Anionic sigmatropic-electrocyclic-Chugaev cascades: accessing 12-aryl-5-(methylthiocarbonylthio)tetracenes and a related anthra[2,3-b]thiophene

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Abstract

1,4-Diols resulting from the double addition of ArCCLi (Ar = Ph, substituted phenyl, 2-thienyl) to ortho-C₆H₄(CHO)₂ undergo cascades to tetracenes on simple admixture of LiHDMS, CS₂ and MeI. Acene formation proceeds by [3,3]-sigmatropic rearrangement of xanthate anions followed by 6π electrocyclisations. The reactions are terminated by E2 or anionic Chugaev-type eliminations. Structural packing motifs and electronic properties are reported for the tetracenes.

Introduction

In recent years polyacenes, especially tetra- and pentacenes, have been in the vanguard of new field effect and other organic electronic based devices [1,2]. Although the simple parent acenes have useful device characteristics in their own right, it is often desirable to be able to tune this performance by use of suitable substituted variants [3,4]. Unfortunately, attaining such derivatives rapidly through simple chemistry is often problematic [5,6]. Cross-coupling approaches (formally an excellent approach for acene library preparation) [7-13] are often hindered by the insolvency, or poor availability, of the parent haloacenes. Conversely, stepwise synthesis of a family of acene derivatives from various acyclic precursors is normally very step intensive. The prevalence of these issues in the synthesis of substituted tetracenes caused Lin [14], building on the anthracene natural product work of Saá [15], to introduce a 1,2-bisallene cascade approach for rapid access to tetracene sulfoxides in 2007 (Scheme 1).

In 2012 Liu used a Pd-based strategy to provide 12-substituted 5-aryltetracenes [after final trapping with RB(OH)₂)] [16]. Both of these reactions rely on the formation of bis-allenes 2, attained by Lin through 2,3-sigmatropic rearrangement of 1a [14] or by Sₛ₂'²' carbonate displacement in 1b by Pd⁰(PPh₃)₃ in Liu’s case [16]. To circumvent reversibility of these pericyclic annulation
strategies Lin relied on PhSOH elimination while Liu relied on ubiquitous palladium β-hydride steps leading to tetracenes 3 and 4. We are interested in very efficient routes to tetracene derivatives containing one or more thiolate (SH) groups for the use in highly electrically conducting organics. In this regard we were attracted by a single result in the early literature [17] showing that traces of allenes related to 2 (X = SCOSMe) were accessible via nominal [3,3]-sigmatropic rearrangements of xanthates. As the thiocarbamate products derived from these are predicted to be easily hydrolysed to thiolates this potentially offers a simple route to a protected SH analogue of 3. Lin’s chemistry [14] cannot be used as no simple method to modify SOPh to SH is available. We proposed that use of starting material xanthate 1c should provide suitably protected 5-thiotetracene derivatives directly (Scheme 2).

The required [3,3]-sigmatropic rearrangements and subsequent 6π electrocyclosations of 1c have precise stereochemical requirements (Scheme 2). Only the meso diastereomer of 1c is predicted by Woodward–Hoffman analyses [18] to deliver anti-6 that is required for facile E2 elimination leading to the desired tetracene 7 under thermal conditions. However, the initially required 1c are typically attained as ca. 1:1 rac/meso mixtures and this might be expected to limit the potential yield of 7 to only 50% under simple heating (in the absence of other factors).

Houk has demonstrated that both electronic donor or acceptor and steric effects favour placing the larger/most electronically biased substituent ‘outwards’ in disrotatory 6π processes [19]. This might also depopulate 5 limiting the final yield of 7. However, the following factors suggested to us the viability of Scheme 2: (i) traces of allenes have been observed when preparing xanthates from propargylic alcohols [17]; (ii) the relative van der Waals volumes of SOPh, Ph, CS₂⁻ and C(=S)SMe (104.2, 76.9, 63.4, and 82.0 Å³, respectively [20]) and related electronic properties [σ(SOMe) +0.52, σ(Ph) +0.06, σ(SCOMe) +0.39 [21]] and the work of Lin [14] suggest that significant populations of intermediate 5, with ‘inward Ph’ should be

Scheme 1: Use of bis-allene intermediates 2 for rapid access to substituted tetracenes [14,16].

Scheme 2: Proposed access to aryl substituted 5-thiolatotetracene derivatives.
accessible; (iii) even if a rac-diol is used in the cascade, the possibility of aromatisation of 6 through Chugaev [22] syn elimination. Finally the system of Scheme 2 provides a unique opportunity to probe if these rearrangements do indeed proceed from the neutral xanthates 1c or via the previously unprecedented 1d–2d–6d anionic cascades.

Results and Discussion

Investigation of the chemistry of Scheme 2 commenced with the preparation of the required diols 8 through simple acetylide addition to o-phthalaldehyde (60–91% yield, see Supporting Information File 1). All of the additions proceeded in high yield, but under all conditions tried, no strong bias to either the rac or meso diastereomer could be realised. The meso enriched diastereomer of 8a could be realised by treating rac/meso mixtures of bis-lithium alkoxide of 8a with freshly prepared anhydrous NBu4F (2 equivalents) [23] (Scheme 3). Acid quench of the resultant purple dianion leads to ca. 5:1 meso:rac 8a. We assign this transformation to an equilibrium between dialkoxide 9 and the benzylic anion 10. Intramolecular proton delivery via cyclic transition state 11 is proposed to favour the meso diastereomer prior to protonic quench. Samples of rac enriched 8a were prepared from Sonogashira coupling of anti enriched 8j. The latter could be prepared directly from o-bromobenzaldehyde as shown (Scheme 3) with ca. 1:7 syn:anti enrichment by recrystallisation from CHCl3. The enantiotopic ArCH signals of rac-8a are split into separate signals upon treatment with Eu(facam)3 confirming it to be the C3 chiral diastereomer while no equivalent splitting in 1H NMR samples of 8a prepared from purple 11 (in line with it being the meso diastereomer). These assignments are in line with the finding of Saá [15]. The chemical shifts of the methine CH/OH proton in rac-8a (δH 6.20) and meso-8a (δH 6.33) reflect an equivalent trend in diols 8b–f where two distinct sets of equivalent signals are seen δH 6.14–6.20 and δH 6.23–6.35. On this basis we assign the higher chemical shift signal to the meso diastereomer.

Cascade optimisation (Table 1) was carried out using 8a in THF unless otherwise stated. Typically diol 8a (ca. 1:1 rac/meso) was deprotonated at an initial low temperature (T1), then treated sequentially with CS2 and MeI before finally being brought to a second higher temperature (T2) to facilitate aromatisation leading to 7a (see Supporting Information File 1 for full optimisation details). Simply allowing –78 °C solutions of the dialkoxide to warm slowly to ambient temperature in the presence of excess CS2 and MeI provided small amounts of tetracene 7a (Table 1, run 1). Formation of the xanthate is favoured at –30 °C but this is slowed at –50 °C (Table 1, runs 2 and 3). The IR νmax [cm⁻¹] (rac-1c: 1035; meso-1c: 1036) of run 2 are consistent with the isolation of xanthate [17].

Table 1: Optimisation of yield of tetracene 7a.  

| Run | Base     | rac.meso  | T1 [°C] | T2 [°C] | 1c [%] | 7a [%]  |
|-----|----------|-----------|---------|---------|--------|---------|
| 1   | NaH      | 1:1.1     | ~78     | 22      | 23     | 9       |
| 2   | NaH      | 1:1.1     | ~30     | 40      | 95     | –       |
| 3   | NaH      | 1:1.1     | ~50     | 40      | 45     | 30      |
| 4   | NaH      | 1:1.1     | 0       | 60      | 30     | 43      |
| 5   | LiHDMS   | 1:1.1     | ~50     | 40      | 39     | 38      |
| 6   | LiHDMS   | 1:1.1     | 0       | 60      | 30b    | 60      |
| 7   | KHDMs    | 1:1.1     | 0       | 60      | 9      | 50      |
| 8   | LiHDMS   | 1:4       | 0       | 60      | 5b     | 38      |
| 9   | LiHDMS   | 8:1       | 0       | 60      | 5b     | 89      |

*aUsing 8a (0.45 mmol) in THF (5.0 mL), with base (2.0 equiv), CS2 (3.0 equiv), MeI (8.0 equiv), see Supporting Information File 1 for details. Determined by NMR spectroscopy. †Isolated yields, except where noted.

Scheme 3: Equilibration to meso species.
All attempts to convert the neutral xanthate 1c (either rac or meso) from Table 1, run 2) to tetracene 7a under thermal or photochemical conditions failed. Either 1c was recovered, or it slowly decomposed under forcing conditions (>200 °C; or 180–365 nm Hg lamp). Exceptionally, traces of 7a were detected in reactions electro-catalysed by Bauld’s catalyst (tris(4-bromophenyl)ammoniumyl hexachloroantimonate) [24] at 25 °C but these showed very poor chemoselectivity. Conversely, rapid one-pot heating of a mixture of all the reaction components maximises the yield of 7a (Table 1, runs 3–6). These results very strongly suggest unprecedented anionic [3,3]-sigmatropic rearrangement starting from 1d; another addition to the body of evidence for the importance of charge upon sigmatropic rearrangements [25,26]. In the subsequent cascade the second 6π electrocyclisation appears rate limiting. The yield of 7a in run 6 (60%) indicates conversion via syn-6d (unprecedented anionic Chugaev elimination) is possible to some extent.

If only E2 termination of the cascade was possible (i.e., via anti-6) a maximum yield of 52% 7a should be realised from the 1:1 rac:meso sample of 8a used. This idea is strongly supported by runs 8 and 9 and the observation that replacing MeI with other alkylating agents (EtBr, BnBr) resulted in only traces of tetracenes. Of the bases screened (see Supporting Information File 1), LiHDMS was superior, only its potassium analogue gave comparable performance (Table 1, run 7).

In all reactions of Table 2 there is some unrecovered material. One common byproduct is an intensely red compound detected at high $R_f$ (0.82, 4:1 pentane/CH2Cl2) in TLC analyses conducted under argon. The very high air sensitivity of this compound prevents its characterisation but it is tentatively ascribed to a mixture (12, Scheme 4) of hydroquinone and its monomethylether on the basis of partial 1H NMR spectrum and ESI mass spectra.

The poorly performing runs of Table 1 also show a broad isolable red band ($R_f$ ca. 0.18, 4:1 pentane/CH2Cl2) whose 1H and 13C NMR and MS data were intractable. For example, the 1H NMR spectrum shows only a broad envelope of signals at δH 7.95–7.20; a number of very similar isomeric species seem to be present. To cast light on these issues model alcohol 13 was treated with NaH/CS2/Mel at −78 °C and the mixture allowed to come to ambient temperature. This resulted in the smooth formation of allene 14. In particular, the presence of allenic and C=O signals in the 13C NMR spectrum at 212.1 and 188.5 ppm and the absence of any alkyne C≡C resonances in the region δC 80–90 are indicative of this transformation. All attempts to isolate 14 resulted only in the rapid formation of red oils whose mass spectra show molecular ions at (14)n ($n = 1–3$). Attempted direct crystallisation provided only trace amounts of cyclobutene 15 which is otherwise unstable in solution (see

| Compound | Precursor diol (8) rac:meso ratio | R1 | R2 | Yield (7) [%] |
|----------|---------------------------------|----|----|---------------|
| 7a       | 1.6:1.0                         | H  | H  | 85            |
| 7b       | 1.9:1.0                         | OMe| OMe| 47            |
| 7c       | 4.8:1.0                         | CF3| H  | 56            |
| 7d       | 1.8:1.0                         | OMe| H  | >99           |
| 7e       | 1.6:1.0                         | F  | H  | 29            |
| 7f       | 1.0:1.1                         | H  | CF3| 44            |
| 7g       | 1.0:1.2                         | H  | OMe| 38            |
| 7h       | 1.0:1.6                         | H  | t-Bu| 22           |
| 7i       | 1.0:1.0                         | –  | –  | 38            |
| 7j       | 1.0:2.0                         | –  | –  | 50            |

*From diol precursor (0.45 mmol) in THF (5.0 mL), with LiHDMS (2.0 equiv), CS2 (3.0 equiv), Mel (8.0 equiv), isolated yields. bEquivalent anti:syn ratio for 8j.*
Its extensive decomposition prevented other characterisation. Based on this model system, it is proposed that intermolecular [2 + 2] reactions of bis-allenes, similar to results in other reported allenic rearrangements to rubrene [27,28], 2c,d result in the formation of numerous stereoisomeric oligomers resulting in the broad uninformative NMR spectra in the cascade byproducts. The structure of 15 is unremarkable except for the presence of a highly elongated C–C bond (1.63 Å) brought on through the steric congestion of the adjacent quaternary centers. A similar situation has been reported [29].

The use of the optimal conditions provided a series of acene derivatives (Table 2). All reactions resulted in chromatographically stable red microcrystalline solids. As anionic Chugaev elimination appeared the preferred aromatisation route from the studies of Table 1 (compare runs 6, 8 and 9), preparations of 7a–c strongly benefit from higher rac:meso ratios that increase the population of the equivalent syn-6 intermediates (Scheme 2). Steric congestion in the anion Chugaev transition state appears to favour this as all these compounds are isolated in good to excellent yields. Conversely 7e–h are isolated in lower yields due to a combination of higher meso content in 8e–h (leading less efficient E2 elimination) and lower steric promotion in the anion Chugaev elimination. Steric, rather than electronic, factors seem to affect the reaction most as evidenced by the quantitative yield of 7d compared to 7b (47%), 7c (56%), 7f (44%) and 7g (38%). The decreasing yields suggest that meta substitution promotes the 6x cyclisation while para electronic affects are minor and unhelpful according to the observed trend. Increasing the reaction temperature, in attempts to facilitate E2 elimination, was generally not useful as this led only to increased amounts of inert xanthates through sulfur alkylation. However, in the case of 7b this approach did allow us to reach 50 ± 4% yields (range for 6 runs).

Compounds 7a, d, f–h and j were subjected to single-crystal X-ray crystallography. This confirmed the molecular connectivity but more importantly allowed insight into their crystal packing features (Scheme 5 and Supporting Information File 1).
across the family of structures. Pairs of 7a associate with slip-stack pairing (C\textsubscript{4a}···C\textsubscript{4b} 3.51−3.72 Å). Each of these (7a)\textsubscript{2} ‘dimers’ is linked to the next through π contacts to the xanthate methyl (C\textsubscript{2a}···MeS 3.38 Å). The ‘gaps’ in the columns are filled by an additional motif (C\textsubscript{2a}···C\textsubscript{3} 3.32−3.59 Å) almost perpendicular to the stacking. In 7d a lattice of (7d)\textsubscript{n} chains propagates through C(11)\textsubscript{a}···MeS (3.39 Å) contacts. Adjacent chains overlap to produce the partial brickwork stack motif showing C\textsubscript{2a}···C\textsubscript{3} 3.51−3.60 Å between the most electron rich and deficient aryl rings. Offset stacking ribbons are found in 7f (i.e., graphic ‘a’ is above ‘b’, etc.). The closest contacts are C−C\textsubscript{edge} at 3.82−3.96 Å and C\textsubscript{3}···F−CF\textsubscript{2} 3.2 Å. Perpendicular ribbons propagate through the crystal linked by inter-digitated xanthates or CF\textsubscript{3} groups. Structure 7f is the only one of the di/trisubstituted family not to show local C\textsubscript{2} symmetry in intermolecular paring of the tetracenes. The structures of 7g,h (Scheme 5) are closely related to those of 7d and 7a, respectively. Finally, the least substituted tetracene 7j forms ribbons of herringbone structures.

Estimates of the HOMO−LUMO data for 7 were taken from UV and CV measurements (see Table 3 and Supporting Information File 1), as well as by DFT calculations. Tetracenes 7d and 7f show the widest range in HOMO−LUMO perturbation while \(E_g\) opt. is ca. 0.4 eV lower that \(E_g\) calcd. across the series. We could not attain the reduction potentials of 7 but from the onset of oxidation data we could estimate the HOMO energy levels in 7 and these followed the same trend as \(E_{HOMO}\) calcd. Preliminary testing of vacuum deposited thin polycrystalline films (ca. 800 nm) of 7a and 7j showed dielectric behaviour (\(\sigma <10^{-10}\) S cm\textsuperscript{−1}) indicating that additional derivitisation and radical cation salt formation is required for the attainment of high electrical conductivity, as in the case of tetrathiotetracene [30].

### Conclusion

Typical [3,3]-sigmatropic rearrangements of xanthates are normally considered to proceed via neutral species (such as 1c).

The tetracenes 7 herein are not formed this way, instead the evidence here strongly suggests that the required [3,3]-6n-6x electrocyclic cascades takes place via anionic xanthate species before final capping with methyl iodide. Final aromatisation through E2 or the anionic equivalent of the Chugaev reaction are also both viable. As neutral Chugaev reactions normally require very high temperatures this alternative approach is attractive as only moderate temperatures are required (60−80 °C). This procedure allows rapid access to mono sulfur-containing acenes, and is applicable to small scale library synthesis. Only low cost reagents are required and otherwise difficult to synthesize hindered 1,3,4,12-tetrasubstituted species can be made straightforwardly.

### Supporting Information

**Supporting Information File 1**

Experimental procedures, characterisation data, X-ray structures, data for the DFT calculations, and NMR spectra.

[http://www.beilstein-journals.org/bjoc/content-supplementary/1860-5397-11-31-S1.pdf]

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### Table 3: Electro-optic properties of 7a–j.

| Compound | \(E_{ox}\) (ox.) [V]\textsuperscript{a} | HOMO/LUMO calcd. [eV]\textsuperscript{b} | \(\nu_{max}\) (vis) [nm]\textsuperscript{c} | \(E_g\) opt. [eV]\textsuperscript{c} | \(E_g\) calcd. [eV]\textsuperscript{c} |
|----------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|
| 7a       | +0.52                           | −5.16−2.51                      | 287             | 2.27            | 2.65            |
| 7b       | +0.22                           | −5.21−2.57                      | 297             | 2.23            | 2.63            |
| 7c       | +1.07                           | −5.23−2.93                      | 297             | 2.18            | 2.60            |
| 7d       | +0.29                           | −4.89−2.36                      | 296             | 2.09            | 2.55            |
| 7e       | +0.65                           | −5.58−2.96                      | 286             | 2.27            | 2.62            |
| 7f       | +0.76                           | −5.61−2.98                      | 290             | 2.24            | 2.63            |
| 7g       | +0.43                           | −5.20−2.69                      | 290             | 2.28            | 2.51            |
| 7h       | +0.55                           | −5.33−2.69                      | 289             | 2.26            | 2.65            |
| 7i       | +0.60                           | −5.27−2.32                      | 283             | 2.49            | 2.95            |
| 7j       | +0.62                           | −5.10−2.40                      | 283             | 2.36            | 2.70            |

\textsuperscript{a}By cyclic voltammetry, referenced against Fc/Fc\textsuperscript{−}.
\textsuperscript{b}DFT: Calculated with the B3LYP-6-31G(d,p) basis set using Gaussian 09 Rev.D.01.
\textsuperscript{c}in CH\textsubscript{2}Cl\textsubscript{2}.
\textsuperscript{d}Determined from the onset (Tauc) of the lowest energy visible absorption band.
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