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PRELIMINARY NOTE

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

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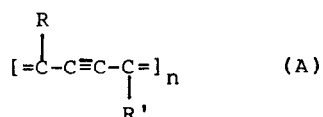
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SUMMARY

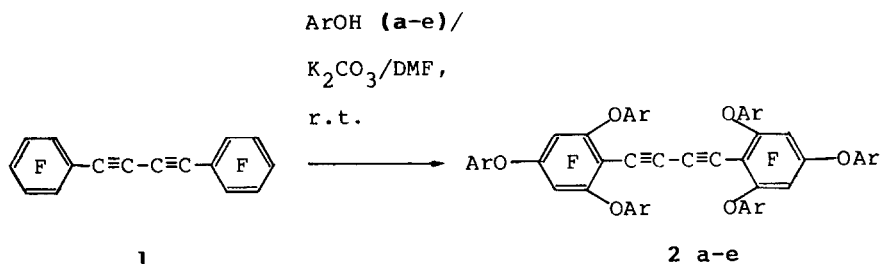
New fluoro-diacetylenes, 1,4-bis(2,4,6-triaryloxy-difluorophenyl)butadiynes, were prepared by nucleophilic substitution reactions on 1,4-bis(pentafluorophenyl)butadiyne, using large excesses of nucleophiles, ArOH, in DMF at room temperature and K_2CO_3 as base.

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

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.



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.



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 /CF₃COOH): 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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