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PRELIMINARY NOTE

Synthesis of Fluoro-diacetylene Monomers: 1,4-Bis(2,4,6-Triaryloxy-difluorophenyl) Butadiynes

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SUMMARY

New fluoro-diacetylenes, 1,4-bis(2,4,6-triaryloxy-difluorophenyl)butadiynes, were prepared by nucleophilic substitution reactions on 1,4-bis(pentafluorophenyl)butadiyne, using large excesses of nucleophiles, ArOH, in DMF at room temperature and K_2CO_3 as base.

Recent work has shown that polydiacetylenes (structure A) with a linear conjugated backbone [1] are highly interesting polymers due to their unique properties involving electrical conductivity [2,3] and their use as novel organic polymers for nonlinear optical materials [4-6]. In order to obtain polydiacetylenes having π-conjugation between the polymer backbone and side groups, many symmetrical and unsymmetrical fluoro-diacetylene derivatives with polyfluoro-aromatic groups directly bound to the butadiyne moiety have been prepared [7-9]. Among them, the fluoro-diacetylenes with aryloxy groups were found to be polymerizable monomers. Polydiacetylenes with extended π-conjugation have been confirmed to have larger third order

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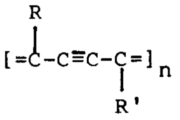
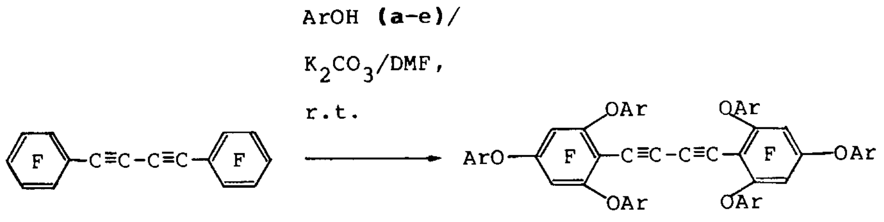
nonlinear optical susceptibilities than those without [6]. In order to enlarge the π-conjugation of polyfluorodiacetylenes further, the diacetylenes with more aryloxy groups will be suitable candidates. In this paper, we wish to report a method for the synthesis of 1,4-bis(2,4,6-triaryloxy-difluorophenyl)-butadiynes from 1,4-bis(pentafluorophenyl)butadiyne.



$$[=\overset{R}{\overset{|}{C}}-C\equiv C-\underset{R'}{\underset{|}{C}}=]_n$$

(A)

1,4-Bis(pentafluorophenyl)butadiyne **(1)** which was prepared by the method reported previously [8] reacted with aryloxides in THF at room temperature to give 1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes in high yield [8]. Further study has now shown that 1,4-bis(pentafluorophenyl)butadiyne **(1)** reacted with large excesses of such nucleophiles, ArOH **(a–e)**, in DMF at room temperature using K_2CO_3 as base to give 1,4-bis-(2,4,6-triaryloxy-difluorophenyl)butadiynes **(2a–e)** in good yield. Fluoro-diacetylenes (2a–e) were synthesized according to the procedures shown in **Scheme 1.**



1

2 a–e

2a, Ar = C_6H_5–; **2b**, Ar = 4-MeO-C_6H_4–; **2c**, Ar = 4-Me-C_6H_4–;
2d, Ar = 3,5-diMe-C_6H_3–; **2e**, Ar = 4-Br-C_6H_4–

Scheme 1.

Generally, the diacetylene monomers are colorless, whilst partially polymerized diacetylenes are either blue or red [10]. The reactivities of diacetylene monomers towards solid-state polymerization are simply determined by the color changes of the monomers upon either thermal annealing or exposure to light. We found that the diacetylenes **2b**, **2c** and **2e** partially polymerized in the solid state upon either thermal annealing or exposure to day-light to give blue crystals which were dissolved in THF to give insoluble blue polydiacetylenes. It is noteworthy that the fluoro-diacetylenes with polyaryloxy groups have higher reactivities towards solid state polymerization. The polymerization and nonlinear properties of these fluoro-diacetylenes are now under study.

TABLE 1

Synthesis of 1,4-Bis(2,4,6-triaryloxy-difluorophenyl)butadiynes **(2a-e)** from 1,4-Bis(pentafluorophenyl)butadiyne **(1)**

Diacetylene **2a-e**	Reaction time (h)	Yield[a] (%)	M.p.[b] (°C)
2a	24	92	205-206
2b	24	90	195-196
2c	24	95	209-210
2d	26	84	245-246
2e	28	85	250-251

[a] Isolated yield.

[b] Uncorrected.

Synthesis of 1,4-bis(2,4,6-triphenoxy-difluorophenyl)butadiyne **(2a)**; A typical procedure: To a stirred solution of 1,4-bis(pentafluorophenyl)butadiyne (**1**; 100mg, 0.26mmol) and K_2CO_3 (1.2 g, 8.7 mmol) in DMF (3 ml) was added phenol (**a**; 0.8 g, 8.5mmol) dropwise over a period of 10 min. After 24 h at room temperature, the mixture was diluted with aq. KOH (10 ml, 1.5M). The yellow precipitate was collected. Recrystallization from acetone-water gave white crystals of 1,4-bis(2,4,6-triphenoxy-difluorophenyl)butadiyne **(2a)** (nc) (199 mg; 92%).

M.p. 205-206°C;

IR (KBr): 1589, 1460, 1390, 1297, 1208, 1164, 1114, 1070, 1023, 989, 961, 889, 810, 759, 746, 718, 686 cm^{-1};

^1H NMR (acetone-d_6/TMS): 7.00-7.75 ppm (m, H_{arom});

^{19}F NMR (acetone-d_6/CF_3COOH): 68.33 ppm (s, F_{arom});

MS m/e 826 (M^+).

$C_{52}H_{30}F_4O_6$				
	Calc.	C 75.54	H 3.63	F 9.20
	Found	C 75.34	H 3.49	F 9.34

Diacetylenes **2d** and **2e** were purified by recrystallization from THF-water. The chemical structures of diacetylenes **2b**, **2c**, **2d** and **2e** were confirmed by IR, ^1H NMR, ^{19}F NMR and MS spectroscopies.

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