A Convenient Synthesis of Aromatic-Ring-Substituted Diacetylenes

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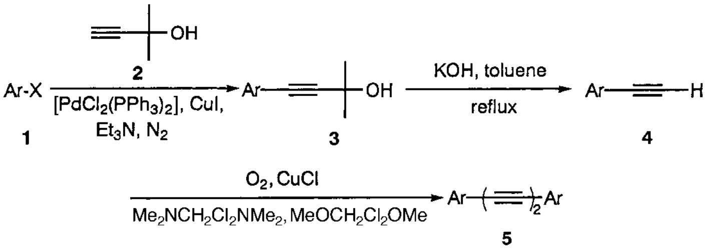
A simple and convenient way for the preparation of symmetrical diarylbutadiynes **5** with improved yields is reported (*Scheme 2*). The reaction time is drastically reduced using this method compared to previously reported procedures.

1. Introduction. – Diacetylenes have generated a lot of interest among researchers during the last two decades due to its peculiar solid-state polymerization behaviour [1][2]. One class of diacetylenes which we have been investigating consists of aryl and heteroaryl moieties directly bound to the diacetylene backbone. The preparation of such diacetylenes **5** using reported procedures involves several steps starting with aryl halide or heteroaryl halide **1** and is generally achieved *via* **3** and **4** following *Scheme 1* [3–6].

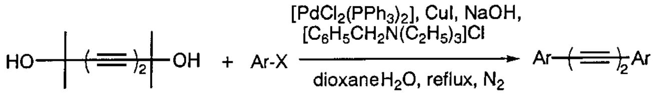
Scheme 1



The coupling reaction of aryl halide **1** with 2-methylbut-3-yn-2-ol (**2**) using the palladium catalyst [3] [$[PdCl_2(PPh_3)_2]$] gives arylalkynol **3**. Depending on the reactivity of the aryl halide, the amount of by-product, 2,7-dimethylocta-3,5-diyne-2,7-diol (**6**), varies. Thus, for thienyl halides, which are comparatively less reactive, a considerable amount of diol is formed, and consequently the yield of **3** decreases [4]. Moreover, this first step takes 5–12 h to go to completion. The next step, the cleavage of acetone, is also time-consuming. In the case of thienyl derivatives, the products **4** have to be distilled at low pressure in spite of rather low boiling points to avoid thermal polymerization. Lots of care, especially for the cooling of the condenser and receiver, has to be taken to get the distilled product, even though some of the product is lost during distillation. The final step, *i.e.*, a coupling reaction using *Hay*'s catalyst [5], is the fastest step, but the yield of the produced diacetylene is not much higher than 40% for aryl- and heteroaryl-substituted compounds. Thus, the overall yield following *Scheme 1* generally does not exceed 28% starting from **1**, while the reaction process is quite long.

We have now developed a simpler synthetic procedure to obtain symmetrically substituted aryl- and heteroaryl-diacetylenes (*Scheme 2*), a procedure which is significantly faster and involves less cumbersome workup processes, and thus is more attractive. The yields of the final products **5** are higher than those obtained *via* the reactions of *Scheme 1*. There are previous reports on the synthesis of alkynes using similar reagents as ours. One of them deals with the synthesis of diarylalkynes starting from aryl halides [7], while the other one describes the preparation of unsymmetrical diarylbutadiynes starting from arylhexadiynols [8]. However, they are not intended for the preparation of symmetrical diacetylenes by a simple procedure.

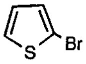
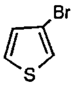
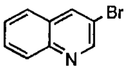
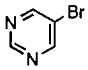
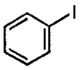
Scheme 2



6 **1** **5**

2. Results and Discussion. – According to *Scheme 2*, we coupled a variety of aryl halides **1** quite efficiently with 2,7-dimethylocta-3,5-diyne-2,7-diol (**6**) (*Table*), the latter being obtained almost quantitatively from **2** within 3 h (see *Exper. Part*). Thus, reaction of **6** with 2 mol-equiv. of **1** in refluxing dioxane in the presence of benzyltrimethylammonium chloride as phase-transfer catalyst, aqueous NaOH solution as base, and a mixture of dichlorobis(triphenylphosphine)palladium(II), and copper(I) iodide as catalyst furnished diacetylenes **5**.

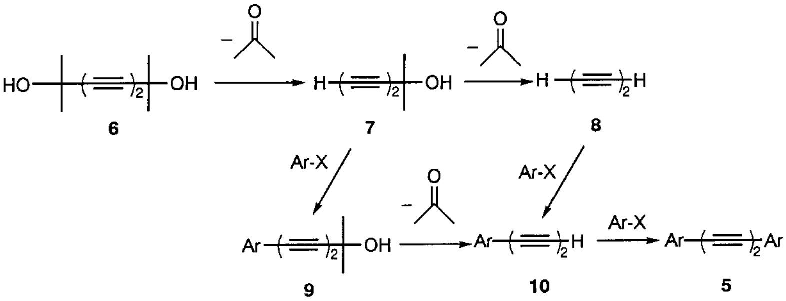
Table. *Reaction Times and Yields for the Transformation* **6** → **5**, *and Melting Points of the Diacetylenes* **5**

Entry	Ar–X (**1**)	Reaction time [min]	Yield [%] of **5**	M.p. [°] of **5**	
				measured	reported
a		90	45	89	88–89 [9]
b		90	44	111	111.5–112.5 [10]
c		120	47	228	227 [11]
d		60	46	171[a])	–[b])
e		60	47	87	87–88 [13]

[a]) Started to sublime at this point. [b]) M.p. was not reported.

The proposed pathway for the reaction process first involves loss of acetone from the diol **6** to give alcohol **7** which can react with the aryl halide yielding aryl alcohol **9** (*Scheme 3*). After a similar cleavage of acetone, **9** is then converted *via* **10** to butadiyne **5**. The intermediates **9** and **10** could be detected in the reaction mixture, suggesting that the reaction proceeds *via* the proposed pathway producing **7** at first. The alternative process from **6** to **10** or **5** *via* **8**, with **8** reacting with the aryl halide, cannot be excluded. However, butadiyne **8** may leave the mixture before reaction because of its low boiling point (estimated 10–20°/760 Torr) [9].

Scheme 3



By-product formation was negligible, and in some cases, the starting material **1** did not react completely, but the unreacted portion could be recovered in such cases. Therefore, the production of **8** is considered to be the main reason for a reduction of the yield of **5**. Nevertheless, the yield of **5** [10–14] starting from **2** *via* **6** was in the range of 38–42% which is significantly higher than that from the previously reported process (*Scheme 1*). Inert atmosphere was absolutely necessary for the reaction **6** → **5** to proceed, and all the reagents had to be purged with N_2 before use.

In conclusion, we have developed a convenient, efficient, and general method for the preparation of symmetrical diarylbutadiynes starting from the corresponding aryl halides and 2,7-dimethylocta-3,5-diyne-2,7-diol.

Experimental Part

2,7-Dimethylocta-3,5-diyne-2,7-diol (**6**). Through a mixture of CuCl (4 g), NH_4Cl (15 g), H_2O (45 ml), and 2-methylbut-3-yn-2-ol (**2**; 0.35 mol), oxygen was bubbled under vigorous stirring. The soln. gradually became warm. After 45 min, more **2** (0.35 mol) was added, and finally, the last portion of **2** (0.35 mol) was added after 90 min. The end of the reaction was indicated by a distinct change of color. The mixture was cooled to *ca.* 20°, and 36% aq. HCl soln. (10 ml) was added while stirring. The mixture was extracted several times with THF, the THF layer dried (Na_2SO_4) and evaporated, and the crude recrystallized from hexane/AcOEt at *ca.* 10°: three crops of needle-shaped colorless crystals. Yield of **6** about quant. M.p. 129° ([9]: 129°–130°).

Diacetylenes **5**: *General Procedure.* A mixture of dichlorobis(triphenylphosphine)palladium(II) (0.07 g, 0.1 mmol), CuI (0.02 g, 0.1 mmol), and benzyltriethylammonium chloride (0.02 g, 0.1 mmol) was flushed with N_2. Separately, **6** (0.166 g, 1 mmol) and aryl halide (2 mmol) in dioxane (5 ml) were purged with N_2 for 15 min. This soln. was then rapidly added to the mixture $[PdCl_2(PPh)_3]/CuI/(PhCH_2NEt_3)Cl$, followed by 5.5N NaOH (2.5 ml) which was added by syringe. The resulting soln. was refluxed under N_2 (TLC monitoring). Upon completion, a sat. NH_4Cl soln. (5 ml) was added, the mixture stirred for *ca.* 30 min at r. t. and then extracted with Et_2O (3 ×). The extract was dried (Na_2SO_4) and evaporated, and the crude product submitted to column chromatography (silica gel, hexane/AcOEt): pure **5**. Yields and data of *2,2′-(buta-1,3-diyne-1,4-diyl)bis[thio-*

phene] (**5a**), *3,3′-(buta-1,3-diyne-1,4-diyl)bis[thiophene]* (**5b**), *3,3′-(buta-1,3-diyne-1,4-diyl)bis[quinoline]* (**5c**), *5,5′-(buta-1,3-diyne-1,4-diyl)bis[pyrimidine]* (**5d**), and *1,1′-(buta-1,3-diyne-1,4-diyl)bis[benzene]* (**5e**): *Table.*

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REFERENCES

[1] 'Polydiacetylenes', Eds. D. Bloor and R. R. Chance, NATO ASI Series, Series E, Applied Sciences No. 102, Martinus Nijhoff, Dordrecht, **1984**.

[2] S. Okada, H. Nakanishi, in 'Polymeric Materials Encyclopedia', Ed. J. C. Salamone, CRC Press, Boca Raton, **1996**, pp. 8393.

[3] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467.

[4] A. Sarkar, P. Sekher, M. B. Kamath, L. P. Bhagwat, K. N. Babu, K. Rajalakshmi, S. S. Talwar, *Indian. J. Chem.*, *Sect. B* **1991**, *30*, 360.

[5] A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320.

[6] A. Vaitiekunas, F. F. Nord, *J. Am. Chem. Soc.* **1954**, *76*, 2733; U. Fritzsche, S. Hünig, *Tetrahedron Lett.* **1972**, *13*, 4831.

[7] A. Caprita, A. Lessi, R. Rossi, *Synthesis* **1984**, 571.

[8] S. A. Nye, K. T. Potts, *Synthesis* **1988**, 375.

[9] L. Brandsma, 'Preparative Acetylenic Chemistry', Elsevier, Amsterdam, 1st edn., 1971.

[10] A. F. Garito, C. C. Teng, K. Y. Wong, O. K. Zhamani, *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 219.

[11] J. L. Buttler, M. Gordon, *J. Heterocycl. Chem.* **1975**, *12*, 1015.

[12] A. Sarkar, K. N. Babu, M. B. Kamath, P. K. Khandelwal, L. P. Bhagwat, S. S. Talwar, in 'Frontiers of Polymer Research', Eds. P. N. Prasad, J. K. Nigam, Plenum, New York, **1991**, p 233.

[13] W. H. Kim, N. B. Kodali, J. Kumar, S. K. Tripathy, *Macromolecules* **1994**, *27*, 1819.

[14] J. B. Armitage, N. Entwistle, E. R. H. Jones, M. C. Whiting, *J. Chem. Soc.* **1954**, 147.

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