resemblance to that of its progenitor **1**, and is formed via a sequence of steps (cf. Scheme I), each of which requires substantial atomic motion and molecular deformation.

We are currently extending our studies on unimolecular solid-state photoprocesses in the hope of finding additional examples of this intriguing phenomenon.

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(10) A variation of this mechanism involves cleavage of the C_4–C_{4a} bond of **4** *prior* to C_2–C_6 bonding. A referee has pointed out that **2** can also be formally derived from **1** via initial C_2–C_6 bonding followed by 1,4-biradical cleavage and cyclization of the resulting ketene. Irradiation of **1** in methanol, however, affords no ketene-derived product; only **2** is produced.
(11) Irradiation of **1** at −25 to −30 °C in hexane gave results identical with those observed in solution at room temperature thus indicating that the solution/solid-state reactivity differences do not arise from the different temperatures employed.
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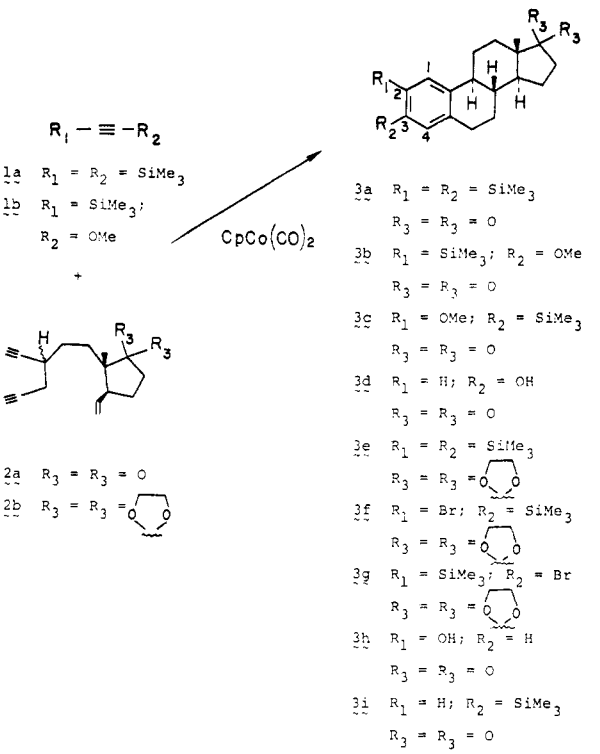
The Cobalt Way to *dl*-Estrone, a Highly Regiospecific Functionalization of 2,3-Bis(trimethylsilyl)estratrien-17-one

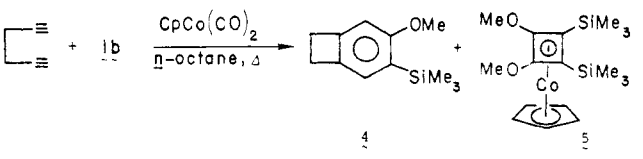
Sir:

The recent literature reveals several approaches to the A-ring aromatic steroid nucleus based on novel BC ring construction via intramolecular cycloadditions to *o*-xylylenes derived from benzocyclobutenes or other precursors.[1] None of these provides an efficient route to the female sex hormone estrone, a prime target in this class of compounds as a synthetic relay point to contraceptive drugs and a challenging structure on which to measure the utility of modern synthetic methodology.



We had recently described[1c] a transition metal catalyzed route to the series based on the cobalt-mediated cooligomerization[2] of bis(trimethylsilyl)acetylene (BTMSA, **1a**) with 1,5-hexadiyne **2a** which provided the one-step construction of rings ABC of the steroid nucleus with essentially complete chemo-, regio-, and stereospecificity. This method appeared to suffer from a lack of convenient methodology to convert the final silylated steroid **3a** into phenolic derivatives, for example the title compound **3d**. We report two solutions to this problem, the first based on the cobalt-catalyzed partially regiospecific cotrimerization of alkoxyacetylene **1b** with **2a** and the second on the highly regiospecific functionalization of bis silyl derivative **3a**.

Acetylene **1b**[3] (prepared from sodium methoxyacetylide generated in situ[4] and trimethylsilyl chloride in 62% yield) was considered a good candidate for cooligomerization with 1,5-hexadiynes since (similar to BTMSA[2]) it appeared to contain sufficient steric bulk to prevent efficient self-trimerization. However, when neat **1b** was cocyclized with 1,5-hexadiyne in



4 5

the presence of catalytic amounts of $CpCo(CO)_2$ under the usual conditions,[2] a quantitative conversion of catalyst to a single, complexed cyclobutadiene isomer **5** was observed.[5,6] The latter is catalytically inert as evidenced by the recovery of starting diyne. Employment of a (optimum) ratio of **1b**:diyne of 4:1 in *n*-octane resulted in the formation of some **4** (15%)[5,6] before all of the cobalt had been removed as **5**. The assignment of structure **5** rests on spectral data,[6] particularly the characteristic molecular ion fragmentation pattern.[7] We noticed an improvement in the outcome of this cyclization when diyne **2a**[1c] was employed in the presence of larger than catalytic amounts of $CpCo(CO)_2$ (>20 mol %). Cooligomerization[2] of **1b** with

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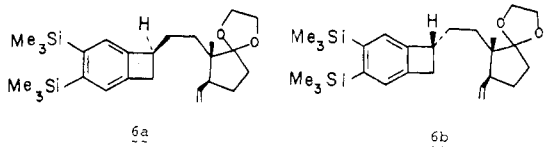
2a and exposure of the resulting mixture (containing intermediate benzocyclobutene regio- and diastereomers) to refluxing decane gave, in addition to **5** and recovered **2a** (52%), a 2:1 mixture of trimethylsilylmethoxyestratrienones **3b** and **3c**[5,6] in 31% yield after column chromatography (silica). Quantitative protodesilylation (1:1 CF_3CO_2H-CCl_4, room temperature, 5 h) furnished 2-methoxyestratrienone and *dl*-estrone methyl ether (ratio 2:1) identified by spectral data (*m/e*, 180-MHz ^1H NMR, ^{13}C NMR, IR) and comparison with authentic material.[10] Although both yield and regioselectivity of this cobalt-catalyzed direct approach to estrone derivatives are unsatisfactory, it would seem that improvements in the procedure might be attainable by choice of a more hindered alkoxyacetylene and a modified diyne precursor.

While the above method held promise, we turned our attention to bis silyl steroid **3a**, a potential estrone precursor if regioselective oxidative phenyl-silicon cleavage could be achieved. In a model system a Baeyer-Villiger approach was successful. Thus, 6,7-bis(trimethylsilyl)tetralin[2b,f] is readily and selectively converted to 6-trimethylsilyl-7-acetoxytetralin in two steps: (1) $CH_3C(=O)Cl$-$AlCl_3$-CCl_4;[2a] (2) $CF_3C(=O)OOH$-Na_2HPO_4 (77%).[5] To apply this sequence to **3a**, protection of the 17-keto function appeared desirable. Ketalization of **2a** ($HOCH_2CH_2OH$-toluene-*p*-TsOH, 24 h, 95%) gave **2b**[5,6] which was subsequently cyclized[1c,2d] in BTMSA (44-h addition) to result in the two diastereomeric benzocyclobutene isomers, **6a** (27.5%) and **6b** (29.1%) (stereochemistry assigned arbitrarily), and steroid **3e** (30%), separated by column chromatography.[5,6] On heating in decane,



6a 6b

either isomer **6a** or **6b** was transformed into **3e** in high yield. The latter was hydrolyzed to estra-1,3,5(10)-trien-17-one with CF_3CO_2H-H_2O. Interestingly, incomplete independent thermolysis of **6a** and **6b** showed that neither one of the two isomers is converted into the other (TLC), suggesting an appreciably lower barrier to intramolecular Diels-Alder reaction than to ring closure once the intermediate *o*-xylylene is generated.[8]

When **3e** was treated with $CH_3C(=O)Cl$-$AlCl_3$, a complex mixture of products ensued. However, bromination (2:1 Br_2-pyridine, CCl_4, room temperature[2a,f]) proceeded with remarkable regioselectivity to produce a mixture of **3f** and **3g** (4:1, based on NMR).[5] Chemical verification of the spectral assignment was obtained by treatment of the latter successively with *n*-butyllithium (1 equiv, THF, −78 °C, 10 min), trimethyl borate[9] (1 equiv, 0 °C, 45 min), CH_3COOH (1. 5 equiv, 1 min), and H_2O_2 (5 equiv, 45 min), separation (PTLC) and characterization[5] of the two resulting trimethylsilylhydroxyestratrienone ketals (68.4% overall combined yield), and subsequent treatment with acid to generate 2-hydroxyestratrienone **3h** (major isomer) and *dl*-estrone **3d**, both identified by their spectral characteristics[5,6] and comparison with authentic materials.[10]

The increased reactivity of the 2 position in **3a** *with respect to electrophilic attack*[11] *can be exploited in a selective dl-estrone synthesis.* Treatment of **3a** with CF_3CO_2H ($CDCl_3$-CCl_4) at −30 °C and monitoring the reaction by NMR gave on completion 3-trimethylsilylestra-1,3,5(10)-trien-17-one (**3i**)[5,6] with 9:1 selectivity (90% yield). Oxidative aryl-silicon cleavage occurs almost quantitatively on exposure to lead tetrakis(trifluoroacetate)[12] to provide *dl*-estrone **3d**. This constitutes the shortest racemic estrone synthesis known to date starting from a monocyclic or an acyclic precursor, respectively: five steps from 2-methylcyclopentenone in 24% overall yield and seven steps from 1,5-hexadiyne in 17% yield.[13] Moreover, it is clear that the cobalt-catalyzed appraoch to the steroid nucleus is readily applicable to A-ring phenolic derivatives. The synthesis of optically active steroids by this method requires an asymmetric synthesis of precursor **2** or modified synthetic methodology involving the cyclization of achiral substrates to chiral polycycles mediated by chiral and optically active metal complexes. Both strategies are under active investigation.

Acknowledgments. We are indebted to E. D. Sternberg for measuring high field NMR spectra and to Professors R. E. Connick and D. S. Noyce for helpful comments. This work was supported financially by the National Institute of Health (GM 22479), Chevron Research Co., and in part by the National Science Foundation, as well as materially by Pressure Chemical Corp., and Silar Laboratories.

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(6) **2b**: colorless liquid; *m/e* (rel intensity) 272 (M^+, 1%), 99 (93%), 55 (100%); ^1H NMR (60 MHz) (CCl_4) δ 5.80 (overlapping (5 lines) ddd, J = 17.5, 10, 9, 1 H), 5.0 (m, 1 H), 4.77 (m, 1 H), 3.81 (br s, 4 H), 2.33 (br s, 4 H), 1.7–2.0 (m, 10 H), 0.87 (s, 3 H); ^{13}C NMR (C_6D_6) δ 139.8, 119.8, 115.7, 86.4, 81.9, 70.4, 64.4, 64.0, 51.0, 48.0, 33.1, 32.6, 32.2, 32.1, 28.7, 25.3, 24.7, 15.7; $\nu_{C\equiv CH}$ 3340, 2155 cm^{-1}. **3b/3c**: colorless oil; *m/e* (rel intensity) 356.2178 (calcd 356.2182, M^+, 11%), 117 (100%); NMR (60 MHz) (CCl_4) δ 7.06 (br s, 0.66 H), 6.81 (br s, 0.33 H), 6.53 (br s, 0.33 H), 6.33 (br s, 0.66 H), 3.73 (br s, 3 H), 1.1–3.0 (m, 15 H), 0.86 (s, 3 H), 0.23 (s, 18 H); $\nu_{C=O}$ 1740 cm^{-1}. **3e**: colorless crystals; mp 109.5–111 °C; *m/e* (rel intensity) 442 (M^+, 13%), 99 (96%), 73 (100%); ^1H NMR (60 MHz) (CCl_4) δ 7.40 (br s, 1 H), 7.13 (br s, 1 H), 3.80 (br s, 4 H), 1.1–3.0 (m, 15 H), 0.83 (s, 3 H), 0.33 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 142.4, 139.6, 136.5, 136.2, 132.6, 119.4, 65.2, 64.5, 49.5, 46.2, 44.2, 38.9, 34.2, 30.8, 29.5, 27.0, 25.6, 22.4, 14.3, 2.48. **3h**: colorless crystals; mp 216–220 °C; *m/e* (rel intensity) 270.1616 (calcd 270.1620, M^+, 85%), 43 (100%); ^1H NMR (180 MHz) ($CDCl_3$) δ 6.94 (d, J = 8.5 Hz, 1 H), 6.75 (d, J = 2.3 Hz, 1 H), 6.60 (dd, J = 8.5, 2.3 Hz, 1 H), 2.82 (m, 3 H), 1.10–2.65 (m, 12 H), 0.89 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.8, 141.1, 129.9, 128.2, 113.0, 112.1, 50.5, 48.0, 44.5, 38.0, 35.9, 31.6, 29.4, 26.6, 25.7, 21.6, 13.8; ν_{OH} 3490 cm^{-1}, $\nu_{C=O}$ 1740 cm^{-1}. **3i**: colorless oil; *m/e* (rel intensity) 326.2060 (calcd 326.2066, M^+, 5%), 28 (100%); ^1H NMR (60 MHz) (CCl_4) δ 7.10 (m, 3 H), 1.1–3.0 (m, 15 H), 0.88 (s, 3 H), 0.24 (s, 9 H); ^{13}C NMR ($CDCl_3$) 140.4, 137.5, 135.7, 134.3, 130.8, 124.8, 50.6, 48.0, 44.5, 38.1, 35.9, 31.6, 29.4, 26.6, 25.6, 21.6, 13.8, −1.1; $\nu_{C=O}$ 1740 cm^{-1}. **4**: colorless liquid; *m/e* (rel intensity) 206 (M^+, 51%), 161 (100%); NMR (60 MHz) (CCl_4) δ 7.21 (br s, 1 H), 6.42 (br s, 1 H), 3.70 (s, 3 H), 3.04 (s, 4 H), 0.25 (s, 9 H). **5**: yellow crystals; mp 83.5–85 °C; *m/e* (rel intensity) 380 (M^+, 90%), 294 ($CpCoMe_3SiC_2SiMe_3$, 79%), 252 ($CpCoMeOC_2SiMe_3$, 31%), 73 (100%); NMR (60 MHz) (CCl_4) δ 4.73 (s, 5 H), 3.30 (s, 6 H), 0.21 (s, 18 H). **6a**: colorless oil; *m/e* (rel intensity) 442.2725 (calcd 442.2722, M^+, 12%), 99 (100%); NMR (60 MHz) (CCl_4) δ 7.22 (br s, 2 H), 5.69 (overlapping (5 lines) ddd, J = 18, 10, 9 Hz), 5.00 (m, 1 H), 4.91 (m, 1 H), 3.73 (br s, 4 H), 3.27 (m, 2 H), 2.63 (m, 2 H), 1.0–2.0 (m, 8 H), 0.84 (s, 3 H), 0.33 (s, 18 H). **6b**: colorless oil; *m/e* (rel intensity) 442.2712 (calcd 442.2722, M^+, 8%), 99 (100%); NMR (60 MHz) (CCl_4) δ 7.22 (br s, 2 H), 5.70 (overlapping (5 lines) ddd, J = 18, 10, 9 Hz, 1 H), 5.01 (m, 1 H), 4.83 (m, 1 H), 3.77 (br s, 4 H), 3.27 (m, 2 H), 2.62 (m, 2 H), 1.0–2.0 (m, 8 H), 0.86 (s, 3 H), 0.33 (s, 18 H).

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(13) This may be compared with the synthesis of *dl*-estrone methyl ether by Torgov,[14] six steps (18%) from 6-methoxy-1-tetralone and improvements thereof,[15] eight steps (27%) from 2-methoxynaphthalene (corresponding to ~45% from 6-methoxytetraline); the synthesis of *dl*-estrone by Johnson and Bartlett,[16] fourteen steps (6.9%) from *m*-hydroxycinnamic acid; and the synthesis of *d*-estrone by Danishefsky and Cain,[17] fourteen steps (7.4%) from 2,6-lutidine, or eleven steps (13%) from 2-methylcyclopentane-1,3-dione.
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(18) (a) Regents' Intern Fellow, 1975–1978; (b) Fellow of the Alfred P. Sloan Foundation, 1976–1980, and Camille and Henry Dreyfus Teacher-Scholar, 1978–1983.

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Substituent Effects in Addition of Carbanions to Arenechromium Tricarbonyl Complexes: Correlation with Arene LUMO

Sir:

The $Cr(CO)_3$ unit activates π-complexed arene ligands (in **1**) toward addition of nucleophiles, leading to analogues (**2**) of Meisenheimer complexes. Oxidation of **2** then gives substituted arenes, from formal replacement of hydride (eq 1).[2] In contrast to classical nuelcophilic aromatic substitution methods, this addition/oxidation pathway does not require a specific leaving group. In this sense, it is parallel with electrophilic aromatic substitution and raises anew the question of selectivity in additions to substituted arenes. The regioselectivity is particularly interesting here since the activating substituent, $Cr(CO)_3$, is symmetrically disposed with respect to the arene ring atoms and presumably activates each of them equally. Then even feeble perturbations from ring substituents could control the site of addition.

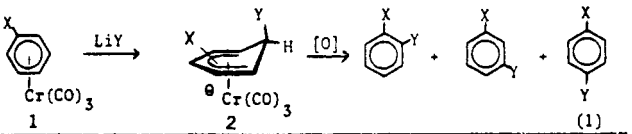
We reported the meta-directing effect (90–100% selective) of a methoxy group,[3] an apparently simple reversal of the usual directing influence in electrophilic substitution, and the less easily explained effect of a methyl group (5–50% ortho, 95–50% meta, 0% para[3]). Here we report reactions of substituted π-arene complexes (i.e., **1**) chosen to probe for factors which influence regioselectivity. Table I presents the results.[4] While we have not proven that the product mixtures are the result of kinetic control, shorter or longer reaction times (0.5 min at −78 °C to 24 h at 25 °C) do not alter the product ratios. With chlorobenzene, longer reaction times can lead to substituion for chloride,[5] but little is seen under the conditions employed here.

Chloride shows a directing effect similar to methyl: little para and similar amounts of ortho and meta (Table I, entries 3, 4, 6, 8) except for bulky anions, where meta is preferred (entries 5, 7). Trimethylsilyl and trifluoromethyl favor para, and naphthalene gives 99% α substitution. The more hindered position is favored with 1,2-dimethoxybenzene, even with a tertiary carbanion (entries 14, 15).[3] The para-directing effect of silicon and the meta-directing effect of methoxy can reinforce to produce a 1,2,3-substitution pattern (entry 18).[6] Steric effects seem to be comparable in magnitude with other directing effects.

A picture for the reaction pathway (**1** → **2**) which emphasizes polar effects is helpful in rationalizing many of the results. This view would take into account the expected electron polarization in **1** or the distribution of negative charge in the cyclohexadienyl unit in **2**. By the usual resonance arguments, the ortho and para positions are electronically similar, opposite from meta. However, the results with certain substrates (toluene, chlorobenzene, *o*-dimethoxybenzene) do not show similar reactivity at ortho and para positions and are not easily fit into this picture.

Table I. Addition/Oxidation of Carbanions with Substituted π-Arenechromium Tricarbonyl Complexes

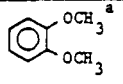
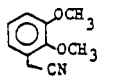
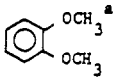
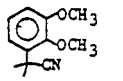
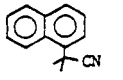
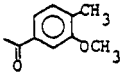
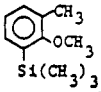
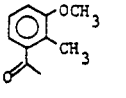
A. Monosubstituted Arene Ligands



1 2 (1)

Entry	Substituent (X)	Carbanion (LiY)	Product Ratios o:m:p (combined yield)
1	CH_3[a]	$LiCH_2CO_2R$	28:72:0 (89%)
2	OCH_3[a]	$LiCH_2CO_2R$	4:96:0 (93%)
3	Cl	$LiCH_2CO_2R$	54:45:1 (98%)
4	Cl	$LiCH(CH_3)CO_2R$	53:46:1 (88%)
5	Cl	$LiC(CH_3)_2CO_2R$	5:95:1 (84%)
6	Cl	$LiCH_2COC(CH_3)_3$	70:24:0 (87%)
7	Cl	$LiC(CH_3)_2CN$	10:89:1 (84%)
8	Cl	Li-(1,3-dithianyl)	46:53:1 (56%)
9	$Si(CH_3)_3$	$LiC(CH_3)_2CN$	0:2:98 (65%)
10	CF_3	$LiC(CN)(OR_1)CH_3$[b]	0:30:70 (33%)
11	$N(CH_3)_2$	$LiC(CH_3)_2CN$	1:99:0 (92%)
12	$C(CH_3)_3$	$LiC(CN)(OR_1)CH_3$[b]	0:35:65 (85%)
13	CH_2CH_3	$LiC(CN)(OR_1)CH_3$[b]	0:94:6 (89%)

B. Polysubstituted Arene Ligands

	Arene Ligand	Carbanion	Major Product (yield)
14		$LiCH_2CN$	 (41%)[c]
15		$LiC(CH_3)_2CN$	 (85%)[d]
16		$LiC(CH_3)_2CN$	 (83%)[e]
17			 (76%)[c]
18			 (82%)[c]

[a] These data are reproduced from ref 3 for comparison. [b] This anion (R_1 = 1-ethoxyethyl) was developed by G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **93**, 5286 (1971); the products are acetophenone derivatives (Y = $COCH_3$) resulting from hydrolysis of the cyanohydrin acetal unit. [c] No other isomers were detected. [d] The 1,2,4-substitution product was obtained in 12% yield. [e] The β-substituted isomer was detected, in 1% yield.

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