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Preparation and Spectra of 9-(*p*-Vinylphenyl)anthracene

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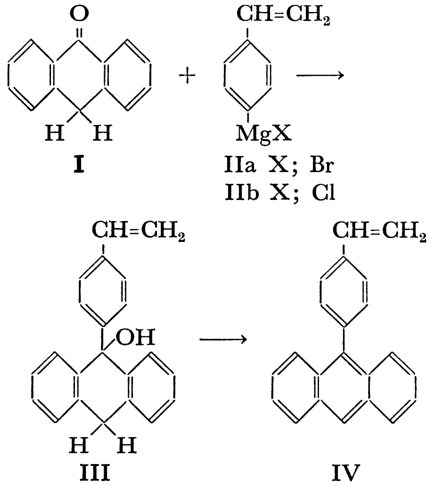
Synopsis. A novel vinyl monomer containing the polyaromatic ring, 9-(*p*-vinylphenyl)anthracene, was prepared by the Grignard reaction of anthrone and *p*-vinylphenylmagnesium halides which could be obtained either from *p*-bromostyrene or *p*-chlorostyrene. The results and the spectra of products are discussed.

Recently, many investigations of organic polymers[1] with polyaromatic rings in the side-chains have been carried out from the optical and electrical interests. 9-(*p*-Vinylphenyl)anthracene (IV) is a promising new vinyl monomer which can be used to prepare one such organic polymer. The authors wish to report on the preparation of IV by the Grignard reaction as follows.



I

IIa X; Br
IIb X; Cl

III

IV

p-Vinylphenylmagnesium halide (IIa) was synthesized by the Grignard reaction of *p*-bromostyrene and magnesium in accordance with Cazes' report.[2] A method using inexpensive *p*-chlorostyrene in place of *p*-bromostyrene was also investigated.

The results are given in Table 1. It was observed that *p*-vinylphenylmagnesium halides can be produced in yields of more than 80% either from *p*-bromostyrene or *p*-chlorostyrene. In the case of *p*-chlorostyrene the yield increased remarkably with the rises in the reaction temperature.

The reaction mixture of *p*-vinylphenylmagnesium halides with I was analyzed by thin layer chromatography(TLC) on alumina, and six spots were detected at R_f 0.94, 0.58, 0.49(main spot), 0.36, 0.25 and at the starting point. These spots were observed in the cases both chlorostyrene or bromostyrene was used. They were assigned to IV, anthraquinone (V), unreacted I, major product III, bianthrone-9-yl (VI) and the polymer of IV, respectively. TLC was presumed to produce V and IV by oxidation or hydration.[3] The spot at R_f 0.25 was identical with that which appeared when purified I was allowed to stand in a benzene solution for several days. It has been reported that I produces bianthrone-9-yl in benzene by photoreaction.[4] Bianthrone-9-yl (VI) was prepared by a known method,[5] and was found to be identical with the product (R_f 0.25) which formed in the reaction mixture. The spots at R_f 0.94 and at the starting point showed a strong blue fluorescence under UV irradiation (366 mm), and therefore, were characterized as polyaromatic compounds.

Table 1. Yields of Grignard reagents from styryl halides

Styryl halide 0.1 mol	Mg mol	THF ml	Reaction temp °C	Reaction time h	Grignard reagent (IIa, IIb) yield, %[a]
p-Bromo	0.1	80	60—65	1.5	90.5 (IIa)
p-Bromo	0.1	80	70—75	1.5	95.5 (IIa)
p-Chloro	0.1	70	60—65	1.5	80.5 (IIb)
p-Chloro	0.2	140	70—75	1.5	94.9 (IIb)

a) Determined by acid titration method.

The overall yield of IV based on I was about 20% when III was separated, purified and then treated with phosphorus pentaoxide (Method A). On the other hand, when the reaction mixture from the reaction of I and *p*-vinylphenylmagnesium halide was directly treated with phosphorus pentaoxide without separating or purifying III, the yield of IV increased to about 40% (Method B). IV was also recrystallized from isopropyl alcohol after treatment with phosphorus pentaoxide without using column chromatography, and a high yield of IV was obtained as shown in Table 2 (the maximum overall yield 44%) (Method C). Table 2 shows the relation of the molar ratio of I to *p*-vinylphenylmagnesium halide and the yield of IV. The yield is maximum at a molar ratio of about 1.3.

In the NMR signals of IV quartet 1H at $\tau=3.24$, doublet 1H at $\tau=4.29$ and doublet 1H at $\tau=4.82$ coincide well with the signals of the α,β-proton of the vinyl group of styrene. Further, the spin-spin coupling constants $J_{\alpha\beta}=1.72$, $J_{\alpha\beta'}=10.8$ and $J_{\beta\beta'}=1.7$ for the

Table 2. Yields of 9-(*p*-vinylphenyl)anthracene (IV) by direct synthesis (Method C)

Starting material	Anthrone (I)/(IIa or IIb)[a] Molar ratio	Reaction time h	Reaction temp °C	Yield of IV % Crude	Pure
IIa	1	3	20—25	19	—
IIa	1	3	Reflux	36	—
IIa	1.3	4	Reflux	52	—
IIa	1.5	4	Reflux	52	36
IIa	2.0	4	Reflux	45	—
IIa	2.5	4	Reflux	13	—
IIb	1.5	4	Reflux	51	44

a) Assuming that Grignard reaction of styryl halide with magnesium gives IIa (or IIb) in quantity.

Table 3. Ultraviolet spectra of 9-phenylanthracene and its derivatives

Compound	Solvent	$\lambda_{\max}$ nm (log ε)					
9-Phenylanthracene[a]	CH_2Cl_2	259 (5.13)	318 (3.09)	332 (3.46)	350 (3.78)	368 (3.97)	387 (3.93)
9-Phenylanthracene[b]	C_2H_5OH	256 (5.09)	—	331 (3.44)	347 (3.77)	365 (3.94)	385 (3.94)
9-(*p*-Vinylphenyl)-anthracene (IV)	CH_2Cl_2	258 (5.12)	—	332 (3.45)	349 (3.81)	367 (4.01)	387 (3.97)
9-(*p*-Vinylphenyl)-anthracene (IV)	C_2H_5OH	256 (5.09)	—	331 (3.44)	348 (3.79)	365 (3.96)	384 (3.98)
9-(*p*-Toryl)anthracene[b]	C_2H_5OH	255 (5.12)	—	331 (3.54)	346 (3.84)	364 (4.00)	383 (3.97)

a) S. C. Dikerman, D. de Souza, and P. Wolf, *J. Org. Chem.*, **30**, 1981 (1965). b) D. Mosnaim, *Tetrahedron*, **25**, 3485 (1969).

vinyl group of IV also coincide well with the coupling constants of styrene.[6,7]

It is known that, when phenyl groups are introduced into anthracene rings, the overall ultraviolet absorption shifts to the longer wavelength region[8,9] and is scarcely affected by the position of the phenyl group or the kind of substitutes bonded to that group. As shown in Table 3, IV shows the same absorption as other 9-monophenylanthracene derivatives in the UV spectra.

Experimental

All compounds were shown to be pure by TLC with alumina B-5 or silica gel C-100 (Wako Pure Chemicals Co., Ltd., Tokyo) as absorbent on glass plates using benzene as the eluent, and with UV and iodine vapor for visualization. IR spectra were recorded using a Hitachi Model EPI-2 IR spectrometer. NMR spectra were recorded on Hitachi Model H-60 NMR spectrometer in deuteriobenzene.

p-Chlorostyrene and p-Bromostyrene[10]: *p*-Chlorostyrene and *p*-bromostyrene were synthesized by dehydration of *p*-hals-(α-hydroxyethyl)benzene with $KHSO_4$. *p*-Chlorostyrene was obtained in yield 67.9%: bp 50.5—51 °C/2 mmHg (lit, 65 °C/4 mmHg). *p*-Bromostyrene was obtained in yield 72.7%: bp 85—85.5 °C/11 mmHg (lit, 87—88 °C/12 mmHg).

9-(p-Vinylphenyl)-9-hydroxy-9,10-dihydroanthracene (III): A solution of 2.75 g of *p*-bromostyrene in 6 ml of THF was added dropwise during 1 h to a mixture of metal magnesium ribbon (0.37 g) and 10 ml of dry THF under mild refluxing. After the magnesium had disappeared, a solution of 2.91 g of I dissolved in 60 ml of dry THF was dropped into the above Grignard reagent (IIa) solution with stirring. The mixture was refluxed for 5 h, cooled and then hydrolyzed with 24 ml of 1.5 M HCl containing ice. An organic layer was extracted with ethyl ether and evaporated to dryness. Recrystallizations with methanol, and petroleum ether-benzene (9:1) in that order, gave 1.12 g (25.1%) of III: mp 132—135 °C; IR bands at 3300 and 1150 cm^{-1} (–OH), 907 and 990 cm^{-1} ($-CH=CH_2$). Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%. Found: C, 88.16; H, 6.74%.

9-(p-Vinylphenyl)anthracene (IV) Method A): Ten grams of phosphorus pentaoxide was added to a solution of 1.12 g of III dissolved in 22 ml of carbon tetrachloride with stirring at room temperature. Stirring was continued overnight. A solution was then extracted with ethyl ether was evaporated to dryness, taken up in toluene and chromatographed over a 2.5×30 cm column containing 42 g of silica gel. Elution of the column with isopropyl alcohol gave a crude product of IV, which was recrystallized twice with isopropyl alcohol, giving 0.77 g (73.2%) of IV: mp 166—168 °C; IR bands at 910 and 995 cm^{-1} ($CH=CH_2$), NMR signals (C_6D_6, internal TMS) τ: 1.67 (s, 1 anthracene ring C-10H), 1.99—2.20 (m, 4 anthracene ring C-1, C-4, C-5, and C-8H), 2.59—2.85 (m, 8 aromatic H), 3.24 (q, 1 vinyl α-H), 4.29 (d, 1 vinyl β-H), 4.82 (d, 1 vinyl β'-H). Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75%. Found: C, 94.26; H, 5.56%.

Method B): In the method described for III, a crude solid of III which was obtained by reaction IIa with I was dissolved in anhydrous benzene containing phosphorus pentaoxide (2% by weight of the benzene) and stirred overnight at room temperature. A solution was then extracted with ethyl ether and evaporated to dryness. The residue was chromatographed as in Method A, giving a crystalline of IV in yield of 40.5% which was recrystallized with isopropyl alcohol.

Method C): In the method described for III, 15.8 g of I in anhydrous benzene (125 ml) was added dropwise to Grignard reagent (IIb) prepared from 14.7 g of *p*-chlorostyrene in THF (50 ml). To the reaction mixture was added 7.6 g of phosphrous pentaoxide in 150 ml of anhydrous benzene with stirring overnight at room temperature. Subsequently, the addition of 332 ml of hexane and filtration left 13.5 g of a solid, which was insoluble in hexane. The filtrate was evaporated to dryness, giving a crude solid of IV which gave 10.0 g (43.7%) of pure product after recrystallization with isopropyl alcohol.

References

1) See, for example, H. Mikawa and S. Kusabayashi, "Semiconductive Polymers," Kohdansha Co., Ltd., Tokyo (1977).

2) J. Cazes, *C. R. Acad. Sci.*, **247**, 1874 (1958).

3) T. Nagai and E. Funakubo, *Kogyo Kagaku Zasshi*, **64**, 1053 (1961).

4) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, **1945**, 657.

5) D. Cohen, L. T. Millar, and K. E. Richards, *J. Chem. Soc.*, **1968**, 793.

6) T. Shimizu, S. Matsuoka, S. Hattori, and K. Senda, *J. Phys. Soc. Jpn.*, **14**, 683 (1959).

7) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959).

8) S. C. Dickerman, D. D. Souza, and P. Wolf, *J. Org. Chem.*, **30**, 1981 (1965).

9) S. C. Dickerman, M. Klein, and G. B. Vermont, *J. Org. Chem.*, **29**, 3695 (1964).

10) C. S. Marvel and G. L. Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).