Thin-layer chromatography was done on precoated Merck silica gel 60 F-264. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian EM 360 in deuteriochloroform with tetramethylsilane as an internal standard. Mass spectra were obtained by using a Hitachi Perkin-Elmer RMU-6E spectrometer.

2-Chloro-9*H*-10-oxaanthracen-9-ol (3a). Xanthone **2a** (10 g, 43.4 mmol) was suspended in 100 mL of methanol that had been saturated with sodium hydroxide at room temperature. Then freshly activated zinc dust[10] (10 g) was added in a single portion. An intense blue color was generated almost immediately. The reaction was checked for starting material once the blue color had disappeared (TLC, CH_2Cl_2) and was normally complete in 2–4 h. The reaction was then concentrated, the residue suspended in methylene chloride and filtered through Celite, and the filter cake washed thoroughly with methylene chloride. The filtrate was washed with water (twice) and brine, dried ($MgSO_4$), and concentrated to provide 9.53 g (94.4%) of crude white solid that was used directly in the next step.

2-Chloro-10-oxoniaanthracene Perchlorate (4a). Crude xanthol **3a** (5.50 g, 21.5 mmol) was treated[8] in 150 mL of diethyl ether at −78 °C with 15 mL of 70% perchloric acid to provide 5.53 g (77.3% from **2a**) of a gold solid. The melting point of this material, even of the same sample, varied over a 20 °C range. DSC analysis indicated that decomposition which occurred before melting was responsible for the variation in melting point.

2-Chloro-10-(dimethoxyphosphinyl)-9,10-dihydro-9-oxaanthracene (5a). Perchlorate **4a** (5.30 g, 16.8 mmol) was treated[8] in 70 mL of acetonitrile with 3.16 g (25.5 mmol) of trimethyl phosphite at room temperature which gave 5.34 g (97.9%) of crude **5a** as a yellowish solid. Recrystallization from methanol gave 3.85 g (70.6%) of white crystals: mp 144.5–146.5 °C; NMR δ 3.55 (d, J_{P-H} = 11 Hz, 3 H), 3.59 (d, J_{P-H} = 11 Hz, 3 H), 4.42 (d, J_{P-H} = 24 Hz, 1 H), 7.22 (m, 7 H); mass spectrum (FD, chloroform solution), m/e 324 (M^+). Anal. Calcd for $C_{15}H_{14}ClO_4P$: C, 55.49; H, 4.35; Cl, 10.92. Found: C, 55.61; H, 4.40; Cl, 10.88.

Condensation of Phosphonates 5 with Aldehydes and Ketones. General Procedure. The phosphonate **5** and the carbonyl compound (1.1 equiv) were dissolved in dry tetrahydrofuran (1 g of carbonyl/10 mL) under a nitrogen atmosphere, and 2.0 equiv of sodium methoxide or 1.1 equiv of sodium hydride (50% dispersion in mineral oil) was added in a single portion. The reactions were monitored for disappearance of starting material by TLC (CH_2Cl_2) and were complete in 2–4 h at room temperature. The reaction mixture was then concentrated, and the residue was dissolved in methylene chloride, washed with water and brine, dried ($MgSO_4$), and concentrated to give the crude product. Recrystallization was normally achieved from an alcoholic solvent.

Acknowledgment. We thank Richard Warren, Gerald Roberts, and Walter Johnson for mass spectra, Gail Johnson and Edith Reich for microanalyses, and Joseph Buckley for DSC analyses. We extend special thanks to Dr. Carl Kaiser for his help in preparing this manuscript.

Registry No. 1c, 60085-78-1; **2a**, 13210-15-6; **3a**, 13209-86-4; **4a**, 81642-92-4; **5a**, 81642-93-5; **5b**, 14110-88-4; **7a**, 81642-94-6; **7b**, 27426-44-4; **8a**, 81642-95-7; **8b**, 27426-40-0; **9a**, 81642-96-8; **9b**, 81642-97-9; **10**, 65674-21-7; **11**, 65674-22-8; **12**, 81642-98-0; **13**, 39730-71-7; **14**, 81642-99-1; **15**, 27980-52-5; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; *N*-methyl-4-piperidone, 1445-73-4; cyclohexanone, 108-94-1; benzaldehyde, 100-52-7.

Supplementary Material Available: Table containing melting point, analytical, and ^1H NMR and mass spectral data for **5a**, **8a**,**b**, and **15** (1 page). Ordering information is given on any current masthead page.

Preparation and Electrophilic Trapping of 7-Lithiated Benzoxazoles Generated via Benzyne Cyclization[1]

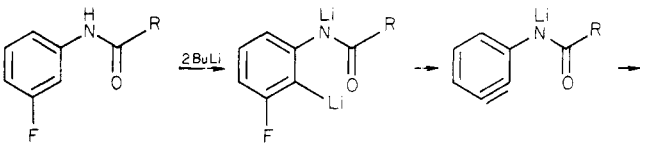
Robin D. Clark* and Joan M. Caroon

Institute of Organic Chemistry, Syntex Research, Palo Alto, California 94304

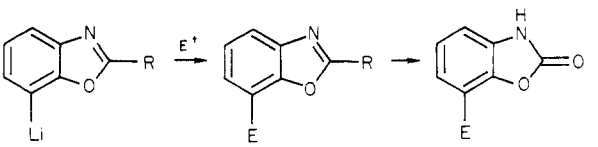
Received January 20, 1982

The intramolecular trapping of a benzyne by a side-chain nucleophile to generate a bicyclic system (benzyne cyclization) is a useful synthetic method.[2] Introduced independently by Huisgen[3] and Bunnett,[4] this sequence has been applied to the synthesis of a number of natural products and to a variety of heterocyclic and homocyclic ring systems.[2] One aspect of the benzyne cyclization, which has apparently not been investigated, is the electrophilic trapping of the anion which is generated by the nucleophilic addition to the benzyne. One intramolecular example of such a trapping has been reported.[5] We now report that in the case of benzoxazole formation, the anion so generated can be trapped with representative electrophiles. This additional feature of the benzyne cyclization has obvious implications for the synthesis of a number of 1,2,3-trisubstituted benzenes and substituted bicyclic systems.

Scheme I



1, R = *t*-Bu
2, R = O-*t*-Bu
3, R = C_6H_5



4, R = *t*-Bu
5, R = O-*t*-Bu
6, R = C_6H_5

7-10[a] **11-14**[b]

[a] For **7**: R = *t*-Bu; E = CH_2CH_3; electrophile = CH_3CH_2I; 89% yield. For **8**: R = *t*-Bu; E = SCH_3; electrophile = $(CH_3S)_2$); 56% yield. For **9**: R = *t*-Bu; E = $CH(OH)(4\text{-}ClC_6H_4)$; electrophile = $4\text{-}ClC_6H_4CHO$; 68% yield. For **10**: R = *t*-Bu; E = $4\text{-}t\text{-}BuC_6H_9OH$; electrophile = $4\text{-}t\text{-}BuC_6H_9O$; 70% yield. [b] For **11**: E = CH_3; electrophile = CH_3I; 85% yield. For **12**: E = $CH(OH)C_6H_5$; electrophile = C_6H_5CHO; 52% yield. For **13**: E = $CONH(4\text{-}ClC_6H_4)$; electrophile = $4\text{-}ClC_6H_4NCO$; 56% yield. For **14**: E = SC_6H_5; electrophile = $(C_6H_5S)_2$; 50% yield.

(1) Contribution No. 622 from the Syntex Institute of Organic Chemistry.

(2) For a useful review see: Kessar, V. S. *Acc. Chem. Res.* **1978**, *11*, 283.

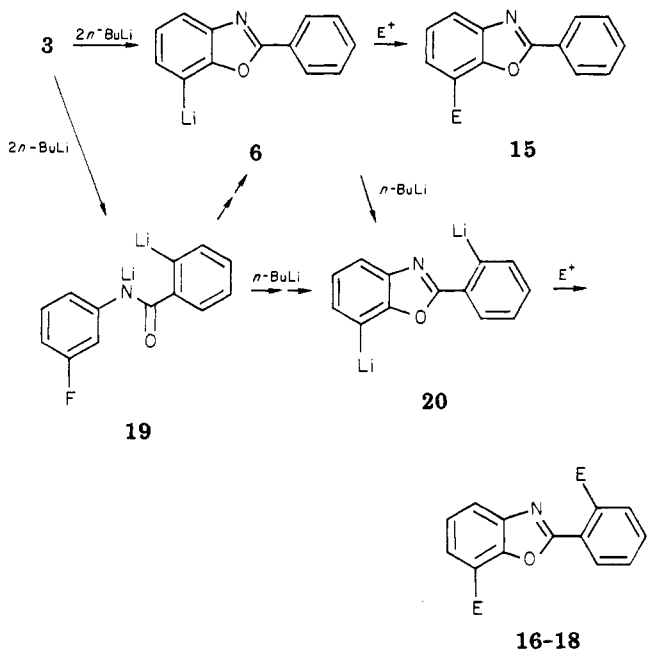
(3) Huisgen, R.; Konig, H. *Angew. Chem.* **1957**, *69*, 268; *Ber.* **1959**, *92*, 203, 429. Huisgen, R.; Konig, H.; Lepley, A. R. *Ibid.* **1960**, *93*, 1496. Huisgen, R.; Saver, J. *Angew. Chem.* **1960**, *72*, 91.

(4) (a) Bunnett, J. F.; Hrutfiord, B. F. *J. Am. Chem. Soc.* **1958**, *80*, 2021, 4745; **1961**, *83*, 1691. (b) Bunnett, J. F.; Skorcz, J. A. *J. Org. Chem.* **1962**, *27*, 3836. (c) Bunnett, J. F.; Kato, T.; Flynn, R. R.; Skorcz, J. A. *Ibid.* **1963**, *28*, 1.

(5) Kessar, S. V.; Pal, D.; Singh, M. *Tetrahedron* **1973**, *29*, 177.

0022-3263/82/1947-2804$01.25/0

Scheme II[a]



[a] For 15 and 16: E = CH(OH)(4-ClC_6H_4); electrophile = 4-ClC_6H_4CHO; 18% and 31% yields, respectively. For 17: E = CH_2CH_3; electrophile = CH_3CH_2I; 48% yield. For 18: E = $CH(OH)C_6H_{11}$; electrophile = c-HxCHO; 50% yield.

Treatment of *N*-pivaloyl-*m*-fluoroaniline (1) with excess *n*-butyllithium (2.5 equiv) in tetrahydrofuran–hexane solution at −20 °C smoothly generated the lithio species 4 (Scheme I). Addition of a variety of electrophiles gave the 7-substituted 2-*tert*-butylbenzoxazoles **7–10**. The powerful activating effect of the *m*-fluoro group on the ortho lithiation[6] is an important feature of the facile benzyne formation. Under the same reaction conditions, the corresponding *N*-pivaloyl-*m*-bromoaniline was converted to 4 at a much slower rate, and even after 12 h at room temperature starting material was not completely consumed.[7] Thus, the *N*-pivaloyl-*m*-bromoaniline apparently required approximately the same conditions for ortho lithiation as did the parent *N*-pivaloylaniline.[8]

Conversion of *N*-(*tert*-butoxycarbonyl)-*m*-fluoroaniline (2) to the 7-lithiated benzoxazole 5 required either 2.5 equiv of *tert*-butyllithium or sequential treatment with 1 equiv of *n*-butyllithium and 1.5 equiv of *tert*-butyllithium at low temperature. Excess *n*-butyllithium does not effect this transformation. This is in accord with the report that ortho lithiation of the parent *N*-(*tert*-butoxycarbonyl)-aniline can be achieved only with *tert*-butyllithium.[9] Addition of electrophiles to 5 gave adducts which were hydrolyzed upon mild acidic workup to afford the 7-substituted 2-benzoxazolinones **11–14**. Since 2-benzoxazolinones can be converted to aminophenols, this synthesis gives access to 6-substituted 2-aminophenols. This complements the ortho functionalization of *N*-pivaloyl-*m*-methoxyaniline which affords the methyl ether of the isomeric 2-substituted 3-aminophenol.[8]

Treatment of *N*-benzoyl-*m*-fluoroanilines (3) with 2.5 equiv of *n*-butyllithium in tetrahydrofuran followed by an aqueous workup cleanly gave the known 2-phenylbenzoxazole.[10] However, electrophilic trapping of the lithio species so generated gave mixtures of mono- and difunctionalized products (e.g., **15** + **16**; Scheme II) which derive from monolithiated species **6** and the dilithiated species **20**. The difunctionalized products predominated in every case. For example, use of 2 equiv of *n*-butyllithium followed by trapping with 1 equiv of *p*-chlorobenzaldehyde led to **16** as the major product in 31% yield along with 18% of **15**, with starting material (3) comprising the remainder of the product. Thus, formation of the dilithio species **20** is considerably faster than conversion of 3 to the monolithiated **6**. Although **20** could be formed via either of the pathways shown, it seems likely that direct deprotonation of **6** is occurring rather than benzyne cyclization of **19** since no substitution products derived from **19** are obtained upon electrophilic trapping. However, it is also possible that **19**, if formed, could undergo fast intramolecular deprotonation ortho to the fluorine leading indirectly to **6**, which could also explain the lack of trapping products from **19**. The ortho-activating effects of the related oxazolines[11] and *N*-phenylbenzamides[12] are well documented. Use of more than 3 equiv of *n*-butyllithium and 2 equiv of electrophile led cleanly to the difunctionalized compounds **17** and **18**.

In summary, these results indicate that benzyne cyclization of a suitably protected *m*-fluoroaniline can be used to functionalize both the ortho and the meta position of the aromatic ring. Of greatest practical utility is the synthesis of 6-substituted 2-aminophenols protected as 2-benzoxazolinones. Numerous other applications of this methodology such as the preparation of 2-benzothiazolinones can be envisioned.

Experimental Section

The melting points were taken on a Fischer-Johns hot stage and are not corrected. The IR spectra were measured with a Perkin-Elmer Model 237 grating infrared spectrometer. The ^1H NMR spectra were recorded on Varian A-60 and HA-100 and Bruker WM 300 instruments. ^{13}C NMR spectra were obtained with a Bruker 90 instrument. Microanalyses were obtained from Syntex Analytical Research. Mass spectra were obtained in either an Atlaswerke CH-4 or CH-7 instrument.

N-Pivaloyl-*m*-fluoroaniline (1, mp 100–101 °C) was prepared from *m*-fluoroaniline and pivaloyl chloride according to the procedure described in ref 8. *N*-(*tert*-Butoxycarbonyl)-*m*-fluoroaniline (2, mp 123–124 °C) was prepared by reaction of *m*-fluoroaniline with di-*tert*-butyl dicarbonate as described in ref

(6) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; p 39.

(7) The formation of 4 and the disappearance of the *N*-pivaloyl-*m*-bromoaniline were monitored by TLC analysis. After 12 h a considerable amount of starting material remained, and the formation of several by-products was noted (possibly derived from transmetalation processes). The rate-limiting step in the conversion of the bromo compound to 4 is most likely the ortholithiation rather than elimination of LiBr although this has not been rigorously demonstrated.

(8) Fuhrer, W.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 1133. Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 45.

(9) Muchowski, J. M.; Venuti, M. C. *J. Org. Chem.* **1980**, *45*, 4798.

(10) Mp 97–98 °C (lit.[4a] mp 99–101 °C).

(11) Meyers, A. I.; Avila, W. B. *J. Org. Chem.* **1981**, *46*, 3881 and references cited therein.

(12) Mao, G. L.; Barnish, I. T.; Hauser, C. R. *J. Heterocycl. Chem.* **1969**, *6*, 475.

(13) A melting point for 11 of 120 °C has been reported: German Offen. 2 131 366. Since we are not able to find commercially available precursors for an unambiguous synthesis of 11, we instead relied on comparison with the isomeric 3-methyl-2-benzoxazolinone (19) for structural confirmation. This material was prepared by catalytic reduction of 2-nitro-3-methylphenol (Aldrich Chemical Co.) followed by treatment with 1,1′-carbonyldiimidazole and had a melting point of 153–155 °C. The TLC mobilities of 11 and 19 are identical, and the isomeric relationship of the two compounds is obvious from a comparison of their ^1H and ^{13}C NMR spectra. for 19: ^1H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 7.00 (s, 3 H), 8.30 (s, 1 H exchangeable); ^{13}C NMR δ 16.1, 107.7, 120.7, 122.6, 125.6, 128.8, 143.8, 157.0.

9. *N*-Benzoyl-*m*-fluoroaniline (**3**, mp 137–138 °C) was prepared by reaction of the aniline and benzoyl chloride in aqueous sodium carbonate solution.

2-*tert*-Butyl-7-ethylbenzoxazole (7). A 1.6 M solution of *n*-butyllithium in hexane (15.6 mL, 25 mmol) was added in a dropwise manner to a solution of **1** (1.95 g, 10 mmol) in THF (50 mL) at −20 °C. The solution was allowed to warm to 0 °C over a period of 1 h. The mixture was cooled to −50 °C, and ethyl iodide (1 mL, 12.5 mmol) was added. After warming to room temperature, the solution was poured into water and extracted with ether. The ether extract was washed with water and brine, dried over sodium sulfate, and evaporated in vacuo. Chromatography on silica gel (14% ether–hexane) afforded 1.80 g of **7** (89%) as a colorless oil: IR (film) 2980, 1560, 1430, 1120, cm^{-1}; NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7.5 Hz), 1.50 (s, 9 H), 2.91 (q, 2 H, J = 7.5 Hz), 7.08 (dd, 1 H, J = 7.8, 1 Hz), 7.20 (dd, 1 H, J = 7.8, 7.8 Hz), 7.54 (dd, 1 H, J = 7.8, 1 Hz). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.79; H, 8.52; N, 6.90.

Compounds **8** (20% ether–hexane), **9** (25% ether–hexane), and **10** (15% ether–hexane) were purified by chromatography on silica gel. **8**: oil; NMR ($CDCl_3$) δ 1.50 (s, 9 H), 2.58 (s, 3 H), 7.17 (dd, 1 H, J = 7.8, 1.2 Hz), 7.23 (dd, 1 H, J = 7.8, 7.8 Hz), 7.51 (dd, 1 H, J = 7.8, 1.2 Hz). Anal. Calcd for $C_{12}H_{15}NOS$: C, 65.15; H, 6.83; N, 6.32. Found: C, 65.00; H, 7.00; N, 6.39. **9**: oil; NMR ($CDCl_3$) δ 1.37 (s, 9 H), 4.35 (s, 1 H, OH), 6.15 (s, 1 H), 7.15–7.50 (m, 7 H). Anal. Calcd for $C_{18}H_{18}ClNO_2$: C, 68.46; H, 5.74; N, 4.43. Found: C, 68.23; H, 5.79; N, 4.35. Compound **10** was separated into two diastereomers, **10a** and **10b**, which were obtained in a ratio of 45:55. **10a**: mp 160–161 °C; NMR ($CDCl_3$) δ 0.94 (s, 9 H), 1.18 (m, 1 H), 1.51 (s, 9 H), 1.54–1.80 (m, 4 H), 1.95 (d, 2 H, J = 12 Hz), 2.16 (td, 2 H, J = 12, 3.7 Hz), 2.31 (s, 1 H, OH), 7.25 (dd, 1 H, J = 7.7, 7.7 Hz), 7.44 (dd, J = 7.7, 0.7 Hz), 7.57 (dd, 1 H, J = 7.7, 0.7 Hz). **10b**: mp 34–35 °C; NMR ($CDCl_3$) δ 0.77 (s, 9 H), 0.90–1.20 (m, 3 H), 1.48 (s, 9 H), 1.78 (m, 4 H), 2.62 (s, 1 H), 2.83 (d, 2 H, J = 11.5 Hz), 7.26 (dd, 1 H, J = 7.7, 7.7 Hz), 7.36 (dd, 1 H, J = 7.7, 1.3 Hz), 7.59 (dd, 1 H, J = 7.7, 1.3 Hz). Anal. Calcd for $C_{21}H_{31}NO_2$: C, 76.55; H, 9.48; N, 4.25. Found: C, 76.82; H, 9.65; N, 3.99.

7-Methyl-2-benzoxazolinone (11). A 1.4 M solution of *tert*-butyllithium in pentane (20 mL, 28 mmol) was added in a dropwise manner to a solution of **2** (2.1 g, 10 mmol) in THF (20 mL) at −70 °C. After 0.5 h at −70 °C the solution was warmed to −25 °C and was maintained at that temperature for 2 h. The dark solution was cooled to −78 °C, and methyl iodide (0.6 mL, 10 mmol) was added. The mixture was stirred for 10 min with warming to −60 °C, and water (1 mL) was added. The solution was poured into cold 1 M aqueous HCl and extracted with ether. The ether was washed with brine, dried over sodium sulfate, and evaporated. Chromatography of the residue on silica gel (15% ethyl acetate–hexane) gave 1.20 g (85%) of **11** as a pale yellow solid: mp 180–181 °C;[13] IR (KBr) 3300, 1750, 1470 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (s, 3 H), 6.93 (s, 3 H), 7.36 (s, 1 H, NH); ^{13}C NMR 16.1, 107.7, 120.7, 122.6, 125.6, 128.8, 143.8, 157.0. Anal. Calcd for $C_8H_7NO_2$: C, 64.43; H, 4.73; N, 9.39. Found: C, 64.36; H, 4.74; N, 9.38.

For the preparation of **12–14** the reaction mixture was allowed to warm to room temperature after addition of the electrophile. Purification of **12** and **14** was effected by silica gel chromatography (15% ethyl acetate–hexane). Crude **13** was purified by trituration with boiling hexane followed by recrystallization from ethyl acetate–ethanol. **12**: mp 129–130 °C; NMR ($CDCl_3$) δ 6.17 (s, 1 H), 6.76–7.67 (m, 10 H). Anal. Calcd for $C_{14}H_{11}NO_3 \cdot 0.5H_2O$: C, 67.20; H, 4.83; N, 5.60. Found: C, 66.90; H, 4.45; N, 5.55. **13**: mp 235–240 °C; NMR (Me_2SO-d_6) δ 7.25 (d, 2 H, J = 6 Hz), 7.36 (d, 2 H, J = 9 Hz), 7.45 (dd, 1 H, J = 6, 6 Hz), 7.78 (d, 2 H, J = 9 Hz), 10.29 (s, 1 H, NH), 11.58 (s, 1 H, NH). Anal. Calcd for $C_{14}H_9ClN_2O_3$: C, 58.28; H, 3.14; N, 9.71. Found: C, 58.47; H, 3.16; N, 9.47. **14**: mp 169–170 °C; NMR ($CDCl_3$) δ 4.00 (s, 1 H, NH), 6.96 (dd, 1 H, J = 7.5, 1 Hz), 6.97 (dd, 1 H, J = 7.5, 1 Hz), 7.06 (dd, 1 H, J = 7.5, 7.5 Hz), 7.25–7.40 (m, 5 H). Anal. Calcd for $C_{13}H_9NO_2S$: C, 64.26; H, 3.73; N, 5.76. Found: C, 64.15; H, 3.76; N, 5.76.

Benzyne Cyclization of 3 and Trapping of 6 and 20. A 1.6 M solution of *n*-butyllithium in hexane (12.5 mL, 20 mmol) was added to a solution of **3** (2.15 g, 10 mmol) in THF (75 mL) at −50 °C. The resulting solution was allowed to warm to 0 °C over 1.5 h and was then cooled to −20 °C. A solution of *p*-chlorobenzaldehyde (1.40 g, 10 mmol) in THF (4 mL) was added, and the mixture was stirred at −10 °C for 0.5 h. The solution was poured into water and extracted with ether. The ether was washed with brine, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel (40% ether–hexane) to give **15** (0.65 g, contaminated with a small amount of **3**, 18% yield) followed by **16**[14] (1.50 g, 31%) as a tan solid. **15**: NMR ($CDCl_3$) δ 2.00 (s, 1 H, OH), 6.23 (s, 1 H), 7.22–7.80 (m, 10 H), 8.10 (dd, 2 H, J = 7.7, 1.5 Hz); MS, m/e 337, 335. **16**: mp 143–144 °C; NMR ($CDCl_3$) δ 3.17 (s, 1 H, OH), 3.30 (s, 1 H, OH), 6.15 (s, 1 H), 6.16 (s, 1 H), 6.19 (s, 1 H), 6.21 (s, 1 H), 6.86 (m, 2 H), 7.11 (m, 2 H), 7.20–7.50 (m, 24 H), 7.58 (m, 2 H), 8.02 (m, 2 H), MS, m/e 477, 475. Anal. Calcd for $C_{27}H_{19}Cl_2NO_3$: C, 68.08; H, 4.02; N, 2.94. Found: C, 67.98; H, 4.11; N, 2.95.

Compounds **17** and **18** were similarly obtained by using 3.1 equiv of *tert*-butyllithium and 2 equiv of electrophile. Purification of both compounds was effected by chromatography on silica gel with 5% ether–hexane for **17** and 25% ether–hexane for **18**. **17**: oil; NMR ($CDCl_3$) δ 1.32 (t, 3 H, J = 7.5 Hz), 1.38 (t, 3 H, J = 7.5 Hz), 2.97 (q, 2 H, J = 7.5 Hz), 3.22 (q, 2 H, J = 7.5 Hz), 7.17 (d, 1 H, J = 7 Hz), 7.22–7.48 (m, 4 H), 7.64 (d, 1 H, J = 7.5 Hz), 8.16 (d, 1 H, J = 7.5 Hz). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.25; H, 7.17; N, 5.24. **18**:[14] mp 135–137 °C; NMR ($CDCl_3$) δ 1.00–2.30 (m, 44 H), 3.00 (m, 2 H, OH), 4.50–4.95 (m, 4 H), 5.80 (m, 2 H, OH), 7.20–7.80 (m, 12 H), 8.15 (m, 2 H). Anal. Calcd for $C_{27}H_{33}NO_3$: C, 77.33; H, 7.88; N, 3.34. Found: C, 77.22; H, 7.95; N, 3.34.

Acknowledgment. We thank Dr. J. M. Muchowski, Dr. M. C. Venuti, and Dr. S. Branz for much helpful discussion on various aspects of this work. The technical assistance of Dr. M. Maddox, L. Kurz, and L. Lightman, as well as other members of Syntex Analytical Research, is gratefully acknowledged.

Registry No. **1**, 81740-17-2; **2**, 81740-18-3; **3**, 1629-15-8; **7**, 81740-19-4; **8**, 81740-20-7; **9**, 81740-21-8; **10a**, 81740-22-9; **10b**, 81740-23-0; **11**, 40925-60-8; **12**, 81740-24-1; **13**, 81740-25-2; **14**, 81740-26-3; **15**, 81740-27-4; (*R**,*R**)-**16**, 81740-28-5; (*R**,*S**)-**16**, 81740-29-6; **17**, 81740-30-9; (*R**,*R**)-**18**, 81740-31-0; (*R**,*S**)-**18**, 81740-32-1; **19**, 21892-80-8; 2-nitro-3-methylphenol, 4920-77-8; aniline, 62-53-3; benzoyl chloride, 98-88-4; 4-*tert*-butylcyclohexanone, 98-53-3; benzaldehyde, 100-52-7; 1-chloro-4-isocyanatobenzene, 104-12-1; cyclohexanecarboxaldehyde, 2043-61-0; CH_3CH_2I, 75-03-6; $(CH_3S)_2$, 624-92-0; 4-ClC_6H_4CHO, 104-88-1; CH_3I, 74-88-4; $(C_6H_5S)_2$, 882-33-7.

(14) Obtained as an inseparable mixture of diastereomers: ^1H NMR signals for both diastereomers are presented.

A Novel and Convenient Synthesis of 2,2,4,5-Tetraaryl-3-oxazolines

G. Prasad and K. N. Mehrotra*

Department of Chemistry, Banaras Hindu University, Varanasi-221005, India

Received January 22, 1982

In the thermal reaction of 2-diazo-1,2-diphenylethanone (**1**) with 1,1-diarylmethanimines to yield *N*-(diarylmethylene)diphenylacetamides, the benzoylphenylcarbene formed from the loss of nitrogen from **1** readily undergoes Wolff rearrangement to give diphenyl ketene, the active reactant.[1] This rearrangement of ketocarbenes has been prevented in the presence of copper powder,[2] cupric chloride,[3] and bis(acetylacetonato)copper(II).[4] Modified

(1) K. N. Mehrotra and G. Prasad, *Bull. Chem. Soc. Jpn.*, **54**, 604 (1981).
(2) P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

0022-3263/82/1947-2806$01.25/0