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Sandeep Kumar [a]

[a] Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore, 560 013, India

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A Simple, Rapid, One-Step Synthesis of Aryl Poly Ethers from Aryl Acetates: Improved Synthesis of Hexaalkoxytricycloquinazoline Derivatives

SANDEEP KUMAR

Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore-560 013, India

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Aryl acetates when heated with alkyl halide in DMSO in the presence of powdered KOH undergo alkylation giving aryl ethers in high yields. Several hexasubstituted tricycloquinazoline and hexasubstituted triphenylene discotic liquid crystals were prepared conveniently from their acetates. Though better direct synthetic methods are available for the synthesis of alkoxy triphenylenes, this method is more efficacious in the case of tricycloquinazoline derivatives and results in several-fold increase in yield.

Keywords: Discotic liquid crystals; aryl ethers; tricycloquinazoline; triphenylene

A large proportion of discotic liquid crystals [1] as well as smectic liquid crystals [2] are poly phenylethers. In the course of our work on the synthesis of discotic liquid crystals, we often faced the problem of clean etherification of poly phenols in good yield. These materials are generally synthesized by the classical methods of etherification using phenols and alkyl halides in the presence of base. Several methods of the preparation of aryl ethers have already been surveyed in text books and reviews [3, 4].

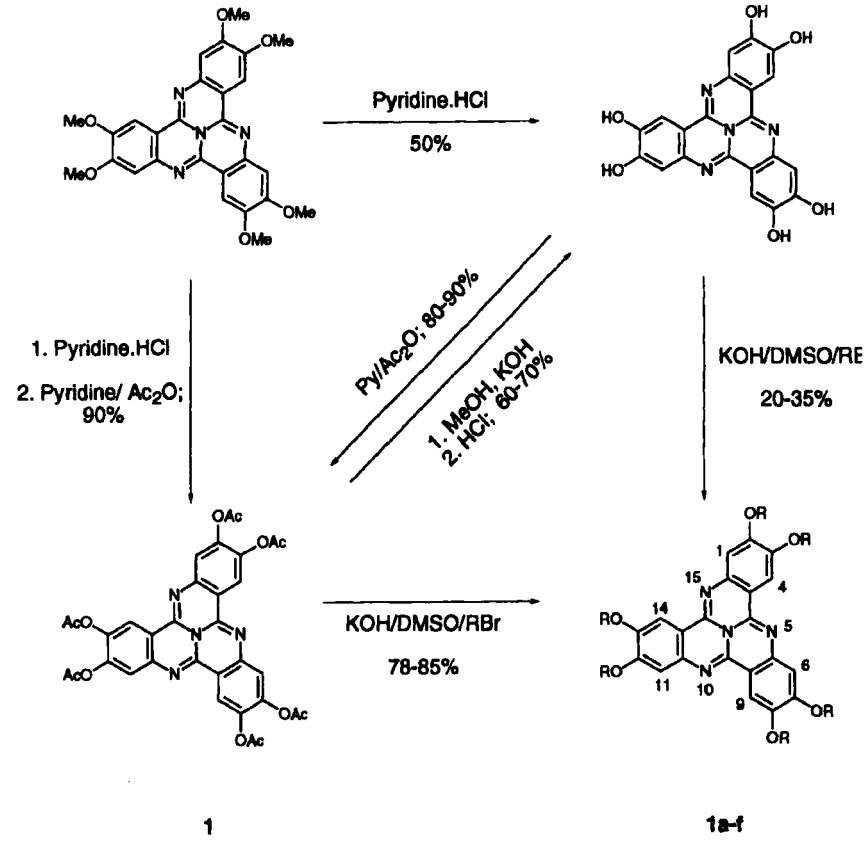
Polymethoxyarenes have been commonly used as precursors for the synthesis of poly ether discogens because aromatic methoxy groups may be easily cleaved to give the corresponding phenols, and the latter are conveniently

alkylated with alkyl halides (Scheme 1). For example hexamethoxy-tricycloquinazoline [5], hexamethoxytriphenylene [6], hexamethoxytruxene [7] have been employed as precursors in the synthesis of various tricycloquinazoline (TCQ), triphenylene and truxene mesogens. These poly phenols are very sensitive to air oxidation and cannot be stored for a long time. The yields of arylpolyethers depend upon the purity of these poly phenols and often very low. Further, because of the partial oxidation and alkylation of phenols, the purification of the products is extremely difficult. In the case of the synthesis of tricycloquinazoline hexaethers we sometimes observed less than 5% yield if stored hexahydroxytricycloquinazoline was used. To overcome this problem, hexaphenols were stored in protected form as acetates and subsequently hydrolyzed back to phenols prior to use. These protection and deprotection steps are wasteful and result in overall poor yields.

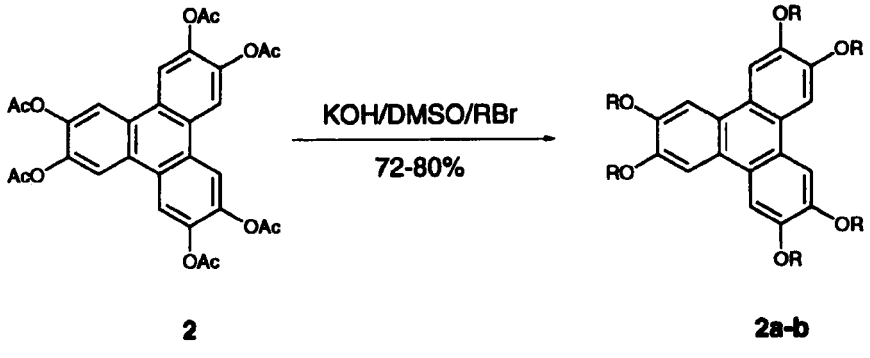
Newer synthetic methods involving phase transfer catalysts for the preparation of phenyl ethers from phenyl acetates have been developed [8]. However, alkylation is rapid and high yielding only with highly reactive halides such as allyl, prenyl or benzyl halides. With normal halides even if using reactive short chain iodides like methyl or ethyl iodides, yields are only moderate and need long reaction time.

We now wish to report a convenient, rapid, high yielding method of synthesis of aryl ethers directly from aryl acetates using potassium hydroxide in dimethylsulfoxide. We have earlier reported the synthesis of homologous 2,3,7,8,12,13-hexaalkoxy and hexathioalkoxy tricycloquinazoline derivatives in low yield [5, 9]. TCQ discotics have recently received increasing attention and the first organic one-dimensional n-conducting discotic liquid crystal based on TCQ has been reported very recently [10]. For various physical studies we were in need of a good amount of pure TCQ derivatives and we achieved this by an improvement in our earlier synthetic method. In a typical procedure, powdered KOH (24 mmol) was mixed with DMSO (5 ml) and stirred at room temperature for 10 min. One mmol of hexaacetoxytricycloquinazoline **1** (Scheme 1) was added followed by alkyl bromide (24 mmol). The reaction mixture was stirred for 4 hr. at 55°C and then worked up by addition of water and extraction with diethyl ether. The crude product was purified by column chromatography over silica gel eluting with hexane-ethyl acetate. Products were characterized by direct comparison with authentic samples as well as by spectral analysis. Similarly different triphynelene derivatives were also prepared from hexaacetoxytriphenylene **2** as shown in Scheme 2. Yields with different alkyl halides are given in Table I.

Better direct synthetic methods are now available for the synthesis of triphenylenes ethers [11–14] but for many other poly ethers such direct



Scheme 1



Scheme 2

TABLE I Alkylation of Arylacetates

Entry	*Hexaacetate*	*Alkyl Bromide*	*Time*	*Product*	*Yield %*
1	1	$CH_3(CH_2)_2CH_2Br$	4hr	1a	85
2	1	$CH_3(CH_2)_3CH_2Br$	4hr	1b	83
3	1	$CH_3(CH_2)_4CH_2Br$	4hr	1c	80
4	1	$CH_3(CH_2)_6CH_2Br$	4hr	1d	80
5	1	$CH_3(CH_2)_7CH_2Br$	4hr	1e	78
6	1	$H_2C=CH(CH_2)_8CH_2Br$	3hr	1f	74
7	2	$CH_3(CH_2)_2CH_2Br$	4hr	2a	74
8	2	$CH_3(CH_2)_4CH_2Br$	4hr	2b	72
9	2	$CH_3(CH_2)_4CH_2Br$	15hr	2b	80

synthesis are not known and these materials are still prepared by the alkylation of corresponding phenols in low to moderate yield. Further, to prepare polymerizable amphiphilic triphenylene derivatives [15], alkylation of functionalized triphenylenes [15, 16] resulted only in poor to moderate yields depending upon the stability of polyphenols [15]. The alkylation of triphenylene hexaacetate with alkyl bromide was also reported [17] earlier and resulted in the isolation of 6% of hexaalkoxy triphenylene, 26% of pentaalkoxy monoacetate and 7% of tetraalkoxy diacetate. In the case of TCQ we achieved more than 70% over all yield of hexaalkoxy TCQ from hexamethoxy TCQ in comparison to about 10% by the best known method.

It is worth mentioning that neither dry solvent nor especially anhydrous reaction conditions were used. As can be seen from Table I, alkylation of arylacetates completed in a short period under mild condition results in high yields with different bromides. A minor increase in the yield was observed on increasing the reaction time (entry 8 and 9).

This method allows one to prepare aryl ethers from aryl acetates in high yields without the use of special dry conditions and catalysts. It may find uses not only in the field of liquid crystals but also in the synthesis of several natural products.

EXPERIMENTAL

General Information

Chemicals and solvents (AR quality) were obtained from E. Merck and used as such without any purification. Column chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 70–230 mesh). Thinlayer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). NMR spectra were measured in deuteriochloroform

on a Bruker 400 or 200 MHz NMR spectrometer. All chemical shifts are reported in δ units downfield from Me_4Si, and J values are given in Hz.

Synthesis of Hexaacetoxy TCQ, 1

Concentrated HCl (22 ml) was added to pyridine (20 ml) with rapid stirring and the mixture was heated to 220°C to remove water. The resultant molten salt was cooled to 140°C, hexamethoxy-TCQ (1 g, 2 mmol) was added and the mixture was heated to 230 °C for 3 h and then cooled to 100 °C. An excess of dry pyridine (10 ml) followed by acetic anhydride (5 ml) was added and the reaction mixture was left at room temperature for 48 h under inert condition. Ice-water was added and the resultant dark green precipitate was collected by filtration, washed with water and with excess of methanol, and dried under vacuum to yield **1** (1.2 g, 90%). 1H NMR ($CDCl_3$): 8.21 (s, 3H, ArH-4, 9,14), 7.35 (s, 3H, ArH-1, 6, 11), 2.34 (s, 18H, $-COCH_3$).

Synthesis of Hexaalkoxy TCQ, 1f

Powdered KOH (135 mg, 2.4 mmol) was mixed with DMSO (2 ml) at room temperature and stirred for 10 min. Hexaactoxy-TCQ (66.8 mg, 0.1 mmol) followed by 11-bromo-1-undecene (560 mg, 2.4 mmol) was added and the reaction mixture was stirred at 55°C for 3 h and then worked up by adding ice-water and extraction with diethyl ether. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate; 9:1) and crystallize with ethyl acetate to afford 98 mg, 74% of 1f in the form of yellow solid. 1H NMR ($CDCl_3$): 7.69 (s,3H,ArH-4,9,14), 6.88 (s,3H,ArH-1,6,11), 5.8 (m,6H,-$C\underline{H}=CH_2$), 4.95 (m,12H,-$CH=C\underline{H}_2$), 4.13 (t,6H,J = 6.4,-OCH_2), 4.09 (t,6H,J = 6.4,-OCH_2), 2.0 (m,12H,-$C\underline{H}_2CH$-), 1.85 (m,12H,-$OCH_2C\underline{H}_2$), 1.3 (s(br),72H,-CH_2). All other derivatives were prepared using the same procedure.

1c: 1H NMR ($CDCl_3$): 7.69 (s,3H,ArH-4,9,14), 6.88 (s,3H,ArH-1,6,11), 4.14 (t,6H,J = 6.5,-OCH_2), 4.10 (t,6H,J = 6.5,-OCH_2), 1.89 (m,12H,-$OCH_2C\underline{H}_2$), 1.2–1.5 (m,36H,-CH_2), 0.90 (t,18H,J = 6.6,-CH_3).

1d: 1H NMR ($CDCl_3$): 7.71 (s,3H,ArH-4,9,14), 6.90 (s,3H,Ar H-1,6,11), 4.13 (t,12H,J = 6.3,-OCH_2), 1.90 (m,12H,-$OCH_2C\underline{H}_2$), 1.30–1.58 (m,60H,-CH_2), 0.89 (t,18H,J = 6.6,-CH_3).

Thermal Behaviour

Phase transition temperature and enthalpy measurements were carried out on 2–3 mg samples using a Perkin-Elmer DSC7 with heating and cooling

rate of 10°C/min. K = crystal, D = columnar and I = isotropic transition. Peak temperatures are given in °C and the number in parentheses indicate the enthalpy difference (ΔH) of transition (k cal/mol). **1a** [5] (Ist heating): K-K 131.6°C (1.8), K-D 239.2°C (3.7), D-I 312.7°C (0.5). **1b** [5] (Ist heating): K-K 138.2°C (1.1), K-D 184.7°C (2.6), D-I 299.2°C (1.1). **1c** (IInd heating): K-D 134.6°C (2.0), D-I 276.1°C (1.8). **1d** (IInd heating): K-D 99.3°C (2.7), D-I 248.7°C (1.9). **1e** [5] (Ist heating): K-D 79.6°C (8.5), D-I 237°C (1.5). **1f** (IInd heating): K-D 55.9°C (9.2), D-D 100.4°C (0.11), D-I 198.7°C (1.7).

Synthesis of Hexahexyloxytriphenylene 2b

Powdered KOH (1.35 g, 24 mmol) was mixed with DMSO (10 ml) at room temperature and stirred for 10 min. Hexaactoxytriphenylene [17] (576 mg, 1 mmol) followed by 1-bromohexane (3.9 g, 24 mmol) was added and the reaction mixture was stirred at 55°C for 15 h and then worked up by adding ice-water and extraction with diethyl ether. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate; 9.5 : 0.5) and crystallized with ethyl acetate-hexane to afford 660 mg, 80% of 2b in the form of white needles.

Thermal Behaviour

2a [18] (Ist heating): K-D 89.3°C (5.6), D-I 145.3°C (4.3). **2b** [18] (Ist heating): K-D 68.8°C (9.2), D-I 99.7°C (1.13).

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References

[1] For a brief review of discotics see S. Chandrasekhar, *Liq. Cryst.*, **14**, 3 (1993).
[2] G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals* (Springer-Verlag, 1988), E. B. Priestley, P. J. Wojtowicz and P. Sheng, eds., *Introduction to Liquid Crystals* (Plenum Press, 1974), H. Kelker and R. Hatz, *Hand Book of Liquid Crystals* (Verlag Chemie, 1980), G. W. Gray, *Thermotropic Liquid Crystals* (J. Wiley & Sons, 1987).
[3] J. March, *Advanced Organic Chemistry*, (J. Wiley & Sons, 1992).
[4] S. Patai, *The Chemistry of Ether Linkage* (Wiley-Interscience, 1967).
[5] S. Kumar, E. J. Wachtel and E. Keinan, *J. Org. Chem.*, **58**, 3821 (1993).
[6] J. Billard, J. C. Dubois, N. H. Tinh and A. Zann, *Nouv. J. Chim.*, **2**, 535 (1978), C. Destrade, M. C. Mondon and J. Malthete, *J. DePhys. Colloque C3, Suppl.au n°4*, **40**, C3–17 (1979).

[7] C. Destrade, J. Malthete, N. H. Tinh and H. Gasparoux, *Phys. Lett.*, **78A**, 82 (1980), W. K. Lee, B. A. Wintner, E. Fontes and P. A. Heiney, *Liq. Cryst.*, **4**, 87 (1989).
[8] S. K. Benerjee, B. D. Gupta and K. Singh, *J. Chem. Soc. Chem. Commun.*, 815 (1982).
[9] E. Keinan, S. Kumar, S. P. Singh, R. Girlando and E. J. Wachtel, *Liq. Cryst.*, **11**, 157 (1993).
[10] N. Boden, R. C. Borner, R. J. Bushby and J. Clements, *J. Am. Chem. Soc.*, **116**, 10807 (1994).
[11] N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge and M. V. Jesuadson, *Liq. Cryst.*, **15**, 851 (1993).
[12] N. Boden, R. J. Bushby and A. N. Cammidge, *J. Chem. Soc., Chem. Commun.*, 465 (1994).
[13] H. Naarmann, M. Hanack and R. Mattmer, *Synthesis*, 477 (1994).
[14] N. Boden, R. J. Bushby, A. N. Cammidge and G. Headdock, *Synthesis*, 31 (1995).
[15] F. Closs, L. Häussling, P. Henderson, H. Ringsdorf and P. Schuhmacher, *J. Chem. Soc., Perkin Trans. I*, 829 (1995).
[16] S. Kumar, P. Schuhmacher, P. Henderson, J. Rego and H. Ringsdorf, *Mol. Cryst. Liq. Cryst.*, (1996, in press).
[17] W. Kreuder and H. Ringsdorf, *Makromol. Chem. Rapid Commun.*, **4**, 807 (1983).
[18] C. Destrade, N. H. Tinh, H. Gasparoux, J. Malthete and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, **71**, 111 (1981).