means of alumina column chromatography. The analytical and hydrogenation results and mass spectra showed that these three compounds had same composition which were dehydrobrominated dimers of compound <u>I</u> .

The structures were strongly suggested by the NMR spectra (Fig.1). The signals of phenyl protons for compounds <u>II</u> and <u>III</u> were separated to two

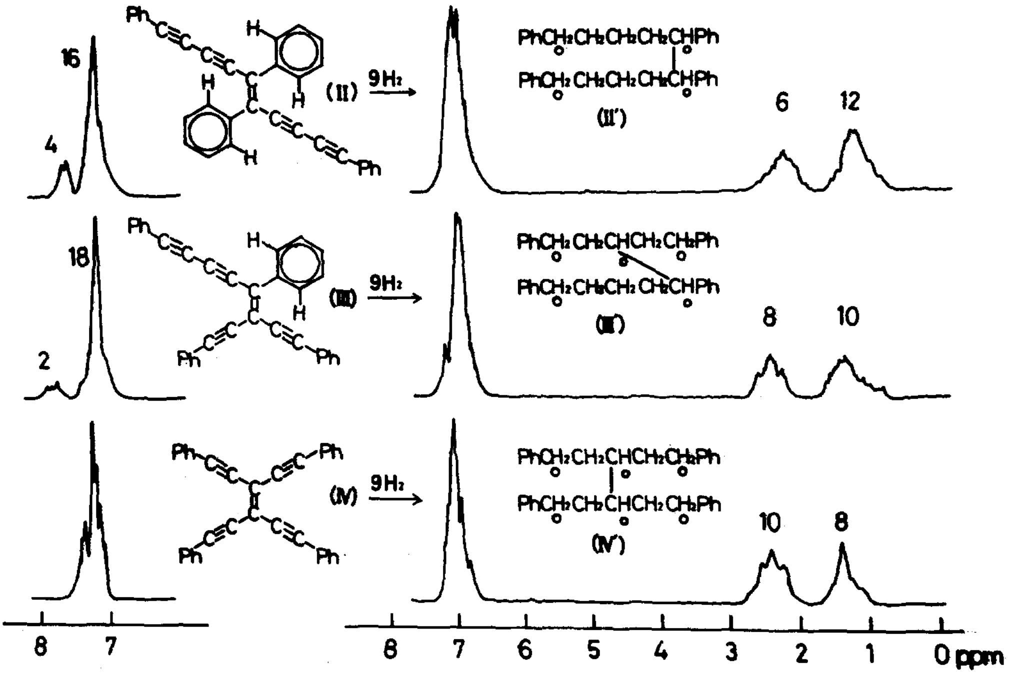
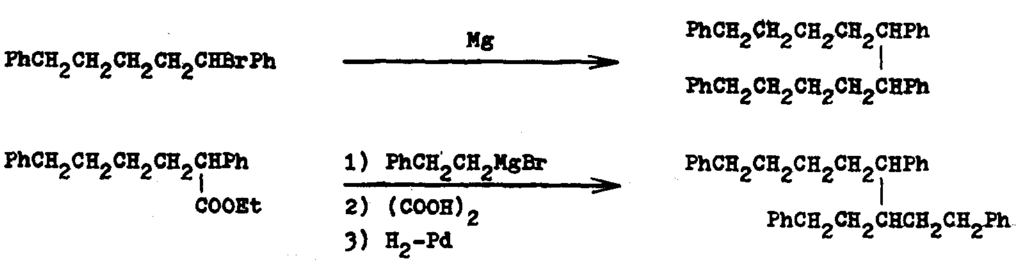


Fig. 1

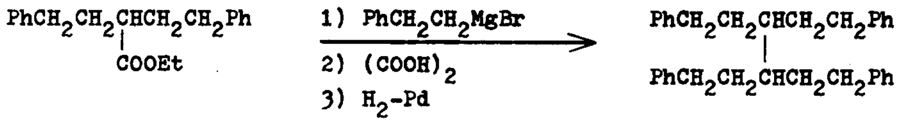
parts. The lower magnetic field signals, 4 protons for compound II and 2 protons for compound III , were assigned to special ortho phenyl protons which were shown by "H" in Fig.1 . The assignment was appreciated by the deshielding effect of acetylenic bond. This phenomenon was also found in several olefines which had phenyl group situated cis to acetylenic bond (2).

The structures were finally confirmed by comparison of the hydrogenated products II' , III' and IV' with the compounds which were prepared by following schemes.



$$PhCH_2CH_2CH_2CH_2CHBrPh \xrightarrow{Mg} \begin{array}{l} PhCH_2CH_2CH_2CH_2CHPh \\ \qquad\qquad\qquad\qquad | \\ PhCH_2CH_2CH_2CH_2CHPh \end{array}$$

$$\begin{array}{l} PhCH_2CH_2CH_2CH_2CHPh \\ \qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\quad COOEt \end{array} \xrightarrow[\substack{2)\ (COOH)_2 \\ 3)\ H_2\text{-}Pd}]{1)\ PhCH_2CH_2MgBr} \begin{array}{l} PhCH_2CH_2CH_2CH_2CHPh \\ \qquad\qquad\qquad\qquad | \\ \qquad PhCH_2CH_2CHCH_2CH_2Ph \end{array}$$



$$\underset{\displaystyle \mathrm{COOEt}}{\mathrm{PhCH_2CH_2\overset{|}{C}HCH_2CH_2Ph}} \xrightarrow[\substack{\text{2) }\mathrm{(COOH)_2}\\ \text{3) }\mathrm{H_2\text{-}Pd}}]{\text{1) }\mathrm{PhCH_2CH_2MgBr}} \begin{array}{c}\mathrm{PhCH_2CH_2CHCH_2CH_2Ph}\\ |\\ \mathrm{PhCH_2CH_2CHCH_2CH_2Ph}\end{array}$$

The IR and NMR spectra of the corresponding compounds were identical, respectively. If the multiplet signals of aliphatic protons at lower magnetic field assigned for benzyl methylene and methyne protons (shown as $\underset{\circ}{H}$ in Fig.1), the NMR spectra were consistent with their structures. Furthermore, compound <u>III</u>' crystallized (mp. 95°) and showed no melting-point depression on admixture with synthetic one.

The electronic spectra of these compounds provided interesting evidence for cross-conjugation. As shown in Fig.2 , they had almost same long-wavelength absorptions in spite of their different linear conjugation length. This would be considered that the all π-electrons in these compounds delocalized at almost same degree for the coplanarity of the cross-conjugation system. It was reported that such effect was not found in the formally cross-conjugated compounds which could not have planar configuration by steric hindrance (3).

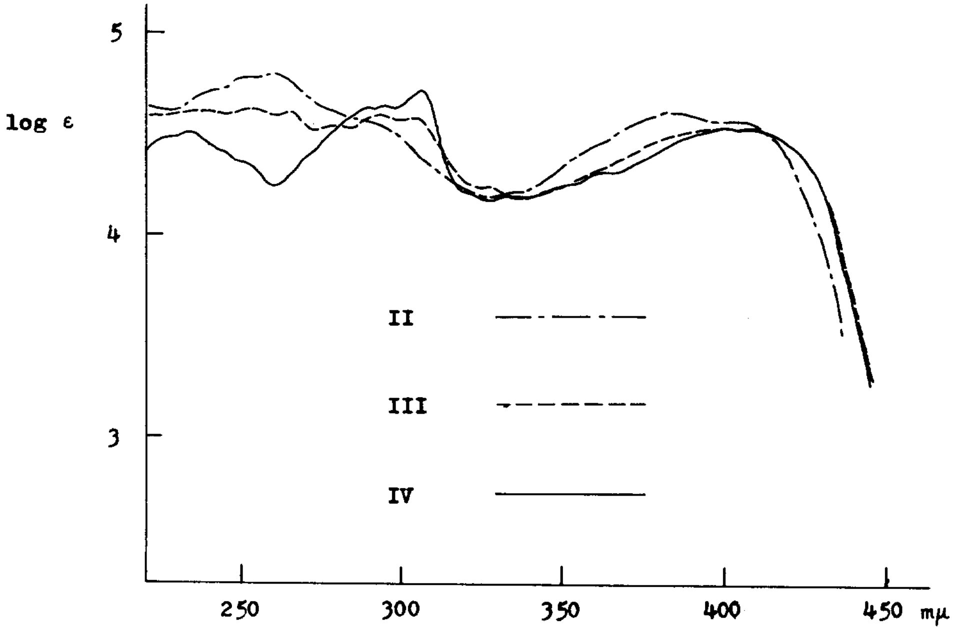


Fig. 2

There is complication in compound IV. Coe and his coworkers treated phenylethynyl copper with tetraiodoethylene and obtained a compound, white crystalline solid, mp. 84~85°, in 40% yield. They claimed it to be tetrakis(phenylethynyl)ethylene (4). This compound corresponded neither to our compound IV nor its isomers. We considered that this compound might be diphenylbutadiyne in view of mp. and UV spectrum (5). The coupling of metal acetylide is well known reaction (6).

The addition of compound IV to 2,4,7-trinitrofluorenone (TNF) in chloroform gave deep red crystalline π-complex, mp. 167°. The composition, determined by analysis, showed 1/2 for IV/TNF. If we used benzene or toluene as solvent in the course of addition or recrystallization, the complex contained another one equivalent mole of solvent molecule. In spite of containing solvent in the complex, their melting points were the same as solvent free ones. Mesitylene was not contained. Differential thermal analyses showed that the solvent were separated by heating at 123° for benzene and 97° for toluene, and then melted at the melting point of the solvent free complex. Although we are undertaking the structural studies, it is apparent that the addition of aromatic solvent molecule to the π-complex is affected by steric effect of their substituents.

Further study for the reaction mechanism, for the syntheses of other tetraethynylethylenes and for their properties is in progress and the results will be reported in near future.

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