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The Preparation of 9-Ethynylanthracene and 9-Ethynyltriptycene and Their Oxidative Coupling

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The formation of 9,10-dichloroanthracene by reaction of 9-acetylanthracene with phosphorus pentachloride is described. 9-Ethynylanthracene and 9-ethynyltriptycene have been prepared according to Köbrich's method. The resulting ethynyl compounds have been converted to the corresponding di-ynes using the Eglinton's oxidative coupling reaction.

The treatment of methyl ketone with phosphorus pentachloride followed by dehydrochlorination using a strong base such as sodium amide in liquid ammonia is a general method of preparation of ethynyl compound. However, evolution of acetyl chloride and chlorine was observed on treatment of 9-acetylanthracene with phosphorus pentachloride. A small amount of crystalline 9, 10-dichloroanthracene could be isolated from the viscous oily reaction product. The mechanism for formation of the dichloroanthracene is not yet clear, but considering a similar reaction of anthracene with phosphorus pentachloride to give 9,10-dichloroanthracene,[1] deacetylation and subsequent chlorination seem to be caused by the catalysis of phosphorus pentachloride. The viscous oily product separated from the dichloroanthracene was treated with sodium amide in liquid ammonia. Chromatographic purification of the reaction product yielded unstable yellow crystals contaminated with some chlorine compound. The IR spectrum of the yellow crystals indicates the presence of 9-ethynylanthracene; however, it was not feasible to remove impurity containing chlorine.

Because of these difficulties, the authors adopted the method of Köbrich[2] for the preparation of 9-ethynyl compounds. As indicated in the following scheme, the reaction of 9-anthracenecarboxaldehyde (I_a) in tetrahydrofuran with chloromethylenetriphenylphosphorane (II) yielded a viscous liquid which is presumably a mixture of *cis* and *trans* isomers of the chlorovinyl compound (III_a). The dehydrochlorination of III_a by means of sodium amide in liquid ammonia yielded 9-ethynylanthracene (IV_a) in a reasonable quantity. The rather rapid decomposition of IV_a even in solution contrasts fairly strongly with the stable nature of other arylacetylene. The oxidative coupling of IV_a according to Eglinton's method resulted in 9,9′-dianthryldiacetylene (V_a) which was shown to be identical with an authentic specimen.[3] Using an analogous procedure, 9-triptycenecarboxaldehyde (I_b)[4] was converted to 9-ethynyltriptycene (IV_b). The ethynyl compound (IV_b) was found to be highly stable compound. The oxidative coupling of IV_b gave 9,9′-ditriptycyldiacetylene (V_b) in a quantitative yield as colorless cubes. The recrystallization of V_b could not be performed because of the extremely poor solubility. The material (V_b) gave satisfactory elemental analysis after digestion with a diluted hydrochloric acid. The unusual thermal stability and the extremely poor solubility seem to be attributable to the rigid and bulky cage structure of the terminal triptycene groups.

Table 1. Hypochromism of 9-substituted triptycenes
λ in nm in ethanol

Triptycene		9-Ethynyltriptycene (IV_b)		9-Formyltriptycene (I_b)	
λ	ε	λ	ε	λ	ε
197	62,900	198	59,000	198	62,500
211	64,200	210.5	63,800	212	64,300
270	3,600	269.5	2,800	270.5	2,400
278	4,900	277	3,600	278	3,000

The hypochromism of electronic spectra of triptycene derivatives substituted with electron attractive group at 9-position as compared with that of parent triptycene has been reported by Theilacker and coworkers.[5] As is shown in Table 1, the electronic spectra of I_b and

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[1] B. M. Mikhailov and M. S. Promyslov, *J. Gen. Chem. (U. S. S. R.)*, **20**, 338 (1950), [*Chem. Abstr.*, **44**, 6408 (1950)].

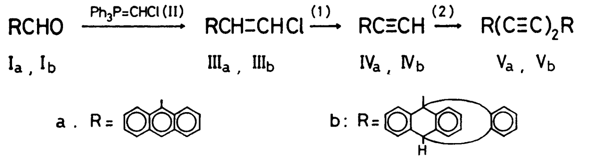
[2] G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, **89**, 689 (1966).

[3] S. Akiyama and M. Nakagawa, This Bulletin, **43**, 3561 (1970).

[4] E. C. Kornfeld, P. Barney, J. Blankley, and W. Faul, *J. Med. Chem.*, **8**, 342 (1965).

[5] W. Theilacker, K. Albrecht, and H. Uffmann, *Chem. Ber.*, **98**, 428 (1965).

$\mathrm{IV_b}$ also show a similar hypochromism in the region of 270—280 nm. However, the strong absorption bands at shorter wavelength region (190—210 nm) exhibit no hypochromism.[6]



Scheme 1. (1) $NaNH_2$/liq. NH_3; (2) $Cu(OAc)_2$/pyridine-methanol. THF=tetrahydrofuran.

Experimental

All the melting points were uncorrected. The IR and nmr spectra were obtained on a Hitachi EPI-2 and a Varian A-60 spectrometers, respectively. A Hitachi EPS-3T spectrometer was used for the electronic spectroscopy except for short-wavelength region. The spectra below 210 nm were measured on a Zeiss PMQ II, M4Q III spectrometer.[6]

Reaction of 9-Acetylanthracene with Phosphorus Pentachloride. A mixture of 9-acetylanthracene, phosphorus pentachloride, and benzene or phosphoryl chloride was heated under reflux until the evolution of gas ceased (*ca.* 1 hr). The reaction mixture was worked up in the usual manner. The yellow fine needles deposited were filtered to remove the viscous oily material and recrystallized to give pure 9,10-dichloroanthracene. As summarized in Table 2, the increase in the ratio of phosphorus pentachloride to 9-acetylanthracene increases the yield of dichloroanthracene.

Table 2. The formation of 9,10-dichloroanthracene

Run	Acetyl-anthracene A (g)	PCl_5 B(g)	B/A (molar ratio)	Solvent[a] (m*l*)	Dichloro-anthracene (g)	Yield based on A (%)
1	1.10	1.0	1	b5	0.07	6
2	1.10	2.1	2	b5	0.09	7
3	1.10	5.2	5	b5	0.17	14
4	1.10	1.0	1	p5	0.02	1
5	1.10	9.15	9	p5	0.23	19

a) b=benzene; p=phosphoryl chloride.

Attempted Synthesis of 9-Ethynylanthracene (IV_a). The viscous oily material mentioned earlier was mixed with a small amount of tetrahydrofuran and added to a suspension of sodium amide in liquid ammonia. After 3 hr, ammonium chloride was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was digested with petroleum ether and subjected to chromatography on alumina. The yellow crystals (mp 54—64°C), thus obtained, were found to be highly unstable and contaminated with chlorine compound.

9-Ethynylanthracene (IV_a). *9-(α-Chlorovinyl)anthracene (III_a)*: An ethereal solution of *n*-butyllithium (1.04N, 28.8 m*l*, 0.03 mol) was added to a suspension of chloromethyltriphenylphosphonium chloride[2] (10.70 g, 0.03 mol) over a period of 30 min at −70°C. After, 20 min, a solution of 9-formylanthracene (6.18 g, 0.03 mol) in tetrahydrofuran (100 m*l*) was added and the cooling bath was removed. The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the viscous oily residue was dissolved in benzene (180 m*l*). The benzene solution was passed through a short column of alumina (40 g). The filtrate was concentrated and the oily residue was re-dissolved in benzene (40 m*l*). The benzene solution was percolated through a layer of alumina (20 g). The light yellow liquid obtained by the concentartion of the filtrate was subjected to the following reaction.

Dehydrochlorination of III_a. A solution of the crude III_a in tetrahydrofuran (25 m*l*) was added over a period of 30 min to a suspension of sodium amide (prepared from 5 g of sodium) in liquid ammonia (200 m*l*) maintained at −65°C. After the mixture had been stirred for 4 hr, the ammonia was allowed to evaporate. A saturated solution of ammonium chloride was added to the residue under cooling with ice-water. The organic solvent and some part of water were removed under reduced pressure, and extracted with ether (200 m*l*). Concentration of the extract gave an oily material, which was dissolved in benzene (50 m*l*) and passed through a short column of alumina (20 g). The oily residue obtained by the concentation of the filtrate was repeatedly digested with petroleum ether (bp 40—60°C, total 800 m*l*). After triphenylphosphine oxide, which deposited on standing the extract, had been removed by filtration, the filtrate was passed through a thin layer of alumina (10 g) and concentrated to yield yellow crystals (3.65 g, 59% based on I_a). The crystals were re-dissolved in petroleum ether, and the chromatographic purification was repeated 3 times. The final filtrate was chilled in an ice-bath to afford IV_a as light yellow needles, mp 76—76.5°C. IV_a gave orange cuprous and yellow silver acetylides.

Found: C, 94.96; H, 5.00%. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98%. IR (KBr-disk): 3290 (-C≡CH) cm^{-1}. NMR (CCl_4): τ 6.16 (s, 1H) (C≡CH), 1.7—2.8 (m, 9H) (aromatic H). UV: $\lambda_{\max}^{n\text{-hexane}}$ (log ε) 218 (4.06), 253 (4.96), 259.5 (5.24), 343 (3.54), 360 (3.90), 379 (4.13), 400 (4.31) nm.

9-Ethynyltriptycene (IV_b). *9-(α-Chlorovinyl)triptycene (III_b)*: The reaction of 9-formyltriptycene[4] (I_b, 5.64 g, 0.02 mol) with chloromethylenetriphenylphosphorane (II) according to the analogous procedure described earlier yielded III_b as a light yellow viscous liqued. Because crystallization was unsuccessful, the liquid was subjected to the subsequent reaction.

Dehydrochlorination of III_b. The dehydrochlorination was performed according to a procedure similar to that used for III_a. The reaction product was digested with benzene (100 m*l*), and the extract was passed through a short column of alumina (15 g). The light brown liquid obtained from the filtrate was re-digested with petroleum ether (bp 60—80°C, 200 m*l*). The extract was percolated through a thin layer of alumina (5 g). The colorless crystals (3.35 g, 60% based on Ib) obtained from the filtrate were dissolved in pertoleum ether (bp 40—60°C), and the solution was passed twice through a short column of alumina to yeild colorless cubes. The crystals were recrystallized from benzene-methanol to give pure IV_b as colorless cubes, mp 222.5—223.5°C.

Found: C, 94.73; H, 5.15%. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07%. NMR (CCl_4): τ 6.77 (s, 1H) (C≡CH), 4.53 (s, 1H) (bridge head H), 1.83—2.93 (m, 12H) (aromatic H). IR (KBr-disk): 3300 (C≡CH) cm^{-1}.

9,9′-Dianthryldiacetylene (V_a). A mixture of IV_a (0.02 g, 1.1 mmol), cupric acetate monohydrate (5.0 g), pyridine (10 m*l*) and methanol (1 m*l*) was stirred for 3 hr at 50°C. The insoluble material was collected by filtration and washed with a small amount of methanol, water, and a small amount of ethanol, successively. The orange tiny cubes (0.20 g, 91%, mp 287—291°C), thus obtained, were dissolved in toluene,

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[6] The authors are indebted to Professor J. Tanaka of Nagoya University for the measurements of spectra at short wavelength.

and passed through a short column of alumina to give orange cubes, mp 290—292°C which were found to be identical with the authentic sample.[3)]

9,9'-Ditriptycyldiacetylene (V_b). The Eglinton's oxidative coupling of analytically pure IV_b (0.60 g) according to a procedure used for V_a gave colorless fine needles in a quantitative yield. The crystals were thoroughly digested with dilute hydrochloric acid to remove inorganic material, and were washed with water, and dried.

Found: C, 95.02; H, 4.81%. Calcd for $C_{44}H_{26}$: C, 95.28; H, 4.72%.

Recrystallization of V_b was infeasible owing to its extremely poor solubility in various organic solvents.