1 H), 4.14 (ddd, J = 12.8, 4.4, 2.4 Hz, 1 H), 3.70 (dd, J = 11.2, 4.4 Hz, 1 H), 2.74 (dq, J = 12.8, 6.9 Hz, 1 H), 1.67 (d, J = 1.0 Hz, 3 H), 1.10 (d, J = 6.9 Hz, 3 H). **3d**: $^1$H NMR (250 MHz, CDCl3, 25 °C) δ 7.20 (s, 1 H), 5.52 (d, J = 5.1 Hz, 1 H), 4.67 (dd, J = 7.9, 2.4 Hz, 1 H), 4.60 (dd, J = 9.6, 3.2 Hz, 1 H), 4.43 (dd, J = 6.3, 4.4 Hz, 1 H), 4.39 (dd, 8.4, 1.8 Hz, 1 H), 4.35 (dd, J = 5.1, 2.6 Hz, 1 H), 3.96 (dd, J = 9.8, 1.7 Hz, 1 H), 2,63 (dq, J = 7.4, 3.1 Hz, 1 H), 1.67 (s, 3 H), 1.55 (s, 3 H), 1.44 (s, 3 H), 1.38 (s, 3 H), 1.35 (s, 3 H), 1.15 (d, J = 7.4 Hz, 3 H); IR ($CDCl_3$) 1663, 1620 cm$^{-1}$; MS, m/e 354 ($M^+$). **3e**: $^1$H NMR (250 MHz, $CDCl_3$, 25 °C) δ 7.12 (s, 1 H) 5.50 (d, J = 4.9 Hz, 1 H), 4.64 (dd, J = 7 = 7.9, 2.3 Hz, 1 H), 4.42 (dd, J = 9.7, 3.1 Hz, 1 H), 4.36 (dd, J = 7.9, 1.5 Hz, 1 H), 4.31 (dd, J = 4.8, 2.5 Hz, 1 H), 4.04 (dd, J = 9.6, 1.3 Hz, 1 H), 2.78 (dq, J = 7.4, 3.2 Hz, 1 H), 1.65–1.26 (m, 18 H); IR ($CDCl_3$) 1665, 1625 cm$^{-1}$; MS, m/e 364 ($M^+$).

**Crystallographic Determination of Compound 3d.** A needle-shaped crystal of dimension 0.6 × 0.6 × 0.4 mm was mounted on a glass rod. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The unit cell was found by using 25 randomly selected reflections and has $a$ = 6.004 (1) Å, $b$ = 16.051 (6) Å, and $c$ = 9.755 (2) Å, with β = 100.17 (2)°. The volume is 925 (1) Å$^3$ and the calculated density is 1.272 g/cm$^3$ for $Z$ = 2. Systematic extinctions, as estimated density and the presence of chirality were the criteria used to establish the space group as $P2_1$, with one molecule of composition $C_{18}H_{26}O_7$ comprising the asymmetric unit.

There were 2493 reflections collected with $2\theta \leq 52°$, with 1712 (69%) observed ($I \geq 3\sigma I$). The structure was solved by direct methods, using MULTAN80.[13] All 25 non-hydrogen atoms were observed on the electron-density map based on the phasing of 158 reflections ($E_{min} \geq 1.59$).

Carbon and oxygen atoms were refined anisotropically. Hydrogen atoms were calculated by using SDP[14] program HYDRO and added to the structure factor calculations. Full-matrix refinement of the non-hydrogen atoms and addition of the hydrogen atoms to the structure factor calculations, without refinement of their positions, has resulted in convergence to a standard crystallographic residual of 0.062 and a weighted residual of 0.075. The indications from residual electrons density point to disorder in the molecule. All intramolecular bond distances and angles are within normal ranges.

A perspective drawing of compound **3d**[15] is given in the text. Tables 1–5[16] containing the final X-ray parameters, bond distances, bond angles, torsional angles, and anisotropic temperature factors are provided as supplementary material.

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**Registry No.** 1, 98703-75-4; **2a**, 100-52-7; **2b**, 93-53-8; **2c**, 60656-87-3; **2d**, 4933-77-1; **3a**, 83378-98-7; **3b**, 80160-78-7; **3c**, 83379-01-5; **3d**, 98687-79-7; **3e**, 98757-20-1; **4a**, 83379-03-7; **4b**, 80160-77-6; **4c**, 83379-05-9; **5**, 72486-93-2; $BF_3$, 7637-07-2; (*E*)-1-methoxy-2-methylpent-1-en-3-one, 56279-35-7; *tert*-butyldimethylsilyl trifluoromethanesulfonate, 69739-34-0.

**Supplementary Material Available:** A prospective drawing of compound **3d** with numbered atoms and tables containing fractional coordinates, temperature factors, bond distances, torsional angles, and anisotropic temperature factors for **1** (7 pages). Ordering information is given on any current masthead page.

(13) MULTAN80 system of computer programs for the automatic solution of crystal structures from X-ray diffraction data: Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M.

(14) Programs used were the Enraf-Nonius SDP program library (version 18).

(15) UPLOT structure plotting package: Kearsley, S. K. Yale University, 1985.

(16) SKKPUB structural parameters and errors: Kearsley, S. K. Yale University, 1985.

# Synthesis of 3,4-Dihydro-3,3,4-trichloroquinolin-2(1*H*)-ones and Their Conversion to Indeno[1,2,3-*de*]quinolin-2(3*H*)-ones

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Recently we treated difluorooxyborane **1a** with sulfuryl chloride to form 3,4-dihydro-3,3,4-trichloroquinolin-2-(1*H*)-one **2a**.[1] Erratic results were encountered in the earlier experiments and have led to the adoption of a procedure using added concentrated $H_2SO_4$ to effect a more rapid and reproducible reaction. Application of the modified method to difluorooxyboranes **1b–e** led to the corresponding formerly inaccessible **2b–e** in 20–70% yields; the structures of the products were assigned from their spectroscopic data.[2]

The function of the acid catalyst may be rationalized in terms of the mechanism[1] suggested for the conversion of **1** to **2**. Ion A (Scheme I), once it is generated from **1** and $SO_2Cl_2$, reacts via two distinct and competitive pathways: with hydrogen chloride it transforms to B (route a), the precursor of amide **3**, otherwise it cyclizes to ion C (route b), furnishing (ultimately) the 3,4-dihydroquinolinone **2**. The postulation that B forms at a significantly faster rate than does C in this dichotomy would account for chlorinated 3-keto amide **3** being the chief product. We speculate further that $H_2SO_4$ (unlike HCl) facilitates ionization of intermediate B to re-form A (Scheme I, route c). The deliberate introduction of an adequate quantity of concentrated $H_2SO_4$ into the reaction (in contrast to the fortuitous production of the acid from $SO_2Cl_2$ in the original[1] procedure) thus results in an increased yield of **2** at the expense of **3**. In support of this analysis, **1b** and $SO_2Cl_2$ were reacted with retention of hydrogen chloride and exclusion of moisture, i.e., under conditions favoring formation of amide(s) **3**, and $H_2SO_4$ was then added to the mixture; the major product was now 3,4-dihydroquinolinone **2b** contaminated with only minor **3a** and **3b**.

In a relatively large scale preparation, **1b** (10.6 mmol) was reacted with an excess of $SO_2Cl_2$ in the presence of concentrated $H_2SO_4$ to provide, after chromatography, **2b** (7.6 mmol). Also eluted from the column were two byproducts, viz., quinolin-2-one **4** and the hitherto inaccessible 3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one (**5**). Product **4** is thought to arise in the reaction by loss of $Cl^+$ from an intermediate species (D, Scheme II),[3] whereas **5** probably resulted from fortuitous hydrolysis of **2b** during workup. Indeed, **5**[4] was subsequently prepared in excellent (~90%) yield by refluxing **2b** in aqueous acetone containing silver nitrate.

Two of the 3,4-dihydroquinolinones, viz., **2b** and **2e**, were tested as precursors for the indeno[1,2,3-*de*]quinolin-2-one **7** system. Compound **2b** in concentrated $H_2SO_4$ reacted in the manner of **2a**[1] likewise affording a ring-cleavage

(1) Staskun, B. *J. Org. Chem.* **1980**, *45*, 2482.

(2) The formulation of **2a** has been confirmed by an X-ray structure determination (Denner, L.; Marais, J. L. C.; Staskun, B., unpublished results).

(3) Staskun, B.; Meltzer, P. C. *Tetrahedron* **1977**, *33*, 2429.

(4) The related 3,4-dihydro-4-hydroxy-1-methyl-4-phenyl-3,3,6-trichloroquinolin-2-one is a possible intermediate in the cyclization of 2-(*N*-methyl)dichloroacetamido-5-chlorobenzophenone (Podesva, C.; Solomon, C.; Vagi, K. *Can. J. Chem.* **1968**, *46*, 435.

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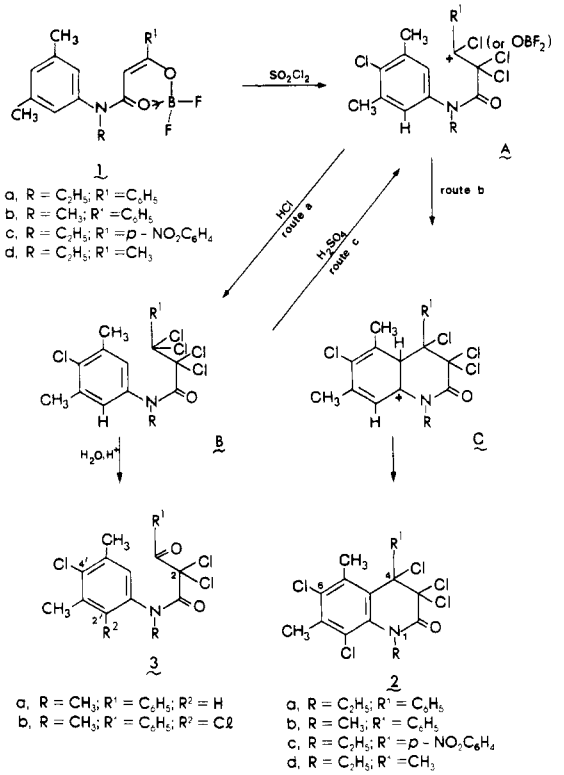
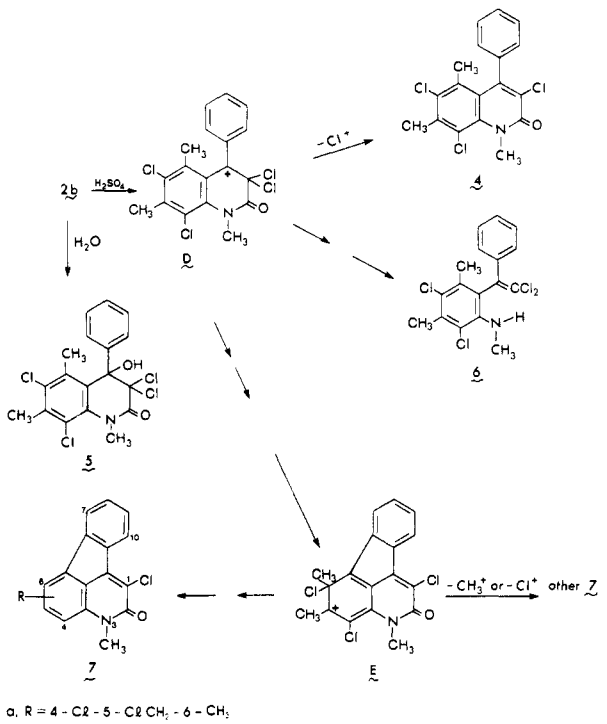
**Scheme I**



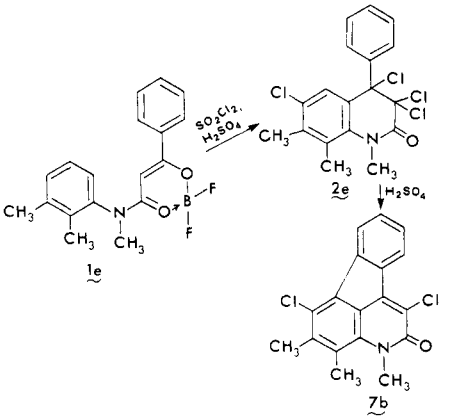
**Scheme II**



product, **6** (Scheme II), along with indenoquinolinone material (TLC showed three components). From the latter mixture was separated (~10%, based on **2b**) the product of multiple substituent migrations,[5] viz., 5-(chloromethyl)indeno[1,2,3-*de*]quinolin-2-one, **7a**. The $^1$H NMR aromatic absorptions of **7a** (Experimental Section) are consistent with the following information: the 1-Cl sub-

(5) Meltzer, P. C.; Staskun, B. *Tetrahedron* **1977**, *33*, 2965; other **7** may arise by loss of either $CH_3^+$ or $Cl^+$ from an intervening species such as **E** (Scheme II).[3]

**Scheme III**



stituent has an anisotropic deshielding effect on the 10-H,[6] while the 6-$CH_3$, to a lesser extent, causes a downfield shift of the 7-H,[7] thereby distinguishing these two protons from the relatively unaffected ones at 8-H and 9-H. The related 4-hydroxydihydroquinolinone **5** formed essentially the same mixture of **6** and **7** (via the common ion D, Scheme II).

By comparison, **2e**, having no C-5 substituent, merely underwent ring junction[3] with loss of HCl (Scheme III) and provided indeno[1,2,3-*de*]quinolinone **7b** in high (~80%) yield.

In summary, we describe a consistent synthesis of the little known and potentially versatile 3,4-dihydro-3,3,4-trichloroquinolinones **2** and report on their conversion to indeno[1,2,3-*de*]quinolin-2-ones **7** and hydrolysis.

## Experimental Section

All melting points were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra (KBr disk) were recorded on a Perkin-Elmer Model 521 spectrophotometer; $^1$H NMR spectra were obtained at 60 MHz with a Hitachi Perkin-Elmer R-20 spectrometer or at 80 MHz with a Bruker (WP 80) instrument, in $CDCl_3$, with $Me_4Si$ as an internal standard. Mass spectra (*m/e*) were measured on a Varian CH-5 spectrometer at 70 eV; the correct Cl isotopic abundance ratios were observed in the compounds described. Elemental analyses were performed at the CSIR, Pretoria. For column chromatography, E. Merck Kieselgel 60 was used; TLC plates (E. Merck silica gel 60 $F_{254}$) were visualized by UV and/or $I_2$. Sulfuryl chloride was purified by distillation.

**Difluorooxyboranes 1b, 1c, 1d, and 1e.** These starting compounds were prepared by N-methylation (with $CH_3I$) or N-ethylation (with $C_2H_5I$) of the appropriate parent difluorooxyborane **1** (R = H).[8] They were crystallized (from ethanol–$H_2O$), and characterized from their $^1$H NMR and MS spectra.

For **1b**: mp 204–205 °C; $^1$H NMR $\delta$ 2.40 (s, 6 H, 2 × $ArCH_3$), 3.50 (s, 3 H, $NCH_3$), 5.55 (s, 1 H, > C=C*H*—), 6.90 (br s, 2 H, aromatic, 2′-H, 6′-H), 7.15 (br s, 1 H, aromatic, 4′-H), 7.2–7.85 (m, 5 H, aromatic); MS, *m/e* 329 ($M^+$).

**Amides 3a and 3b from *N*-Methyldifluorooxyborane 1b.** An excess of $SO_2Cl_2$ (1.5 mL; ~18 mmol) was added in one portion to **1b** (300 mg, 0.91 mmol) contained in a 25-mL conical flask. After the initial brisk gas evolution had mostly subsided (0.5–1 min), the flask was sealed (with a glass stopper), and the reaction was left at room temperature for 3 h. Ice and water were added, and the mixture was stirred to decompose unreacted $SO_2Cl_2$. The reaction product was extracted into $CHCl_3$, and the organic phase was washed with water, dried ($MgSO_4$), and evaporated to yield a colorless gum [~400 mg; TLC (benzene) showed two major

(6) Meltzer, P. C.; Staskun, B. *J. Org. Chem.* **1977**, *42*, 2977.
(7) Cerfontein, H.; Koeberg-Telder, A.; Laali, K.; Lambrechts, H. J. A. *J. Org. Chem.* **1982**, *47*, 4069.
(8) Staskun, B. *J. Org. Chem.* **1979**, *44*, 875.

components (**3a** and **3b**) and negligible **2b**]. The amides were separated on a column (benzene).

**2,2,4′-Trichloro-*N*,3′,5′-trimethylbenzoylacetanilide (3a)** (160 mg; $R_f$ 0.28) crystals (from $C_2H_5OH$–$H_2O$): mp 123–124 °C; IR 1700 (keto CO) and 1660 (amide CO) $cm^{-1}$; NMR $\delta$ 2.25 (s, 6 H, 2 × Ar$CH_3$), 3.30 (s, 3 H, N$CH_3$), 6.60 (s, 2 H, 2′-H and 6′-H), 7.3–8.2 (m, 5 H, ArH); MS, *m/e* 383 (3Cl, $M^+$), 196, (1Cl, 3,5-$(CH_3)_2$-4-$ClC_6H_2N(CH_3)C{\equiv}O^+$), 168 (1Cl, 196 – CO), 105, 77.

**2,2,2′,4′-Tetrachloro-*N*,3′,5′-trimethylbenzoylacetanilide (3b)** (50 mg; $R_f$ 0.37): colorless gum; NMR $\delta$ 2.35 (s, 3 H, Ar$CH_3$), 2.50 (s, 3 H, Ar$CH_3$), 3.30 (s, 3 H, N$CH_3$), 6.85 (br s, 1 H, 6′-H), 7.2–7.7 (m, 3 H, ArH), 7.9–8.3 (m, 2 H, ArH); MS, *m/e* 417 ($M^+$, minor peak), 382 (3Cl, M – 35), 312 (M – 105, minor peak), 278 (2Cl), 242 (2Cl), 230 (2Cl, 3,5-$(CH_3)_2$-2,4-$(Cl)_2C_6HN(CH_3)C{\equiv}O^+$), 202 (2Cl, 230 – CO), 105, 77.

The reaction between $SO_2Cl_2$ (1.5 mL) and **1b** (300 mg) was repeated; however, after about 15 min had elapsed concentrated $H_2SO_4$ (~0.03 mL) was introduced into the solution which was swirled and left as before (for 2 h). Addition of ice and water followed by stirring gave a colorless, granular solid (~320 mg) which was collected by filtration. TLC (benzene) showed this to be a mixture with **2b** as the major constituent (ca. >50%).

**3,4-Dihydro-3,3,4,6,8-pentachloro-4-phenyl-1,5,7-trimethylquinolin-2(1*H*)-one (2b).** The preparation of **2b** illustrates the following general procedure: an excess of sulfuryl chloride (10 mL, ~130 mmol) was added in one portion to *N*-methyldifluorooxyborane **1b** (3.50 g, 10.6 mmol) contained in a 200-mL conical flask; an immediate and vigorous evolution of $HCl/SO_2$ occurred. When this had mainly subsided (~1 min) concentrated $H_2SO_4$ (0.1–0.2 mL) was added; the container was stoppered with cotton wool, and the now dark-green colored reaction mass from which there was renewed[9] effervescence was allowed to remain at room temperature for 2 h. The discolored and turbid mixture was treated with ice and water and stirred to obtain a colorless solid. This product was collected by filtration, washed with water, and air-dried [4.67 g; TLC (benzene) showed a mixture with the title compound **2b** (highest $R_f$) as the major component]. The crude product was chromatographed (benzene) to give dihydroquinolinone **2b** (3.32 g, 72%; $R_f$ 0.53), colorless cubes (from ethanol–$CHCl_3$), mp 197–199 °C: IR 1715 (amide CO) $cm^{-1}$; NMR $\delta$ 1.72 (s, 3 H, Ar$CH_3$), 2.60 (s, 3 H, Ar$CH_3$), 3.50 (s, 3 H, N$CH_3$), 7.18–7.6 (m, 4 H, ArH) 7.9–8.2 (m, 1 H, ArH); MS, *m/e* 435 (5Cl, $M^+$), 400 (4Cl, M – 35), 365 (3Cl, M – 70), 330 (2Cl, 365 – 35).

Anal. Calcd for $C_{18}H_{14}Cl_5NO$: C, 49.40; H, 3.22; Cl, 40.51; N, 3.20. Found: C, 49.06; H, 3.06; Cl, 40.56; N, 3.18. Elution of the column was continued with $C_2H_5OH$, and the appropriate fractions were combined and evaporated to afford **4** and **5**, respectively.

**3,4-Dihydro-4-hydroxy-4-phenyl-3,3,6,8-tetrachloro-1,5,7-trimethylquinolin-2(1*H*)-one (5)** (100 mg; $R_f$ 0.18, colorless needles (from $C_2H_5OH$), mp 220–221 °C: IR 3430 (OH), 1680 (amide CO) $cm^{-1}$; (Bruker) NMR $\delta$ 2.27 (s, 3 H, Ar$CH_3$), 2.58 (s, 3 H, Ar$CH_3$), 3.27 (s, 1 H, OH; removed with $D_2O$), 3.50 (s, 3 H, N$CH_3$), 7.33 (s, 5 H, ArH); MS, *m/e* 417 (4Cl, $M^+$), 382 (3Cl, M – 35).

Anal. Calcd for $C_{18}H_{15}Cl_4NO_2$: C, 51.58; H, 3.60; Cl, 33.83; N, 3.34. Found: C, 51.99; H, 3.80; Cl, 33.64; N, 3.45.

**4-Phenyl-3,6,8-trichloro-1,5,7-trimethylquinolin-2(1*H*)-one (4)** (580 mg; $R_f$ ~0.1), buff-colored plates (from $C_2H_5OH$–$H_2O$), mp 150–151 °C: IR 1650 (amide CO) $cm^{-1}$; NMR $\delta$ 1.80 (s, 3 H, Ar$CH_3$), 2.65 (s, 3 H, Ar$CH_3$), 3.90 (s, 3 H, N$CH_3$), 7.1–7.6 (m, 5 H, ArH); MS, *m/e* 365 (3Cl, $M^+$), 337 (3Cl, M – 28), 330 (2Cl, M – 35).

Anal. Calcd for $C_{18}H_{14}Cl_3NO$: C, 58.96; H, 3.85; Cl, 29.01; N, 3.82. Found: C, 59.18; H, 3.81; Cl, 29.07; N, 3.90.

**Hydrolysis of 2b to 5.** Compound **2b** (1 g) was dissolved in acetone (100 mL) under reflux, after which distilled water (30 mL) was added followed by $AgNO_3$[10] (2.6 g). The mixture was refluxed for 4 h, cooled somewhat, and filtered. The filtrate was diluted with distilled water (250 mL) and left at room temperature for several hours. The separated solid (**5**, 0.87 g; TLC (benzene) showed negligible contaminant) was collected by filtration, washed with water, dried (50 °C), and identified from its IR and NMR spectra.

**3,4-Dihydro-4-phenyl-3,3,4,6-tetrachloro-1,7,8-trimethylquinolin-2(1*H*)-one (2e).** Reaction of **1e** (0.50 g; mp 184–186 °C) with $SO_2Cl_2$ (1.5 mL) and concentrated $H_2SO_4$ (0.03 mL) as with **1b**, for 2 h gave, after treatment with ice and water, a solid product [0.60 g; TLC (benzene) showed a mixture]. Chromatography (benzene) yielded the title compound **2e** (200 mg); colorless crystals (from ethanol), mp 193–194 °C: IR 1710 (amide CO) $cm^{-1}$; NMR $\delta$ 2.4 (two nearly coincident singlets, 6 H, 2 × Ar$CH_3$), 3.45 (s, 3 H, N$CH_3$), 7.0 (s, 1 H, 5-H), 7.2–7.8 (m, 4 H, ArH), 8.1–8.3 (m, 1 H, ArH); MS, *m/e* 401 (4Cl, $M^+$, minor peak), 366 (3Cl, M – 35), 331 (2Cl, M – 70).

**3,4-Dihydro-5,7-dimethyl-1-ethyl-4-(*p*-nitrophenyl)-3,3,4,6,8-pentachloroquinolin-2(1*H*)-one (2c).** Reaction of difluorooxyborane **1c** (0.70 g; mp 126–127 °C) with $SO_2Cl_2$ (3 mL) and concentrated $H_2SO_4$ (0.03 mL) for 4.5 h, as with **1b**, afforded a product (0.86 g; TLC (benzene) showed a mixture) from which the title compound **2c** (highest $R_f$; 200 mg) was isolated by chromatography (benzene); pale yellow crystals (from $CHCl_3$–$C_2H_5OH$), mp 209–210 °C: IR 1705 (amide CO) $cm^{-1}$; Bruker NMR $\delta$ 1.25 (t, 3 H, $CH_2CH_3$), 1.73 (s, 3 H, Ar$CH_3$), 2.63 (s, 3 H, Ar$CH_3$), 4.2 (8-line multiplet, 2 H, $CH_2CH_3$), 7.3 (d, 1 H, ArH), 8.1 (m, 1 H, ArH), 8.3 (m, 2 H, ArH); MS, *m/e* 494 (5Cl, $M^+$), 459 (4Cl, M – 35), 431 (M – 28 – 35), 424 (3Cl, M – 70), 396 (3Cl, 424 – 28).

Reaction of **1c** (300 mg) with $SO_2Cl_2$ (1 mL) with retention of HCl and exclusion of $H_2SO_4$, for 3.5 h, afforded a mixture (~300 mg) of the acyclic amides **3** (R = $CH_3$; $R^1$ = *p*-$NO_2C_6H_4$; $R^2$ = H and Cl, respectively), as evidenced from TLC and MS.

**3,4-Dihydro-1-ethyl-3,3,4,6,8-pentachloro-4,5,7-trimethylquinolin-2(1*H*)-one (2d).** Compound **1d** (3.0 g, 10.7 mmol; mp 136–137 °C) was reacted with $SO_2Cl_2$ (9 mL, ~110 mmol) and concentrated $H_2SO_4$ (0.2 mL), as with **1b**, for 3 h. Following treatment with ice and water the product mixture was extracted into $CHCl_3$. The solvent was evaporated, and the residue was chromatographed (benzene) to afford the title quinolinone **2d** as a pale yellow gum (1.9 g, 4.9 mmol; $R_f$ 0.56), sparingly soluble in cold $C_2H_5OH$: IR 1710 (amide CO) $cm^{-1}$; NMR $\delta$ 1.10 (t, 3 H, $CH_2CH_3$), 2.40 (s, 3 H, $CH_3$), 2.52 (s, 3 H, $CH_3$), 2.60 (s, 3 H, $CH_3$), 4.05 (m, 2 H, $CH_2CH_3$); MS, *m/e* 421 (M + 34; minor peak), 387 (5Cl, $M^+$), 352 (4Cl, M – 35), 324 (4Cl, 352 – 28), 289 (3Cl, M – 28 – 70).

**Ring-Cleavage, Cyclization of Compound 2b.** Concentrated $H_2SO_4$ (3 mL) was added to a mixture of **2b** (1.5 g, 3.45 mmol) and $Ag_2SO_4$ (0.7 g, 2.24 mmol), and the resulting permanganate-colored mass was heated at ~95 °C (oil bath) for 3 min with intermittent stirring; relatively little HCl was evolved as compared to the reaction without $Ag_2SO_4$ (which gave a similar result). The orange mixture was diluted with ice and water, and the bright yellow, sparingly soluble material was extracted into $CHCl_3$. The organic phase was washed with water, dried ($MgSO_4$), and evaporated to leave an orange gum (1.2 g). TLC [benzene–acetone (10:1)] showed a mixture with **6** (highest $R_f$) as a major constituent along with (at least) three yellow/orange spots including **7a**. The product was chromatographed (benzene) to give **1-phenyl-1-[3′,5′-dichloro-4′,6′-dimethyl-2′-(methylamino)-phenyl]-2,2-dichloroethene (6)** as a colorless gum (250 mg, 0.67 mmol) which solidified on trituration with $C_2H_5OH$, colorless needles (from $C_2H_5OH$–acetone), easily soluble in acetone, sparingly soluble in $C_2H_5OH$, mp 72–74 °C: IR 3400 (NH), 1580 (C=C) $cm^{-1}$; Bruker NMR $\delta$ 2.34 (s, 3 H, $CH_3$), 2.50 (s, 3 H, $CH_3$), 2.81 (s, 3 H, $CH_3$), ~3.5 (br s, 1 H, N*H*, removed by $D_2O$), 7.2–7.4 (m, 5 H, ArH); MS, *m/e* 373 (4Cl, $M^+$), 338 (3Cl, M – 35), 337 (3Cl, M – 36), 322 (3Cl, 337 – 15).

Anal. Calcd for $C_{17}H_{15}Cl_4N$: C, 54.43; H, 4.03; Cl, 37.80; N, 3.74. Found: C, 54.35; H, 3.73; Cl, 37.72; N, 3.70.

Elution of the column was continued with benzene–acetone (10:1) but did not lead to a clean separation of the indenoquinolinone **7** components. The yellow fractions were recombined and evaporated, and the solid residue (0.52 g; TLC showed three yellow/orange spots) was rechromatographed [benzene–ethyl acetate (1:1)] to provide a sample (~50 mg) of **5-(chloromethyl)-1,4-dichloro-3,6-dimethylindeno[1,2,3-*de*]quinolin-2(3*H*)-one (7a)** sparingly soluble in cold $CHCl_3$, $C_2H_5OH$, and

(9) This may be indicative of (renewed) nuclear chlorination (e.g., at 6-H and/or 8-H, leading to **2b**).

(10) Wasserman, H. H.; Mariano, P. S.; Keehn, P. M. *J. Org. Chem.* 1971, *36*, 1765.

benzene, yellow needles (from $C_2H_5OH$–$CHCl_3$); mp 258–262 °C: IR 1650 (amide CO), 760 $cm^{-1}$; Bruker NMR ($CDCl_3$ + TFA to clear) δ 2.78 (s, 3 H, $ArCH_3$), 4.15 (s, 3 H, $NCH_3$), 4.96 (s, 2 H, $ArCH_2Cl$), 7.3–7.7 (m, 2 H, ArH), 7.8–8.0 (m, 1 H, 7-H), 8.25–8.4 (m, 1 H, 10-H); MS, *m/e* 363 (3Cl, $M^+$), 328 (2Cl, M – 35).

**1,6-Dichloro-3,4,5-trimethylindeno[1,2,3-*de*]quinolin-2-(3*H*)-one (7b).** Dihydroquinolinone **2e** (80 mg) was covered with concentrated $H_2SO_4$ (0.5 mL) and the permanganate-colored mixture was stirred and heated at 80–85 °C for 5 min; the reaction mass turned orange and liberated HCl. After having been cooled somewhat, water was added and the canary-yellow solid was collected by filtration, washed with water, and dried at 50 °C (60 mg; TLC [benzene–$C_2H_5OH$ (100:1) or $CHCl_3$] showed virtually only **7b**), yellow crystals (from $CHCl_3$–$C_2H_5OH$), mp 291–293 °C: IR 1635 (amide CO) $cm^{-1}$; Bruker NMR δ 2.47 (s, 3 H, $ArCH_3$), 2.59 (s, 3 H, $ArCH_3$), 3.86 (s, 3 H, $NCH_3$), 7.4–7.5 (m, 2 H, ArH), 8.2–8.3 (m, 2 H, ArH); MS, *m/e* 329 (2Cl, $M^+$), 314 (2Cl, M – 15), 294 (1Cl, M – 35).

**Action of $H_2SO_4$ on 5.** 4-Hydroxydihydroquinolinone **5** (100 mg) was reacted (for 2 min, no $Ag_2SO_4$) with concentrated $H_2SO_4$ (0.3 mL) as described for **2b**; a parallel and control run was conducted with **2b** 100 mg). The washed and dried ($MgSO_4$) $CHCl_3$ extract (15 mL) from **5** was examined by TLC [benzene–acetone (10:1) and $CHCl_3$] which revealed a product mixture (of **6** and **7**) virtually identical in composition with that derived from **2b**.

**Registry No.** **1b** (noncoordinate entry), 98539-86-7; **1b** (coordinate entry), 98526-28-4; **1b** (R = H) (noncoordinate entry), 98526-11-5; **1b** (R = H) (coordinate entry), 68682-89-3; **1c** (noncoordinate entry), 98526-08-0; **1c** (coordinate entry), 98526-29-5; **1c** (R = H) (noncoordinate entry), 98526-12-6; **1c** (R = H) (coordinate entry), 98526-31-9; **1d** (noncoordinate entry), 98526-09-1; **1d** (coordinate entry), 68682-93-9; **1d** (R = H) (noncoordinate entry), 98526-13-7; **1d** (R = H) (coordinate entry), 98539-87-8; **1e** (noncoordinate entry), 98526-10-4; **1e** (coordinate entry), 98526-30-8; **1e** (R = H) (noncoordinate entry), 98526-14-8; **1e** (R = H) (coordinate entry), 98526-32-0; **2b**, 98526-17-1; **2c**, 98526-21-7; **2d**, 98526-24-0; **2e**, 98526-20-6; **3** (R = Me, $R^1$ = *p*-$NO_2C_6H_4$, $R^2$ = H), 98526-22-8; **3** (R = Me, $R^1$ = *p*-$NO_2C_6H_4$, $R^2$ = Cl), 98526-23-9; **3a**, 98526-15-9; **3b**, 98526-16-0; **4**, 98526-18-2; **5**, 98526-19-3; **6**, 98526-25-1; **7a**, 98526-26-2; **7b**, 98526-27-3.

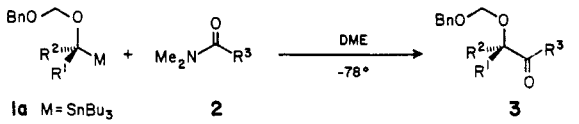
# Communications

## A Trialkylstannane-Mediated Approach to Acyloin Products

*Summary:* α-Alkoxy organolithium compounds, generated through the treatment of the corresponding tri-*n*-butylstannane with *n*-BuLi, smoothly condense with *N,N*-dimethylamides to afford α-alkoxy carbonyl products. This condensation is functionally equivalent to a regiocontrolled acyloin condensation.

*Sir:* Contemporary targets of total synthesis have stimulated intense interest in the development of carbon–carbon bond-forming processes that generate carbon skeletons bearing a variety of oxygenation patterns. Impressive advances have been recorded for the assembly of substrates bearing 1,3-oxygen relationships through the aldol condensation[1] and related methodologies.[2] In contrast, relatively less study has been devoted toward the realization of general methods of forming carbon–carbon bonds resulting in vicinal oxygenation.[3,4] Given the synthetic versatility of α-alkoxy carbonyl compounds,[5] the bond-forming strategy embodied in the acyloin condensation[6] offers an attractive approach to compounds bearing contiguous oxygen substitution. With this in mind, we wish to report on a trialkylstannane-mediated condensation that efficiently affords protected α-alkoxy carbonyl products in a manner formally equivalent to an acyloin condensation.

Table I. Intermolecular Acylation of α-Alkoxy Organolithium Species 1b[a]



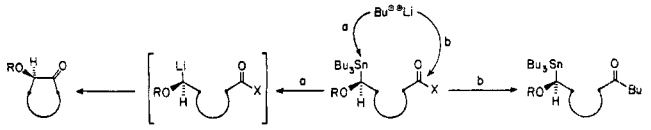

1a M = $SnBu_3$ 2 3

1b M = Li

| entry | $R^1$ | $R^2$ | $R^3$ | yield,[b] % |
|---|---|---|---|---|
| 1 | $C_2H_5$ | H | H | 67 |
| 2 | $Me_2CH$ | H | H | 78 |
| 3 | $Me_2CH$ | H | Ph | 74 |
| 4 | $Me_2CH$ | H | $C_2H_5$ | 67 |
| 5[c,d] | Ph | Me | $C_2H_5$ | 63 |
| 6 | $CH_2(CH_2)_3CH_2$ | | $C_2H_5$ | 68 |
| 7 | $Me_2CH$ | H |  | 80[e] |

[a] 1a (M = $SnBu_3$) → 1b (M = Li) via 1 equiv of *n*-BuLi, DME, −78 °C. [b] After column chromatography. [c] Using the methoxymethyl protecting group. [d] M = $SnMe_3$ in 1a. [e] Isolated as a mixture of diastereomers.

**Scheme I**

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