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ADSORPTIVE CYCLIZATION REACTION ; DIBENZOFURANACETYLENES FROM 1,6-BIS(o-METHOXYARYL)-1,6-DIPHENYL-2,4-HEXADIYNE-1,6-DIOLS

Shinjiro Kobayashi, Masuo Shinya and Hiroshi Taniguchi
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka, Japan.

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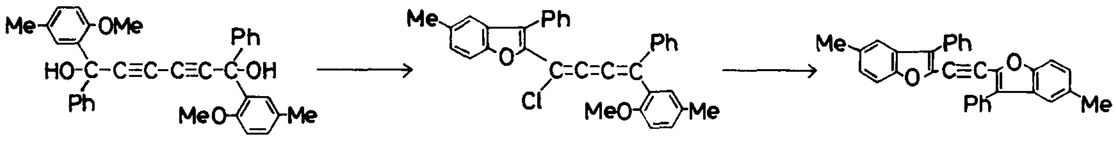
By treatment with hydrobromic acid in acetic acid, 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol has been shown to rearrange to 1,1,6,6-tetraphenyl-3,4-dibromo-1,2,4,5-hexatetraene (1). This is one of the well-known rearrangement reactions of propargyl alcohols to haloallenes (2). However, we found that the dibenzofuranacetylene IIIa was unexpectedly obtained in the eluate from alumina column chromatography of the product of the hexadiynediol Ia, which had o-methoxyaryl groups at both 1 and 6-positions, under the similar condition as the above reaction. By isolation of the benzofuranbutatrienechloride IIa as the intermediate product, it was proved that this unusual intramolecular cyclization reaction proceeded by two steps, the second one proceeding easily by adsorption of IIa on adsorbent such as alumina and silica-gel.

Here, we wish to report the chemical evidence for this novel adsorptive cyclization reaction.



Ia IIa IIIa

The reaction of Ia with two equivalent moles of concentrated hydrochloric acid in the acetic acid-benzene solution at room temperature afforded a deep red solution. After usual work-up, recrystallization of the raw product gave orange crystals (IIa), $C_{33}H_{25}O_2Cl$, mp 118-121°C (3), in 75% yield. Its structure was determined by the following spectral results. The peak at 2030 cm^{-1} in infrared spectrum was assigned to butatriene stretching vibration (4) and its electronic spectrum (in cyclohexane, 270 nm (ε 27,000) and 440 nm (ε 36,000)) was similar to that of tetraarylbutatriene (2). The nmr spectrum (in $CDCl_3$, 7.73 τ(3H) for methyl proton in benzofuran ring, 7.58 and 7.62 τ(3H) for methyl proton in phenyl ring, 6.30 and 6.40 τ(3H) for methoxy proton and 2.3-3.7 τ(16H) for aromatic proton) showed that the crystals were the mixture of cis and trans-isomers of IIa.

When the benzene solution of IIa was allowed to stand in contact with alumina at room temperature, the absorption at 440 nm disappeared gradually and a new absorption appeared at 360 nm. After 15 hours yellow crystals, mp 220-222°C, $C_{32}H_{22}O_2$, was isolated quantitatively. The compound was identified as the dibenzofuranacetylene IIIa by the above analysis and the following hydrogenation result. The crystals absorbed two equivalent moles of hydrogen on palladium-black and afforded fluorescent crystals, mp 153-155°C, $C_{32}H_{26}O_2$. The similarity of its electronic spectrum (in cyclohexane, 258 nm (ε 32,400), 279 nm (ε 17,600), 284 nm (ε 15,400) and 292 nm (ε 14,600) to that of benzofuran supported to its structure.

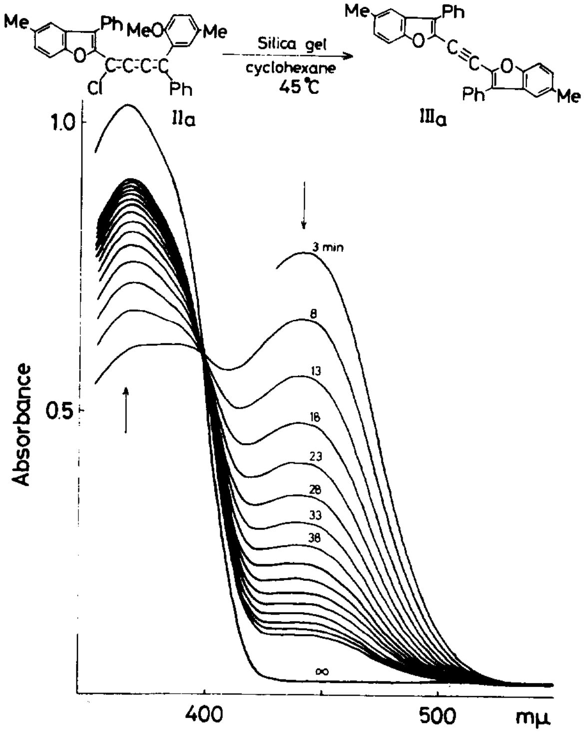
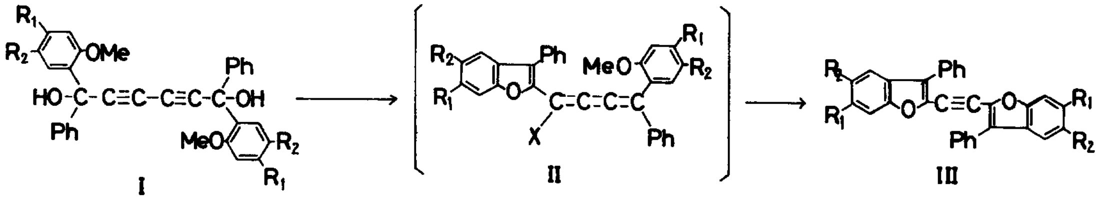


Fig. 1

This novel cyclization reaction was not influenced by the quality of alumina (acidic, neutral or basic) and was also achieved by use of silica-gel. However, no reaction was observed when ethanol was used for solvent instead of hexane and/or benzene. The measurement of adsorption equilibrium showed that the butatrienechloride IIa was strongly adsorbed in the hexane and/or benzene solution but was not in the ethanol solution. The cyclization occured by adsorption of <u>IIa</u> on the surface of adsorbent such as alumina and silica-gel.

The electronic spectrum of the butatrienechloride <u>IIa</u> adsorbed on silica-gel in the cyclohexane solution was measured for various time period at 45°C (5). As shown in Fig. 1, this cyclization reaction proceeded with the regular change of the adsorption at 440 nm and the appearance of the isosbestic point at 397 nm.

The related hexadiynediols <u>Ia-f</u>, which had o-methoxyaryl groups, also afforded the dibenzofuranacetylenes <u>IIIa-f</u> through the raw butatrienechloride II in contact with alumina in the benzene solution, respectively, as shown in the following table. The corresponding bromides <u>IIa-c</u>, which were prepared by treatment of <u>Ia-c</u> with concentrated hydrobromic acid, were also converted to <u>IIIa-c</u> in the same method, respectively.



	R_1	R_2	II X	II λ_{max}(nm)$^{i)}$	III mp (°C)	III yield(%)$^{ii)}$
a	H	Me	Cl Br	443 446	220—222	42 43
b	H	MeO	Cl Br	450 452	200	40 38
c	H	H	Cl Br	440 442	186—188	60 27
d	H	Cl	Cl	440	——$^{iii)}$	15
e	Me	H	Cl	445	189—191	60
f	MeO	H	Cl Br	460 ——	166—168	34 8$^{iv)}$

i) was measured in benzene.

ii) was obtained when the raw halide in benzene (1 mmole/50 ml) was in contact with alumina (10 g) for 15 hours.

iii) was sublimes at near 280°C.

iv) was obtained from the solvolysis reaction.

Although the purification of some butatrienehalides was unsatisfactory, the qualitative reactivities of the halides could be compared by measurement of the change of the absorption maxima at near 450 nm of the halides. The result was summarized as follows; i) the bromide was more reactive than the corresponding chloride and ii) the substituent effect at 5 and 6-positions of the benzofuran ring was the following order; 6-MeO > 6-Me > 5-Me > H > 5-MeO > 5-Cl. The electron donating group which was more effective at 6-position than at 5-position activated the halide in this adsorption reaction.

The difficulty of purification of the halides, especially of the bromides, would be attributed to their reactivities. When the compound If was treated with two equivalent moles of hydrobromic acid in the acetic acid-benzene solution for two hours the dibenzofuranacetylene IIIf was directly formed. The bromide IIa gave also the dibenzofuranacetylene IIIa in methanolysis catalized by silver acetate. These results implied that the butatrienehalide II was subjected to solvolysis and gave III, the same product as the adsorption reaction. Both solvolysis and adsorption reactions are of interest in connection with the butatrienyl cation as intermediate.

The phenomenon of high activation of usually unreactive unsaturated halide by adsorption is very interesting. We are undertaking for this mechanistic study and now consider that the carbon and halogen bond in the butatrienehalide may be activated by the polarity of adsorbent and the resulting butatrienyl cation will be subjected to the attack of the lone pair in the methoxy group which is favourably located to the vacant orbital of the cation.

REFERENCE

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2. H.Fischer in The Chemistry of Alkene (Ed. S.Patai), Interscience Publishers, New York, 1964, Chap. 13, p 1025.
3. The melting points of all compounds in this paper are uncorrected.
4. H.Fischer and H.Fischer, Tetrahedron Letters, No 6, 435 (1969).
5. The spectrum was measured for the resulting slurry which consisted of IIa 1x10^{-3}mmole / silica-gel 1g / cyclohexane 6ml.