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A New Approach to the Functionalization of Phenanthrenequinone

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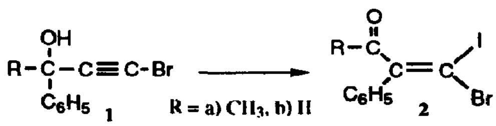
Abstract: The bromoethynyl adduct of fluorenone was converted to 10-((Z)-bromoiodomethylidene)phenanthren-9-one by means of the iodonium-generating reagent, iodine and Koser's reagent.

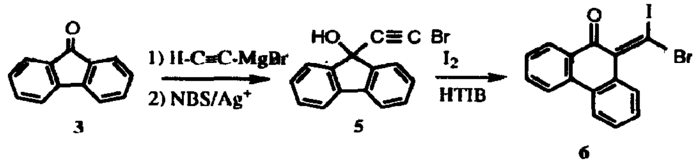
Mixed β,β-dihaloenones represent stepping stones to a wide variety of diaryl or dialkyl enones by means of organometallic exchanges catalyzed by palladium complexes.[1] Lately we have found a facile methodology for the generation of β,β-bromoiodoenones from ketones which have been converted to bromoethynyl adducts, which in turn are treated with iodine and stoichiometric amounts of Koser's reagent (HTIB, [hydroxy(tosyloxy)iodo]benzene)[2] or N-iodosuccinimide and catalytic amounts of HTIB. Examples of such conversions for linear systems are the conversion of 4-bromo-2-phenyl-3-butyn-2-ol (**1a**) to (Z)-4-bromo-4-iodo-3-phenyl-3-buten-2-one (**2a**) and the change of 3-bromo-1-phenylpropynol (**1b**) to (Z)-3-bromo-3-iodo-2-phenylpropenal (**2b**).[3,4]



Extensions to bromoethynylcyclopentanol ring expansions were successful.[5] A bicyclic systems based on camphor also led to a ring expansion.[6] In all cases the reactions proceeded in high yields and the principal product was the (Z)-isomer, the iodo atom syn to the carbonyl. Attempts to derive the (E)-isomers by bromination of an iodoalkynol led to mixtures wherein the (Z)-isomer predominated.

In this paper we present the results of the bromoethynyl adduct of fluorenone, which leads to a functionalized phenanthrenequinone. Data supports a ring expansion. This should not be viewed as an obvious extension since the iodinating agents such as iodine and HTIB have the capability of iodinating aromatic rings.[7] Furthermore, the constrained nature of fluorenol's ring could complicate the process of aryl shifts.

Fluorenone (**3**) was treated with ethynylmagnesium bromide to form the known 9-hydroxy-9-ethynylfluorene (**4**).[8] This compound was converted in 87% yield to the bromoalkynol **5** by N-bromosuccinimide (NBS) and catalytic amounts of silver nitrate in acetone.[9] Analytical data for the white crystalline **5** were as follows: mp. 122-4°C; anal, CH; ^{1}H-NMR (CDCl$_3$) δ multiplets at 7.70, 7.66, 7.62, 7.59, 7.43, 7.40, 7.37, 7.34, 7.30 and a singlet at 2.5; ^{13}C-NMR (CDCl$_3$) δ 146.83, 139.52, 130.34, 129.08, 124.74, 120.74, 80.42, 76.52, 44.84; IR (nujol) 3540 (s, -OH), 2200 (m, -C≡C-Br), 1610 (m), 1070 (s), 1020 (m), 900 (m), 770 (s), 750 (s) cm^{-1}; GC/MS, m/z (rel. int.) 180 (100, (M-HC≡C-Br)$^{+}$), 152 (50). The ^{1}H-NMR spectrum of **5** differed from that of **4** in the loss of the alkynyl proton at 2.71 ppm but its ring multiplets had the same shapes as those of **4** but were shifted upfield by 0.02 to 0.03 ppm. Similar slight differences of the aromatic carbons of **4** and **5** were noted in the ^{13}C-NMR spectra. The noteworthy differences of the IR spectra was the amplification of the alkynyl stretch of **5** due to the presence of bromine atom.



With **5** in hand, treatment with iodine and HTIB followed to afford a yellow solid melting at 131-3°C in 85% yield. Characterization of the principal product as 10-((Z)-bromoiodomethylidene)phenanthren-9-one (**6**) was based on the following data: anal. CH; ^{1}H-NMR ($CDCl_3$) δ multiplets at 8.07, 8.03, 7.98, 7.94, 7.91, 7.87, 7.83, 7.80, 7.09, 7.65, 7.61, 7.49, 7.45, 7.42, 7.38, 7.36, 7.32, 7.27; ^{13}C-NMR ($CDCl_3$) δ 190.39, 159.41, 144.97, 136.84, 135.02, 131.30, 130.85, 130.58, 130.18, 129.01, 127.97, 125.07, 123.69, 60.08; IR (nujol) 1670, 1590, 1530, 1270, , 1230, 1080, 1040, 940, 760, 745, 720 cm^{-1}; GC/MS, m/z (rel. int.) 410/412 (20, M$^+$), 283/285 (25, (M-I)$^+$), 255/257 (20, (M-I-CO)$^+$), 176 (100). The IR spectrum displays the unsaturated enone and is in agreement with the value of 1678 cm^{-1} reported for the related 10-(dibromomethylidene)phenanthren-10-one.[10] That there was a ring expansion of **5** to **6** received chemical proof when it was noted that ozonolysis of **6** afforded phenanthrenequinone **7**. Matches with authentic material were made by IR spectrum (1678 and 1595 cm^{-1}), ^{1}H-NMR (multiplets at 8.21, 8.17, 8.04 8.00, 7.76, 1.72, 7.68, 7.51, 7.47, 7.43, 7.26) and GC/MS (208 (20, M$^+$), 180 (100, M-CO)$^+$, 152 (50). The assignment of the (Z)-stereochemistry is based on all the reactions to date with iodonium-induced shifts or ring expansions.[3-6] Shifts occur *anti* to the iodine atom.

The value of **6** as a synthon rests on its flexibility via organometallic exchanges to generate compounds related to the anticancer therapeutic tamoxifen.[11] It provides entries into other substituted polynuclear aromatic hydrocarbons whose bases are phenanthrenes.

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