07487, and by the U.S. Army Research Office is gratefully acknowledged. The Columbia group acknowledges similarly support by the National Science Foundation and the Air Force Office of Scientific Research.

Registry No. Cyclooctatetraene, 629-20-9; semibullvalene, 6909-37-1.

A New Synthesis of Anthraquinones

John A. Rieck and John R. Grunwell*

Chemistry Department, Miami University,
Oxford, Ohio 45056

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As part of a program to synthesize naturally occurring quinones such as frenolicin[1] and the nanaomycins,[2,3] diethyl glutaconate was reacted with 2-butyryl-1,4-naphthoquinone in order to elaborate the dihydropyran ring system. Instead of dihydropyran formation the anthraquinone **2** (Scheme I) was found. This discovery amounts to a new annelation procedure for the synthesis of anthraquinones.

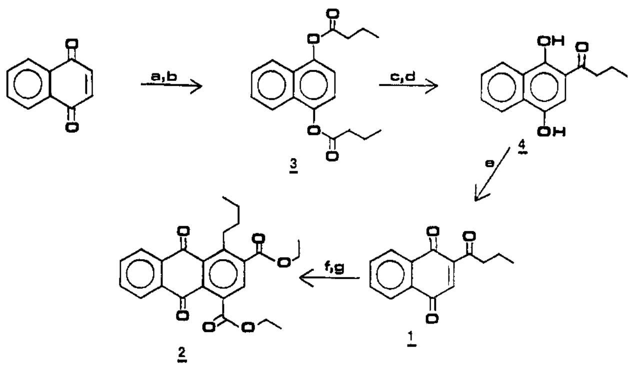
The synthesis of 2-butyryl-1,4-naphthoquinone is summarized in Scheme I. The Fries rearrangement of the dibutyrate **3** followed by hydrolysis of the rearranged ester and oxidation of the naphthalenediol **4** with silver carbonate adsorbed on Celite gave **1**.

The structural assignment of **2** was based on spectral data. The mass spectrum of **2** displayed an intense molecular ion at *m/e* 349 and ions at *m/e* 365 (loss of CH_3CH_2 from the propyl side chain) and 349 (loss of CH_3CH_2O from one of the carbethoxyl groups). The ^1H NMR spectrum in CCl_4 gave an AA′BB′ pattern centered at 7.9 ppm and a singlet at 7.75 ppm. The ester methylene hydrogens appeared as overlapping quartets centered at 4.45 and 4.40 ppm and the propyl methylene hydrogens adjacent to the benzene ring appeared as a triplet centered at 3.35 ppm. The ^{13}C NMR spectrum showed four carbonyls at 184 and 182.5 (quinone carbonyls) and 169 and 167 ppm (ester carbonyls). The ester and propyl methylenes as well as the three methyl resonances occurred as expected.

The formation of **2** can be rationalized according to Scheme II. The base-catalyzed addition of diethyl glutaconate to **1** gave the anion **5** which subsequently underwent proton transfer to produce the anion **6**. The anion **6** condensed intramolecularly with loss of water to form the anthrahydroquinone **7** which was probably air oxidized to the quinone **2**. The anion **6** may also transfer hydride to unreacted **1** to form a quinone which could lose a proton to form an anion capable of condensation with the acyl carbonyl to give the anthraquinone **2**. The former scheme seems more likely because proton-transfer reactions such as those involved in the conversion of **6** to **7** are expected to be faster than bimolecular hydride-transfer reactions.

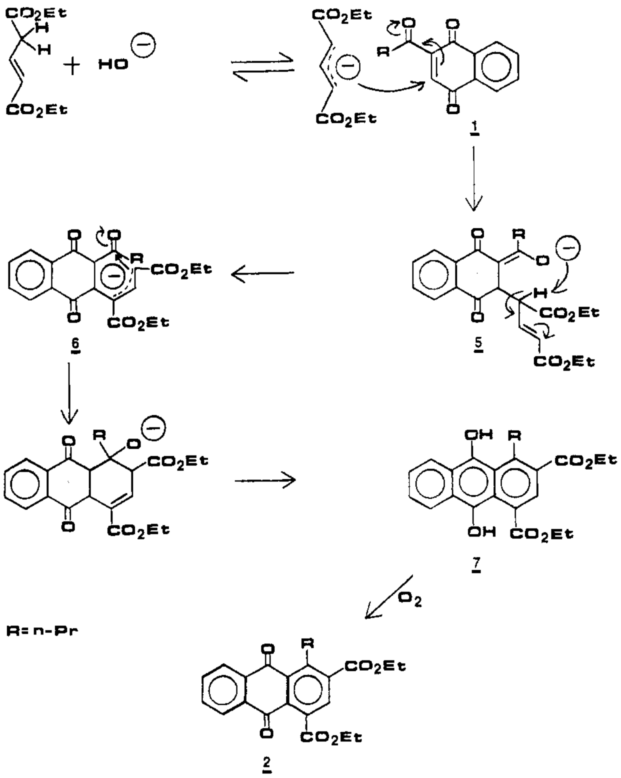
In summary, this annelation reaction should provide new methodology for the future synthesis of anthraquinones.

Scheme I



[a] a, $Na_2S_2O_4$; b, $(CH_3CH_2CH_2CO)_2O$, H_2SO_4; c, $AlCl_3$; d, CH_3OH/HCl, then H_2O; e, Ag_2CO_3/Celite; f, diethyl glutaconate/NH_4OH; g, O_2.

Scheme II



Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer IR-237. Mass spectra were taken on a single-focusing Hitachi RMU-6 spectrometer while proton NMR spectra were run with a JEOL-C-60M spectrometer and carbon-13 NMR were taken on a Bruker WH-90 with Me_4Si as an internal standard. Microanalysis was performed by Galbraith Laboratories, Inc.

1,4-Naphthalenediol Dibutyrate (3). To a flask containing 79.1 g (0.5 mol) of 1,4-naphthoquinone, previously recrystallized from acetone several times, and 500 mL of water was added 115 g (0.66 mol) of sodium hydrosulfite. The mixture was stirred for 2 h under N_2 and then extracted five times with 100 mL of ether. The ether extracts were combined and the ether was evaporated under vacuum. The crude naphthohydroquinone was dried under high vacuum (2.0 × 10^{-4} mm) for several days in the dark and was reacted with 158.2 g (1.0 mL) of butyric anhydride and 2 drops of concentrated H_2SO_4. The mixture was heated for 2 h under N_2 on a steam bath, and after cooling the crude ester was crystallized by the addition of a methanol–water solution. The solid was distilled and the fraction boiling at 184–189 °C (2.5 × 10^{-2} mm) was recrystallized from methanol to give 120.1 g (78%) of the white diester: mp 47–48 °C (lit.[4] mp 41–42 °C); ^1H NMR (CCl_4) δ 0.98 (9 H, t), 1.75 (4 H, m), 2.50 (4 H, t), 7.05 (2 H, s), 7.48 (4 H, m); IR (neat) 1760 cm^{-1}; mass spectrum, *m/e* 300, 231, 162, 144, 132, 115, 102, 71, 55, 43.

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2-Butyryl-1,4-naphthohydroquinone (4). The butyrate ester, 50 g (0.166 mol), was mixed with 60.0 g (0.45 mol) of anhydrous aluminum chloride to produce a brilliant yellow mixture which was added in small amounts with stirring to a 1-L beaker suspended in an oil bath heated to 115 °C. Heating was continued for 0.5 h after the last addition. The glossy solid produced by the reaction was ground to a fine powder which was added to 1.2 L of ice containing 60 mL of concentrated HCl. The mixture was extracted with diethyl ether. The ether solution then dried over $MgSO_4$ and evaporated to give 32 g of crude butyrylnaphthalenediol monobutyrate which was refluxed for 3 h in 350 mL of anhydrous methanol containing 5% dry hydrogen chloride. Water was added and the resultant mixture refluxed for another 3 h, poured onto cold ice water, and extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated to give a mixture of the desired hydroquinone and its 4-methyl ether. The hydroquinone was separated by fractional crystallization from chloroform to give 25.1 g (50%) of yellow crystals: mp 147–148.5 °C (lit.[5] mp 147–148 °C); IR (KBr) 3315, 1630 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 1.01 (t, 3 H), 1.75 (2 H, m), 3.02 (2 H, t), 7.20 (1 H, s), 7.90 (4 H, m), 8.70 (1 H, s), 13.23 (1 H, s), the last two resonances disappear upon addition of D_2O; mass spectrum, *m/e* 250, 229, 196, 186, 158, 131, 104, 102, 101, 76, 75, 51, 43.

2-Butyryl-1,4-naphthoquinone (1). The hydroquinone 4 (11.0 g, 0.048 mol) and 43.4 g of silver carbonate (adsorbed on Celite, assuming 1 mm of silver carbonate per 0.57 g of reagent is 0.076 mol of silver carbonate) was stirred at reflux under N_2 for 2 h in 1.5 L of dichloromethane. The mixture was filtered and washed three times with 100 mL of dichloromethane. The solvent was evaporated and the residue was recrystallized several times from petroleum ether (30–60 °C) to give 5.05 g (46%) of yellow needles: mp 54.5–55.5 °C (Lit.[5] mp 55–56 °C); IR(neat) 1695, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1./0 (3 H, t), 1.80 (2 H, m), 2.95 (3 H, t), 7.10 (1 H, s), 8.05 (4 H, m).

2,4-Dicarbethoxy-1-propyl-9,10-anthraquinone (2). To a solution containing 2.80 g (0.015 mol) of diethyl glutaconate and 1.89 g (0.008 mol) of 2-butyryl-1,4-naphthoquinone dissolved in 30 mL of methanol was added 10 mL of concentrated ammonium hydroxide. The reaction mixture turned brown. After 10 min, 100 mL of water was added and the mixture extracted three times with 100 mL of ether. The aqueous layer was acidified with dilute H_2SO_4 and extracted three times with 100 mL of ether. The ether solutions were dried ($MgSO_4$), filtered, and evaporated. A brown residue resulted from the basic extract which crystallized slowly on standing. This material was recrystallized from acetone to give 1.05 g (33%) of the light yellow anthraquinone: mp 77.5–79 °C; IR (KBr) 1730, 1670 cm^{-1}; mass spectrum, *m/e* 394, 365, 349; ^{1}H NMR (CCl_4) δ 1.1 (3 H, t), 1.4 (6 H, t), 1.6 (2 H, m), 3.35 (2 H, t), 4.45 (4 H, q), 7.75–8.1 (5 H, m); ^{13}C NMR ($CDCl_3$) 14.0 (q), 14.6 (q, 24.5 (t), 33.3 (t), 62.0 (t), 126–147 (aromatic carbons), 167.0 (s), 169.0 (s), 169.0 (s), 182.5 (s), 184 (s). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.02; H, 5.63; Found: C, 70.23; H, 5.78.

Registry No. 1, 65781-70-6; 2, 74007-41-3; 3, 40036-53-1; 4, 72827-02-2; 1,4-naphthoquinone, 130-15-4; butyric anhydride, 106-31-0; diethyl glutaconate, 2049-67-4.

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Stereochemistry in the Reduction of Vinyl Bromides with Lithium Aluminum Hydride

Sung-Kee Chung

Department of Chemistry, Texas A&M University,
College Station, Texas 77843

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Complex metal hydrides such as lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) have proven to be extremely versatile reagents for the reduction of a wide variety of organic functional groups.[1] Although they are generally believed to react as nucleophilic hydride donating species, the detailed mechanistic picture of the reduction is far from clear, especially in the reduction of aryl, vinyl, bridgehead, and cyclopropyl halides which are normally inert to the S_N processes.[2] In a recent report we have shown that $LiAlH_4$ reduction of aryl bromides proceeds most likely via a radical mechanism. We have further suggested that the metal hydride might serve not only as an efficient hydrogen atom donor to the radical intermediate but also as an electron-transfer reagent in the initial production of the radical.[3] As an extension of this mechanistic scheme, we have now examined the stereochemical outcomes in the $LiAlH_4$ reduction of vinyl bromides.

Table I

run	substr	molar ratio of $LiAlD_4$/substr	conditions[a]	d_1/d_0[b]	ratio of 4a/4b[c]
1	1a (trans)	4.0	ether, rt	63/37	50/50
2[f]	1a	8.0	ether, rt	77/23	48/52
3[f]	1a	4.0	THF, rt	59/41	52/48
4	1a	4.0	THF, Δ	60/40	90/10
5	1a	4.0[d]	THF, Δ	5/95	
6	1a	1.05[e]	benzene, Δ	72/28	50/50
7	1a	5.0[e]	benzene, Δ	76/24	50/50
8	1a	2 mmol of 1a, 1 g of Zu-Cu	EtOD, Δ (10 mL)	72/28	95/5
9	1b (cis)	4.0	ether, rt	65/35	48/53
10	1b	4.0	THF, rt	55/45	50/50
11[f]	1b	4.0	THF, Δ	56/44	16/84
12	1b	4.0[d]	THF, Δ	2/98	

[a] Reactions were run under an Ar atmosphere at a 0.1 concentration of the substrate for periods well over half the reaction time; rt = room temperature. [b] Determined by mass spectral analysis on a Hewlett-Packard GC/MS data system, Model 5982-A, and corrected for the amount of natural abundance of M + 1. [c] Determined by NMR analysis and corrected for the amounts of styrene-d_0 present based on the ratios of d_1/d_0. [d] $LiAlH_4$ was used, and the reaction was quenched by addition of D_2O. [e] $(n\text{-Bu})_3SnD$ was used. [f] Averaged values of d_1/d_0 and 4a/4b from two runs.

The energy barrier of the configurational inversion for the vinyl radical has been determined to be ca. 2 kcal/mol by kinetic ESR experiments,[4] and the value is comparable to 4.3 kcal/mol calculated by the semiempirical MINDO method.[5] On the other hand, the configurational stabilities of vinyl anions have long been established experi-

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