136 (100), 84 (23); ^{1}H NMR ($CDCl_3$) δ 7.3-8.0 (m, Ph, 5 H), 0.7-1.5 (m, CH_3, 12 H). Pyridine was distilled over CaH_2.

The laser flash photolysis setup uses a crossed-beam arrangement. The sample, in a 10- × 10-mm cell, was excited at 355 nm by single light pulses (200 ps; 5-30 mJ) provided by a frequency tripled mode-locked Nd-YAG laser (Quantel). The detection system (pulsed Xe arc, monochromator, photomultiplier, and Tektronix 7912 transient recorder) has a response time around 4 ns.

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Registry No. 1, 139409-05-5; 2, 139409-06-6; TME, 563-79-1; (trichloroethenyl)benzene, 700-60-7; 1-chloro-1-(α,α-dichlorobenzyl)-2,2,3,3-tetramethylcyclopropane, 139409-07-7; pyridine, 110-86-1; (α,β,β-trichlorophenethyl)pyridinium ylide, 139409-08-8.

Tandem-Addition Rearrangements in the Reaction of 2-Butenoic Acid and *N*-(4-Methoxyphenyl)-2-butenamide with Methyl-Substituted Benzynes

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We[1] showed recently that *N*-(4′-methoxyphenyl)-2-butenamide dianion (**1**) and 2-butenoic acid (crotonic acid) dianion (**2**) react with various methoxy-substituted arynes to yield the corresponding 4-aryl derivatives of 3-butenoic acid, presumably by the usual aryne arylation mechanism. We report herein that these dianions also react with the methyl-substituted benzynes, i.e., 3,6-dimethylbenzyne (**3a**) and 3,4,5,6-tetramethylbenzyne (**3b**), to give predominantly rearranged cyclic products. Thus, treatment of 1 equiv of **1** in THF, prepared from equivalent molar amounts of *N*-(4′-methoxyphenyl)-2-butenamide and LDA, with aryne **3a**, generated from LDA (2 equiv) and 2-chloro-1,4-dimethylbenzene (1 equiv) (−50 °C to room temperature) yields the *N*-(4′-methoxyphenyl)-2-carboxamide of 4,7-dimethyl-1-(2′,5′-dimethylphenyl)indan **5a** (51%) and an inseparable 1:1 mixture of propenamide **6a** and *N*-(4′-methoxyphenyl)-3-butenamide (6% overall yield), after proton quench. Additionally, **1** reacts with 3,4,5,6-tetramethylbenzyne (**3b**) to give the rearranged 2-propenamide (**6b**) (55%); however, no indan derivative analogous to **5a** was observed. The IR, ^{1}H NMR, ^{13}C NMR, and mass spectra of rearranged products are consistent with proposed structures. Single-crystal X-ray crystallography[2] further supports the structure of indane **5a** whose ORTEP[3] plot is shown in Figure 1.

A possible mechanism for the formation of the rearranged products **5** and **6** is shown in Scheme I. Accordingly, dianion **1** adds to aryne **3** to give the usual aryne–nitrile anion adduct **8**. This initially formed adduct then undergoes a 5-*exo*-*trig*[3] cyclization to the benzocyclobutane intermediate **9**, which yields the rearranged benzyl dianion **10** upon ring opening. This tandem-addition rearrangement (TAR) sequence is similar to that proposed by

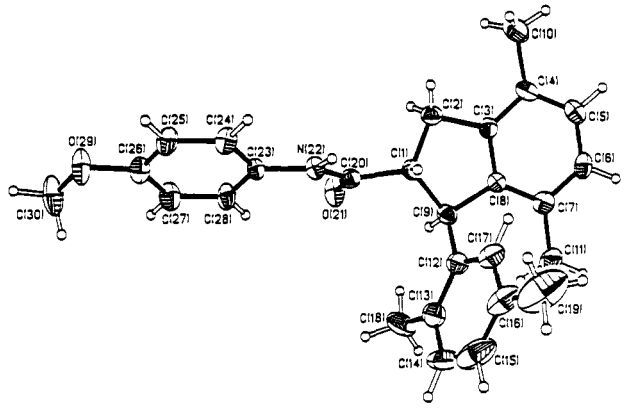

Figure 1. ORTEP plot of compound **5a**.

Meyers[4] and extensively studied by our group.[5] The rearranged dianions are converted either exclusively (in the case of **10b**) or partly (in the case of **10a**) to the appropriate 3-aryl-2-propenamide **6**, after proton quench. The dianion **10a** undergoes a 5-*endo*-*trig*[3] cyclization to yield indan dianion **11**,[6] which upon addition of another molecule of **3** and proton quench supplies indan **5a**. The inability of **10b** to yield an indan derivative similar to **5a** probably reflects the decreased stability of the CH_2Li group in **10b** when compared to that in **10a** which is brought about by the greater number of electron-donating methyl groups in former when compared with the latter. Furthermore, the greater propensity of the methyl-substituted arynes **3a** and **3b**, when compared with the methoxy-substituted arynes, to participate with dianion **1** in the tandem-addition rearrangement pathway most likely reflects the greater nucleophilicity of the 2-lithiated cyclization site of the initially formed adduct **8**, engendered by the electron-donating methyl groups on the benzene ring.

2-Butenoic dianion **2** also reacted readily with aryne **3a** to give predominantly 5,8-dimethyl-2-naphthol (**12a**) (50%) and trace amounts (<3%) of 4-(2,5-dimethylphenyl)-3-butenoic acid; neither an indane derivative analogous to **5a** nor a 3-(2,3,6-trimethylphenyl) derivative of 2-propenoic acid was obtained. The reaction of **2** with **3b** gave mainly intractible tars from which a small quantity of 5,6,7,8-tetramethyl-2-naphthol (**12b**) (8%) could be extracted. The formation of the 2-naphthols indicates that the benzocyclobutane intermediates **13a** and **13b** open directly to the dihydronaphthalenes **14a** and **14b**, respectively, which are converted to the respective 2-naphthols **12a** and **12b** by well-established pathways (Scheme II). The greater tendency for the ring intermediates derived from crotonic acid dianions (**13a** and **13b**) to form naphthalene derivatives when compared with those derived from *N*-(4-methoxyphenyl)-2-butenamide (**10a** and **14b**) most likely reflects the greater electrophilicity of the carbonyl group of the acid when compared with that of the amide. Attempts to isolate the conjugate acid of indane **11** by periodic trapping were unsuccessful.

In conclusion, we have extended the TAR reaction to include α,β-unsaturated amides and acids and have uncovered novel chemistry of the key benzocyclobutane ring

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(2) Crystal data for $C_{27}H_{29}NO_2$ (**5a**): monoclinic $P2_1/c$, a = 9.429 (2) Å, b = 26.588 (7) Å, c = 9.705 (3) Å, β = 110.32 (2)°, V = 2282 Å^3, Z = 4, D_c = 1.16 g cm^{-3}, R = 0.052, R_w = 0.060 for 1281 reflections [$I \geq 3\sigma(I)$] collected on a Nicolett $R3m/\nu$ diffractometer with graphite-monochromated Mo Kα radiation.

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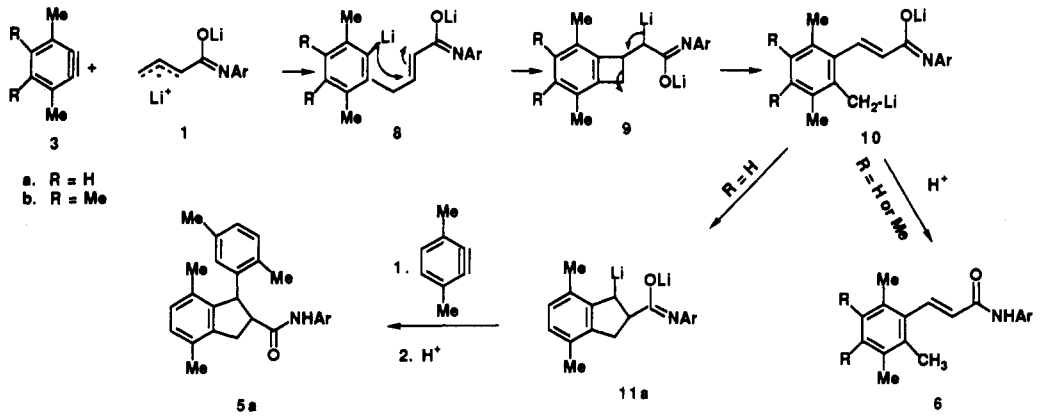
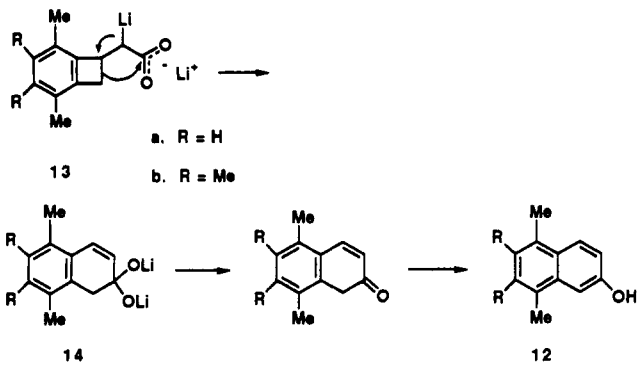
Scheme I



Scheme II



dianion intermediates proposed in these reactions.

Experimental Section

Melting points were determined on an electrothermal apparatus and are uncorrected. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (200 MHz) spectra were obtained in $CDCl_3$, and the chemical shifts were related to TMS. E. Merck silica gel 9385 (230–400 mesh) was used for flash chromatography. THF and *i*-Pr_2NH were obtained from Aldrich Chemical Co. and were thoroughly dried and distilled prior to use. Most of the other organic starting materials were also obtained from Aldrich Chemical Co. 2-Bromo-1,4-dimethyl benzene,[5c] 1-bromo-2,3,4,5-tetramethylbenzene,[5c] and *N*-(4-methoxyphenyl)-2-butenamide[1] were on hand from previous studies.

General Procedure for the Reaction of Dianions 1 and 2 with Arynes 3a,b. The reactions were carried in the usual way,[1] and the products were obtained in pure form by flash chromatography using a 5:95 mixture of acetone/hexane as eluent.

***N*-(4-Methoxyphenyl)-4,7-dimethyl-1-(2′5′-dimethylphenyl)indan-2-carboxamide (5a)**: yield 503 mg, 51%; mp 210–211 °C, ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3 H), 2.20 (s, 3 H), 2.32 (s, 3 H), 2.38 (s, 3 H), 3.10 (m, 1 H), 3.30 (s, 2 H), 4.9 (bd, 1 H), 6.8–7.1 (m, 7 H), 7.3 (d, 2 H, *J* = 8 Hz); IR ($CDCl_3$) 3428, 1681, 1598, 1513 cm^{-1}. Anal. Calcd for $C_{27}H_{29}NO_2$: C, 81.16; H, 7.31, N, 3.50. Found: C, 81.31; H, 7.39; N, 3.45.

***N*-(4-Methoxyphenyl)-3-(2,3,4,5-pentamethylphenyl)-2-propenamide (6b)**: yield 178 mg, 55%; mp 237–238 °C; ^{13}C NMR ($CDCl_3$) δ 16.39, 16.77, 17.88, 55.42, 114.18, 121.72, 126.99, 131.20, 132.61, 133.04, 134.77, 135.80, 143.59, 156.56, 163.60; IR ($CHCl_3$) 34331, 1670, 1597, 1512 cm^{-1}. Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67, H, 10.02, N, 5.57. Found: C, 71.98, H, 10.14, N, 5.75.

5,8-Dimethyl-2-naphthol (12a): yield 860 mg, 50%; mp 112–113 °C; ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 2.61 (s, 3 H), 5.07 (s, 1 H), 7.06–7.17 (m, 3 H), 7.29 (s, 1 H), 7.81 (d, 1 H, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 19.31, 107.22, 116.71, 124.17, 126.76, 127.02, 128.14, 130.88, 132.35, 152.96; IR ($CHCl_3$) 3328, 1592, 1458 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.32. Found: C, 83.91; H, 7.39.

5,6,7,8-Tetramethyl-2-naphthol (12b): yield 18 mg, 8%; mp 115–117 °C; ^{1}H NMR δ 2.38 (s, 3 H), 2.40 (s, 3 H), 2.52 (s, 3 H), 2.58 (s, 3 H), 7.04 (d, 1 H, *J* = 9 Hz), 7.33 (d, 1 H, *J* = 2 Hz), 7.94 (d, 1 H, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 15.30, 17.08, 17.46, 106.96, 115.81, 126.36, 126.89, 127.30, 128.75, 130.65, 132.69, 133.77, 152.46; IR ($CHCl_3$) 3314, 1617, 1459 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.10; H, 8.39.

Acknowledgment. This work was supported in part by Grants from the Welch Foundation of Houston, TX, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 139409-00-0; 2, 83439-40-1; 3a, 59309-68-1; 3b, 76054-72-3; 5a, 139409-01-1; 6a, 139409-02-2; 6b, 139409-03-3; 12a, 102273-84-7; 12b, 139409-04-4; 2-chloro-1,4-dimethylbenzene, 95-72-7.

Supplementary Material Available: Positional coordinates, bond lengths, bond angles, and equivalent isotropic thermal parameters of non-hydrogen atoms of 5a as determined by X-ray crystallography (3 pages). Ordering information is given on any current masthead page.

Halogenation and Oxidation of 2,5-Bis(ethoxycarbonyl)-3,4-dialkylpyrroles. A Possible Route to Side-Chain Functionalized 3,4-Dialkylpyrroles

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It is well-known that in the pyrrole nucleus, the reactivity of the α-position greatly exceeds that of the β-position, thus making the synthesis of β-substituted pyrroles an extremely difficult task, requiring the study and the development of particular synthetic procedures.[1] This situation also extends to side-chain reactivity; alkyl groups bonded to the α-position of the pyrrole nucleus are much more reactive than those bonded to the β-position. Thus, α-alkylpyrroles readily undergo oxidation,[2] halogenation,[3,4] aminoalkylation,[5] and isotope exchange[6] reactions. In

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