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Preparation of 9-Butadiynyltriptycene and 9,9'-Ditriptycyltetraacetylene

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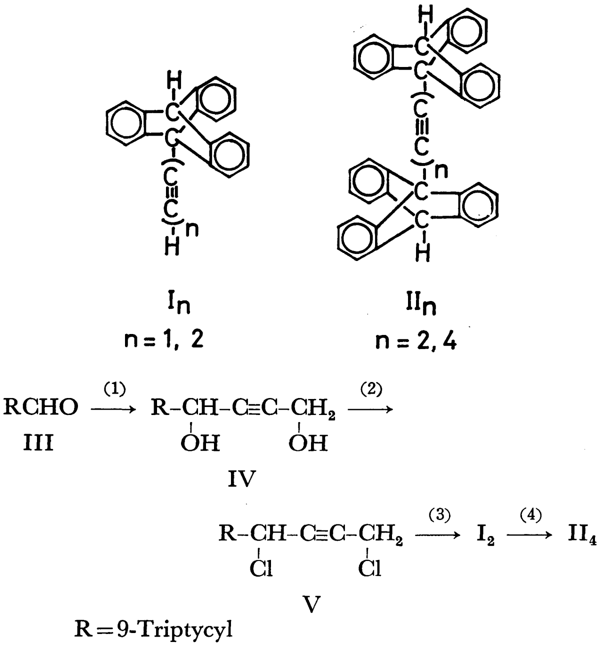
The preparation of 9-ethynyltriptycene (I_1) and 9,9'-ditriptycyldiacetylene (II_2) was given in a previous paper.[1] The present paper deals with the preparation of their higher analogues, 9-butadiynyltriptycene (I_2) and 9,9'-ditriptycyltetraacetylene (II_4), which was performed according to the following scheme.



I_n $n=1, 2$ II_n $n=2, 4$

$$\underset{\text{III}}{\text{RCHO}} \xrightarrow{(1)} \underset{\text{IV}}{\text{R-}\underset{\text{OH}}{\text{CH}}\text{-C}\equiv\text{C-}\underset{\text{OH}}{\text{CH}_2}} \xrightarrow{(2)}$$

$$\underset{\text{V}}{\text{R-}\underset{\text{Cl}}{\text{CH}}\text{-C}\equiv\text{C-}\underset{\text{Cl}}{\text{CH}_2}} \xrightarrow{(3)} I_2 \xrightarrow{(4)} II_4$$

R = 9-Triptycyl

(1): $BrMgC\equiv C\text{-}CH_2OMgBr$; (2): $SOCl_2$-pyridine; (3): $NaNH_2$ in liq. NH_3; (4): $Cu(OAc)_2$-pyridine

Scheme

9-Butadiynyltriptycene (I_2) was found to be highly stable in sharp contrast to the instability of other butadiynyl compounds such as phenanthryldiacetylene[2] and pyrenyldiacetylene.[3] The oxidative coupling of I_2 by Eglinton's method afforded highly stable and scarcely soluble II_4 in a quantitative yield. Theilacker and co-workers have pointed out that the introduction of an electron-attractive group at 9-position of triptycene nucleus causes an appreciable hypochromism of long wavelength absorption.[4] As shown in the Table, I_2 exhibits more enhanced hypochromism in a long wavelength region than I_1.[1]

The unusually high stability of I_1,[1] I_2, II_2,[1] and II_4, which can be attributed to the rigid and bulky cage structure of the triptycyl group, indicates the possibility of preparing much higher members of this class of polyacetylene. However, this seemed impracticable in view of the extremely poor solubility of II_4.

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

Triptycene		I_1		I_2	
λ	ε	λ	ε	λ	ε
197	62900	198	59000	198	62200
211	64200	210.5	63800	211	65200
270	3600	269.5	2800	270	2500
278	4900	277	3600	277.5	3200

Experimental

All the melting points were uncorrected. The IR and NMR spectra were measured with Hitachi EPI-2 and Varian A-60 spectrometers, respectively. The UV spectra were obtained on Hitachi EPS-3T and Zeiss PMQII,M4QIII spectrometers.

1-(9-Triptycyl)-2-butyne-1,4-diol (IV). To an ice-cooled solution of bis-Grignard derivative of propargyl alcohol [prepared from magnesium, 2.30 g; ethyl bromide, 10.5 g; propargyl alcohol, 2.69 g and tetrahydrofuran, 70 ml] was added over 20 min period a solution of 9-formyltriptycene[5] (III, 4.51 g, 0.061 mol) in the same solvent (150 ml). The cooling bath was then removed and the mixture was stirred overnight at room temperature. A saturated solution of ammonium chloride was added to the reaction mixture and the aqueous layer was extracted with benzene. The residue obtained by evaporating the combined organic layer *in vacuo* was mixed with benzene (30 ml) to give IV as colorless crystalline powder in a quantitative yield. A solution of IV thus obtained in tetrahydrofuran was passed through a thin layer of alumina. A small amount of benzene was added to the concentrated filtrate to yield pure IV, colorless tiny cubes, mp 284—285 °C, IR (KBr-disk): 3560—3050 (O-H), 1063, 1023 (C-O) cm^{-1}.

Found: C, 85.16; H, 5.56%. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%.

9-Butadiynyltriptycene (I_2). A solution of thionyl chloride (3.57 g, 0.03 mol) in tetrahydrofuran (5 ml) was added over a 20 min period to an ice-cooled solution of IV (3.38 g, 0.01 mol) in a mixture of pyridine (2.37 g, 0.03 mol) and tetrahydrofuran (40 ml). After the mixture had been stirred for 2 hr at 55 °C, cracked ice was added and extraction was carried out with benzene (150 ml). The extract, after being washed and dried, was concentrated under reduced pressure. A solution of the residue (crude V) in tetrahydrofuran (5 ml) was added to a solution of sodium amide [prepared from sodium, 3.0 g, 0.13 g-atom] in liquid ammonia (150 ml) at

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[1] S. Akiyama, F. Ogura, and M. Nakagawa, This Bulletin, **44**, 3443 (1971).

[2] S. Akiyama and M. Nakagawa, *ibid.*, **44**, 2237 (1971).

[3] K. Nakasuji, S. Akiyama, and M. Nakagawa, *ibid.*, **45**, 875 (1972).

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

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

-70 °C. After being stirred for 2 hr, the ammonia was allowed to evaporate. The residue was mixed with a saturated solution of ammonium chloride and the organic solvent was removed under reduced pressure. Insoluble material was collected by filtration, washed with water and dried. The material was crystallized from benzene–cyclohexane to give faint brown crystalline powder, 1.52 g (50%). A solution of crude I_2 in carbon tetrachloride was percolated through a thin layer of alumina. Concentration of the filtrate afforded colorless cubes which were recrystallized from benzine to give pure I_2, mp 189—191 °C, IR (KBr-disk): 3285 (≡C–H), 2245 (C≡C) cm^{-1}, NMR ($CDCl_3$): τ 2.25—3.08 (m, 12H, aromatic H), 4.65 (s, 1H, bridgehead H), 7.67 (s, 1H, –C≡C–H).

Found: C, 95.65; H, 4.59%. Calcd for $C_{24}H_{14}$: C, 95.33; H, 4.67%.

9,9′-Ditriptycyltetraacetylene (II_4). Treatment of analytically pure I_2 with cupric acetate monohydrate in pyridine afforded colorless tiny cubes in a quantitative yield, mp >300 °C, IR (KBr-disk): 2230 (C≡C) cm^{-1}. The crystals were digested with dilute hydrochloric acid and washed with water to remove a trace of inorganic material. Recrystallization of II_4 was found to be unfeasible on account of extremely poor solubility.

Found: C, 95.22; H, 4.38%. Calcd for $C_{48}H_{26}$: C, 95.65; H, 4.35%.