Synthesis of Nuclear Monobromobenz[a]anthracenes[1]

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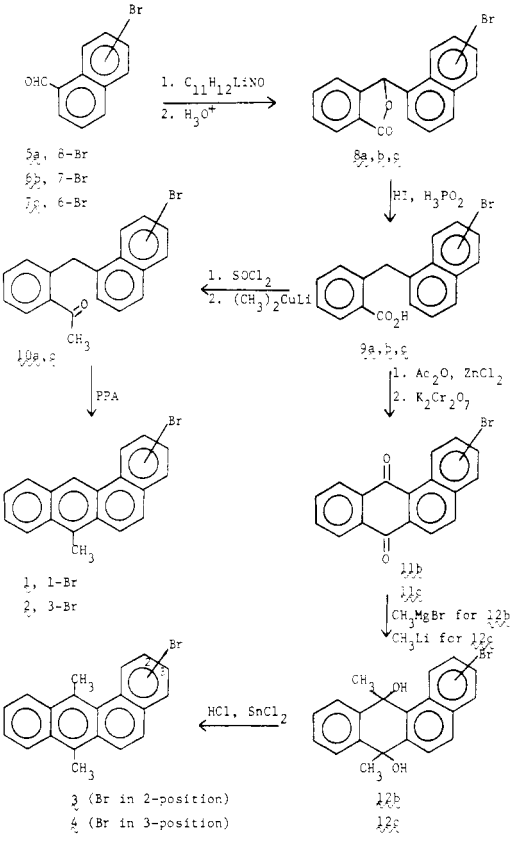
The reasons for synthesizing nuclear monobromo derivatives of methylated benz[a]anthracenes have been outlined.[3] Some difficulty in making these compounds arose from the failure of amino and hydroxy derivatives of benz[a]anthracenes to give bromo compounds as can be accomplished in the naphthalene series.[3] In this paper the syntheses of 1-bromo-7-methylbenz[a]anthracene, **1**, 3-bromo-7-methylbenz[a]anthracene, **2**, 2-bromo-7,12-dimethylbenz[a]anthracene, **3**, and 3-bromo-7,12-dimethylbenz[a]anthracene, **4**, are described.

The successful syntheses of **1**, **2** and **4**, and **3** stemmed from 8-bromo-1-naphthaldehyde, **5**, 6-bromo-1-naphthaldehyde, **7**, and 7-bromo-1-naphthaldehyde, **6**, respectively, by reactions with the lithium derivative of 4,4-dimethyl-2-phenyl-2-oxazoline[4] as shown in Scheme I.

The loss of bromine from lactones **8a–c** on reduction to **9a–c** was avoided by relatively short (4–5 h) treatment with anhydrous hydriodic–hypophosphorous acid in glacial acetic acid (see Experimental Section). In the conversion of **9a,c** to the methyl ketones **10a,c**, the use of methyllithium caused much loss of bromine. However, the reaction of the acid chlorides with lithium dimethylcuprate[5] gave high yields of the desired **10a,c**. Since treatment of **11b** with methyllithium resulted in almost complete loss of bromine, methylmagnesium bromide was used to afford a low yield of **12b**, which was converted[6] smoothly to **3**. Reaction of **11c** with methyllithium afforded **12c**, which was transformed into **4** by the use of $SnCl_2$–HCl.[6] The sensitivity of the bromine in **11b** toward methyllithium stands in marked contrast to the stability of the bromine in 4-bromo-7,12-benz[a]anthraquinone[3] and the fair stability of the bromine in **11c** in the same reaction. The bromo aldehydes **6b** and **7c** were prepared from 6-bromo-1-methylnaphthalene, **19**, and 7-bromo-1-methylnaphthalene[7] as described. 8-Bromo-1-naphthaldehyde, **5a**, was prepared from 8-bromo-1-naphthoic acid[8] (the synthesis of which has been improved) by treatment with borane–dimethyl sulfide–trimethyl borate reagent[9] at reflux in THF (no reaction at room temperature for 3.5 h) to yield (8-bromo-1-naphthyl)methanol. The latter could be oxidized in high yield to 8-bromo-1-naphthaldehyde by *N*-chlorosuccinimide–dimethyl sulfide reagent[10a] or by pyridinium dichromate.[10b]

Scheme I



Experimental Section[11]

3-(4-Bromophenyl)-1-butanol* (13). *p*-Bromoacetophenone was converted into 3-(4-bromophenyl)butanoic[12] acid in high overall yield as described[13] except that a better yield (82%) in the reaction of 1-(4-bromophenyl)ethyl bromide with diethyl sodiomalonate was obtained when run at 0–5 °C for 12 h with 0.001 mol of dicyclohexyl-18-crown-6 ether followed by 12 h at room temperature. Reduction of 3-(4-bromophenyl)butanoic acid with borane–dimethyl sulfide (no trimethyl borate used) gave pure **13**, bp 120–122 °C (0.4 mm), as a colorless viscous liquid: NMR ($CDCl_3$) δ 1.10–1.30 (d, 3 H, CH_3), 1.53–1.93 (q, 2 H, CH_2), 2.20–2.35 (d, H, OH), 2.50–3.03 (m, H, CH), 3.30–3.60 (t, 2 H, CH_2), 6.87–7.47 (m, 4 H, Ar H).

4-(4-Bromophenyl)pentanenitrile* (15). To a stirred solution of 22.90 g of **13** and 24 g of triethylamine in 120 mL of CH_2Cl_2 at 0–5 °C was added 12.6 g of mesyl chloride during 15 min. After 2h at this temperature the usual workup yielded 30.3 g (99%) of viscous **14**,[14] which was dissolved in 200 mL of dry acetonitrile containing 13 g of dry KCN and 3.7 g of dicyclohexyl-18-crown-6 ether. The mixture was stirred at room temperature for 4 h and refluxed for 2 h. After removal of the acetonitrile under vacuum the usual workup gave 22.3 g (93%) of **15**: bp 156–160 °C (0.9 mm); NMR ($CDCl_3$) δ 1.17–1.37 (d, 3 H, CH_3), 1.63–2.35 (m, 4 H, CH_2CH_2), 2.50–3.07 (m, H, CH), 6.93–7.53 (m, 4 H, Ar H).

4-(4-Bromophenyl)pentanoic Acid (16). Hydrolysis of 56.9 g of **15** with a solution of 90 g of KOH in 90 mL of water and 90

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(11) All compounds marked with an asterisk gave correct (±0.3%) analysis by the Galbraith Laboratories, Knoxville, TN. All compounds gave NMR, IR, and MS spectra consistent with the assigned structures. All melting points are uncorrected. The term "worked up in the usual way" means that ether–benzene solutions of the products were washed with alkali and/or acid and saturated salt solution and filtered through a cone of $MgSO_4$. The solvent was then distilled or rotary evaporated. All dry ether was distilled from butylmagnesium bromide.

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0022-3263/83/1948-2926$01.50/0

mL of ethanol for 2 days afforded 60.0 g, (97.7%) of **16**, mp 63–65 °C, good enough for the next step. The analytical sample, mp 67–68 °C, was obtained by one crystallization from hexane: *m/e* calcd for $C_{11}H_{13}BrO_2$ 256.009 938, found 256.010 614.

7-Bromo-1-oxo-4-methyl-1,2,3,4-tetrahydronaphthalene* (17). Cyclization of 62.0 g of **16** by heating in 650 g of PPA at 100 °C for 2 h yielded 49.7 g (86%) of **17**: mp 50–52 °C. Distillation afforded 43.1 g (75%) of pure **17**: mp 53–55 °C, bp 135–137 °C (0.2 mm).

7-Bromo-1-hydroxy-4-methyl-1,2,3,4-tetrahydronaphthalene (18). To a stirred solution of 2.52 g of $NaBH_4$ in 250 mL of methanol was added 20.0 g of **17** in three portions during 15 min. After 16 h at room temperature the methanol was vacuum evaporated. The usual workup yielded 19.8 g (98%) of **18**, mp 98–100 °C, good enough for the next step. A pure sample (mp 101–103 °C; *m/e* calcd for $C_{11}H_{13}BrO$ 240.015 024, found 240.015 466) was obtained by crystallization from benzene–petroleum ether (30–60 °C): no carbonyl absorption in IR.

6-Bromo-1-methylnaphthalene (19). A stirred solution of 19.8 g of **18** in 250 mL of benzene containing 1.6 g of *p*-toluenesulfonic acid was held at reflux for 2 h while allowing the water formed to distill, and then 40.7 g of chloranil was added in portions over 15 min. After refluxing for 24 h the cooled mixture was treated with 500 mL of hexane and filtered. The organic layer was washed with dilute NaOH containing some sodium hydrosulfite. After the usual workup there was obtained 16.4 g (89%) of crude **19**, which was vacuum distilled, bp 117–120 °C (0.6 mm), to give 14.9 g (81%) of **19**: *m/e* calcd for $C_{11}H_9Br$ 219.988 811, found 219.989 450; NMR ($CDCl_3$) δ 2.43 (s, 3 H, CH_3), 7.03–7.85 (m, 6 H, Ar H).

6-Bromo-1-(bromomethyl)naphthalene (20). A mixture of 11.05 g of **19**, 10.0 g of *N*-bromosuccinimide, 0.5 g of benzoyl peroxide in 300 mL of CCl_4 was refluxed for 6 h. The cooled mixture was filtered and the filtrate passed through a short column of alumina. After removal of the CCl_4, the residue, 13.65 g (91%) of **20** (mp 105–107 °C) was used in the next step. The analytical sample (*m/e* calcd for $C_{11}H_8Br_2$ 297.899 377, found 297.899 939; mp 109–110.5 °C) was obtained by one crystallization from benzene–petroleum ether (bp 30–60 °C).

6-Bromo-1-naphthaldehyde (7c). A mixture of 6.20 g of hexamethylenetetramine and 12.0 g of **20** in 48 mL of $CHCl_3$ was warmed to reflux for 90 min. After cooling and filtration the solid adduct was collected and held at reflux in 48 mL of 50% acetic acid for 90 min. Chromatography of the product, isolated in the usual way, over a short column of silica gel using benzene yielded 6.7 g (71%) of **7c**: mp 73–74 °C; *m/e* calcd for $C_{11}H_7BrO$ 233.968 076, found 233.968 835.

3-(6-Bromo-1-naphthyl)phthalide (8c). To a stirred solution of 3.50 g of 4,4-dimethyl-2-phenyl-2-oxazoline in 100 mL of dry ether at −10 to −5 °C under nitrogen was added 17.2 mL of *n*-butyllithium (1.4 M) in hexane. After 4 h at this temperature was added 4.7 g of **7c** in 40 mL of THF in one portion. After 1 h at −5 °C the mixture was left at room temperature for 16 h. The usual workup afforded 8.75 g of an oily product which was heated in 90 mL of 95% alcohol containing 10 mL of concentrated H_2SO_4 for 16 h. On cooling, 4.62 g (68%) of **8c**, mp 134–135 °C, suitable for further work was obtained. The analytical sample, mp 136–137 °C, was obtained by one crystallization from benzene–heptane: *m/e* calcd for $C_{18}H_{11}BrO_2$ 337.994 284, found 337.995 356.

***o*-[(6-Bromo-1-naphthyl)methyl]benzoic Acid* (9c).** To a stirred solution of 60 mL of 57% HI and 30 mL of H_3PO_2 at room temperature was added with some cooling 270 mL of acetic acid containing 140 mL of acetic anhydride followed by 5.0 g of **8c**. After refluxing for 5 h the clear solution was cooled and diluted with 500 mL of water. The precipitate was collected and dissolved in 100 mL of 5% K_2CO_3 and this solution was poured on excess HCl to yield 4.7 g (93%) of pale yellow **9c**, which on crystallization from benzene–hexane yielded 4.45 g (88%) of pure **9c**: mp 173–174 °C; *m/e* calcd for $C_{18}H_{13}BrO_2$ 340.009 938, found 340.010 633.

***o*-[(6-Bromo-1-naphthyl)methyl]acetophenone (10c).** To the acid chloride formed by heating for 18 h 1.02 g of **9c** with 1.07 g of thionyl chloride in 30 mL of CH_2Cl_2 containing a drop of DMF was added the lithium dimethylcopper reagent made from 13.9 mL of 1.4 M methyllithium reagent and 1.7 g of cuprous iodide[5] in 35 mL of ether at −5 °C during 4–10 min. After 15 min the mixture was treated with 9 mL of methanol and worked up as usual to yield 0.82 g of oily **10c** after chromatography over silica gel, using hexane–benzene: *m/e* calcd for $C_{19}H_{15}BrO$ 338.030 673, found 338.031 522.

3-Bromo-7-methylbenz[*a*]anthracene* (2). A mixture of 800 mg of **10c** and 20 mL of PPA was held at 100 °C for 2 h. The usual workup afforded, after chromatography of the crude product over silica gel and crystallization from alcohol–CH_2Cl_2, 528 mg (70%) of pale yellow plates of **2**: mp 164–165 °C.

8-Bromo-1-naphthoic Acid. A solution of 340 g of sodium bromide and 84 g of bromine in 620 mL of water was added during 2 h to a stirred suspension at 0 °C of 186 g of anhydro-8-hydroxymercuric-1-naphthoic acid[8] in 760 mL of acetic acid and 120 mL of water in a 5-L three-necked flask. The mixture was then heated to 100 °C for 2.5 h, cooled, and poured on ice. The solids were collected, washed well with water, dissolved in NaOH, filtered, and reprecipitated by addition to dilute HCl. The crude acid thus obtained (76.7 g, 60%) was well dried for conversion into the acid chloride.

8-Bromo-1-naphthaldehyde (5a). To a stirred refluxing solution under N_2 of 3.77 g of 8-bromo-1-naphthoic acid in 20 mL of dry THF and 10 mL of trimethyl borate was added during 20 min 18 mL of 2 M BH_3·Me_2S in THF.[9] After the mixture was held at reflux for 2.5 h, 15 mL of methanol was added and the product isolated as usual. From the alkaline extract there was recovered 0.31 g of starting bromo acid and 2.88 g (88% based on recovered acid) of (8-bromo-1-naphthyl)methanol, mp 81.5–83.0 °C, suitable for further use. On one recrystallization from cyclohexane a purer sample (mp 83–85 °C; *m/e* 235.984 598, calcd for $C_{11}H_9BrO$ 235.983 726) was obtained. In the best of several experiments 2.4 g of *N*-chlorosuccinimide in 60 mL of toluene was placed in a 100-mL three-necked flask with 1.35 mL of dimethyl sulfide[12] and cooled to −30 ± 5 °C. A solution of 2.13 g of (8-bromo-1-naphthyl)methanol in 20 mL of toluene was added during 30 min. After 4 h at −25 °C, 1.5 mL of triethylamine was added and the cooling bath was removed. After standing overnight at room temperature the solid was filtered and the filtrate rotary evaporated. The residue was taken into ether–benzene (filtration of solid) and worked up as usual (wash with dilute HCl) to yield a solid that gave only one spot on TLC. Chromatography over silica gel using CH_2Cl_2 afforded 1.882 g (89%) of **5a**: mp 82–85 °C; *m/e* 233.967 521, calcd for $C_{11}H_7BrO$ 233.968 076. The oxidation of (8-bromo-1-naphthyl)methanol could also be carried out by using pyridinium dichromate[10b] in almost as good a yield.

3-(8-Bromo-1-naphthyl)phthalide (8a). In an experiment the same as for **8c**, there was obtained 4.49 g (66%) of **8a**, mp 179–181 °C, suitable for further work. A sample recrystallized from heptane–benzene melted at 183–184 °C: *m/e* 337.995 092, calcd for $C_{18}H_{11}BrO_2$ 337.994 289.

***o*-[(8-Bromo-1-naphthyl)methyl]benzoic Acid (9a).** In an experiment analogous to that for **9c**, 3.00 g of **8a** was converted into 2.62 g (87%) of **9a**, mp 174–177 °C, suitable for further work. A purer sample (mp 177–179 °C; m/e 340.010 633, calcd for $C_{18}H_{13}BrO_2$, 340.009 938) was obtained by recrystallization from benzene–hexane.

***o*-[(8-Bromo-1-naphthyl)methyl]acetophenone (10a).** In the best of several attempts a solution of lithium dimethylcopper reagent was prepared from 7 mL of methyllithium (1.4 M) solution and 0.86 g of CuI in 20 mL of ether at 0 °C and was cooled to −78 °C under nitrogen. A solution of the acid chloride from 0.51 g of **9a**, prepared as described for **9c**, in 10 mL of ether was added during 5 min. After 20 min the mixture was quenched with 5 mL of methanol and worked up as usual to give 246 mg (48%) of oily ketone **10a** after column chromatography over silica gel, using 7:3 hexane–benzene: IR absorption at 1690 cm^{-1}; NMR ($CDCl_3$) δ 2.55 (s, 3 H, CH_3), 5.23 (s, 2 H, CH_2), 6.63–7.90 (m, 10 H, Ar H).

1-Bromo-7-methylbenz[*a*]anthracene* (1). A mixture of 240 mg of **10a** in 10 g of PPA was held at 100 °C for 3 h. After the usual workup there was obtained 202 mg (89%) of **1**: mp 144–146 °C. This was converted into a picrate, mp 136.5–138 °C, which was decomposed by chromatography over basic alumina, using benzene–heptane, and recrystallized from alcohol–CH_2Cl_2 to yield 0.11 g (48% based on **10a**) of **1**: mp 151.5–153.0 °C.

2-Bromo-7,12-benz[*a*]anthraquinone (11b). A solution of 4.6 g of **9b**,[3] 90 mL of acetic anhydride, 46 mL of acetic acid, and

0.9 g of $ZnCl_2$ was refluxed for 1 h, cooled, and treated with 10 mL of water, and 5.0 g of powdered $K_2Cr_2O_7$ was added at once. This mixture was refluxed for 1 h, then cooled, and poured into ice and 20 mL of concentrated H_2SO_4. After the usual workup and crystallization from benzene was obtained 4.1 g (90%) of yellow **11b**: mp 258–259 °C; *m/e* 335.979 286, calcd for $C_{18}H_9BrO_2$ 335.978 640.

2-Bromo-7,12-dihydro-7,12-dihydroxy-7,12-dimethylbenz[*a*]anthracene (12b). To a suspension of 1.00 g of **11b** in 40 mL of benzene and 10 mL of THF was added 7.2 mL of 2.5 M methylmagnesium bromide in ether (Aldrich) and the mixture was held at reflux for 16 h and worked up as usual to give 0.972 g (89%) of crude diol, which on trituration with 10 mL of benzene followed by washing with hexane gave 0.345 g (32%) of **12b**: mp 218–219 °C dec. In the IR there was strong OH absorption and no carbonyl band: *m/e* 353.018 597, calcd for $C_{20}H_{17}BrO_2$ 353.017 763.

2-Bromo-7,12-dimethylbenz[*a*]anthracene* (3). To the clear solution of 1.7 g of $SnCl_2$ in 30 mL of ether containing 1.5 mL of concentrated HCl was added 300 mg of **12b** in two portions during 5 min. After 20 min the mixture was worked up as usual, chromatographed over basic alumina, and crystallized from EtOH–CH_2Cl_2 to obtain 0.16 g (59%) of **3**: mp, 91–92.5 °C.

3-Bromo-7,12-benz[*a*]anthraquinone (11c). By treatment of 2.5 g of **9c** essentially as described for **9b** was obtained 2.20 g (89%) of **11c** (mp 219–220 °C; *m/e* 335.9764, calcd for $C_{18}H_9BrO_2$ 335.9785) after chromatography over basic alumina ($CHCl_3$).

3-Bromo-7,12-dimethylbenz[*a*]anthracene* (4). To a solution of 1.00 g of **11c** in 40 mL of THF under nitrogen was added 4.5 mL of 1.48 M methyllithium in ether. After 20 h at room temperature the mixture was treated with water and worked up as usual to yield a mixture containing dimethyl diol. A solution of the crude diol in 20 mL of ether was added to a stirred solution of 5.0 g of $SnCl_2$ and 3 mL of concentrated HCl in 20 mL of ether. After 20 min, the products, isolated as usual, were chromatographed over basic alumina to yield **4**, which was purified by vacuum sublimation to give 0.33 g (33% from **11c**) of **4**: mp 159–160 °C.

Registry No. 1, 86456-53-3; 1·picrate, 86456-54-4; 2, 86456-55-5; 3, 78302-37-1; 4, 78302-38-2; **5a**, 85864-82-0; **6b**, 81830-59-3; **7c**, 86456-56-6; **8a**, 86456-57-7; **8b**, 86470-91-9; **8c**, 86456-58-8; **9a**, 86456-59-9; **9a** (acid chloride), 86456-73-7; **9b**, 81846-82-4; **9c**, 86456-60-2; **9c** (acid chloride), 86456-72-6; **10a**, 86456-61-3; **10c**, 86456-62-4; **11b**, 49600-95-5; **11c**, 78302-29-1; **12b**, 86456-63-5; **12c**, 86456-64-6; **13**, 20005-55-4; **14**, 86456-65-7; **15**, 86456-66-8; **16**, 31042-07-6; **17**, 51644-34-9; **18**, 86456-67-9; **19**, 86456-68-0; **20**, 86456-69-1; **20**·hexamethylenetetramine, 86456-70-4; *p*-bromoacetophenone, 99-90-1; 3-(4-bromophenyl)butanoic acid, 53086-46-7; 1-(4-bromophenyl)ethyl bromide, 24308-78-9; diethyl malonate, 105-53-3; diethyl 2-[1-(4-bromophenyl)ethyl]malonate, 59771-11-8; 4,4-dimethyl-2-phenyl-2-oxazoline, 19312-06-2; 6-bromo-α-[2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]-1-naphthalenemethanol, 86456-71-5; 8-bromo-1-naphthoic acid, 1729-99-3; anhydro-8-hydroxymercuric-1-naphthoic acid, 6314-27-8; (8-bromo-1-naphthyl)methanol, 14938-58-0; methyl bromide, 74-83-9.

Molecular Geometries and Relative Stabilities of Acyclic π-Conjugated C_6H_8 Dianions. A Simple Prediction and ab Initio Molecular Orbital Study

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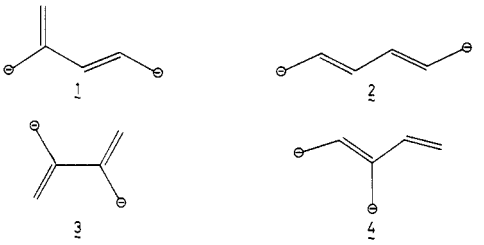
π-Conjugated dianions of acyclic hydrocarbons were recently subjected to theoretically and experimentally rigorous investigations.[1-8] The stability of the cross-conjugated trimethylenemethane dianion relative to the linearly conjugated butadiene dianion has been well established.[1-5] Attention is here concentrated on the relative stabilities and molecular geometries of the higher homologues. All isomers of acyclic C_6H_8 conjugated dianions, **1–4**, have been prepared by Bates et al.[5-7]



Recently, we showed[4] that *acyclic* conjugated molecules contain *cyclic* interactions among the orbitals of the component systems such as lone-pair electrons and bonds and that the extent of the electron delocalization is under the control of the orbital-phase continuity–discontinuity properties. The phase requirements for the delocalization are the same as those in cyclic conjugated systems: (i) the electron-donating (occupied) orbitals out of phase; (ii) the electron-accepting (unoccupied) oribitals in phase; (iii) the donating and accepting orbitals in phase. Two principles important for the present purpose can be drawn from the requirements. The electron delocalization from the geminal anionic centers to the double bond is favored by the orbital phase continuity as was shown for trimethylenemethane dianion while that from the vicinal ones as in butadiene dianion is disfavored by the phase discontinuity.[4] The difference is produced by the bond polarization allowed in the trimethylenemethane dianion and forbidden in the butadiene dianion. The electron delocalization from the anionic center to a distant bond across another is favored by the phase continuity for linear conjugation while disfavored by the phase discontinuity for cross-conjugation.

There are a number of Kekulé structures for each isomer. The two anionic centers are assumed to be separated from each other as far as possible in the main Kekulé structures as shown by **1–4**.[9] All contain butadiene structures with anionic centers in the different positions. The degree of electron delocalization is primarily determined by the delocalization of anionic lone-pair electrons to the adjacent double bonds. This delocalization is not restricted by the orbital-phase properties except for **4**. The Kekulé structure **4** contains a butadiene dianion unit where the delocalization is disfavored (the first principle). Therefore, **4** is predicted to be the least stable dianion. Secondarily, the whole delocalization is determined by the distant delocalization of the anionic lone pairs beyond a bond. The distant delocalization is depressed by the cross-conjugation for both anionic lone pairs in **3**, for one in **1**, and for neither in **2** (the second principle). The stability is then expected to increase in the order **3** < **1** <

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