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.

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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

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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

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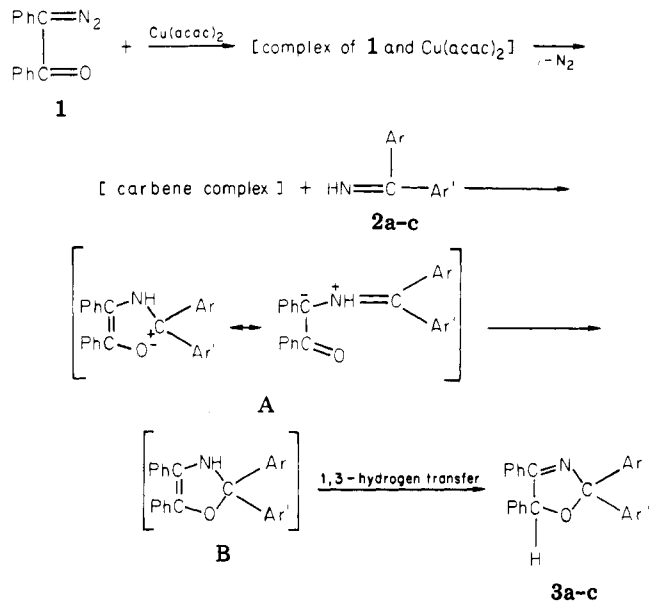
Scheme I[a]



[a] a, Ar = C_6H_5, Ar' = C_6H_5; b, Ar = p-Me-C_6H_4, Ar' = C_6H_4-Me-p; c, Ar = C_6H_5, Ar' = C_6H_4-Cl-p.

carbenes, produced in the copper complex-catalyzed decomposition of diaryldiazomethanes, have been known to possess electrophilic character.[5,6] The present study describes a single-step direct synthesis of 2,2,4,5-tetraaryl-3-oxazolines (3) from bis(acetylacetonato)copper(II)-catalyzed thermal decomposition of 2-diazo-1,2-diphenylethanone (1) in the presence of diarylmethanimines (2).

Treatment of 1 with **2a–c** in the presence of bis(acetylacetonato)copper(II) in dry benzene afforded 2,2,4,4-tetraaryl-3-oxazolines (**3a–c**). The structures of the products were assigned on the basis of analyses[7] and spectral data. The probable reaction route for the formation of products **3a–c** is shown in Scheme I.

The synthesis of oxazolines apparently involves the formation of a complex of 1 with bis(acetylacetonato)-copper(II). Similar complexes of diazoacetophenone[4] and diphenyldiazomethane[5,6] with copper salts have been reported earlier. Loss of nitrogen may give the carbene complex with the copper salt, which reacts with imines **2a–c** to lead to zwitterionic intermediate A. A subsequent collapse may form oxazolines B, followed by a 1,3-hydrogen transfer to yield the products **3a–c**. A similar ionic intermediate has been proposed earlier[6] in the bis(acetylacetonato)copper(II)-catalyzed reaction of diaryldiazomethanes with **2**.

Experimental Section

Melting points were determined on a Buchi capillary apparatus and are uncorrected. UV spectra were recorded on a Cary-14 spectrophotometer. IR spectra were determined on a Perkin-Elmer 621 spectrophotometer. ^1H NMR spectra were recorded using a Varian A-60D spectrometer. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as internal standard. Microanalyses were performed by Coleman carbon–hydrogen and nitrogen analyzers. Mass spectra were obtained on a CEC 110 double-focusing, high-resolution mass spectrometer.

Synthesis of 3. A solution containing 2.5 g (11.3 mmol) of 2-diazo-1,2-diphenylethanone (1) in 20 mL of dry benzene was added slowly to a stirred suspension of 0.4 g (1.4 mmol) of bis(acetylacetonato)copper(II) in 20 mL of dry benzene and 3.0 g (16.4 mmol) of 1,1-diphenylmethanimine (**2a**) at reflux temperature. The contents acquired a brown color with evolution of nitrogen. Stirring was continued until the color of the reaction mixture became blue (~8 h). The contents were chromatographed on an alumina column (1.8 × 20 cm, 60 g). Elution with benzene (100 mL) left bis(acetylacetonato)copper(II) adsorbed in the column. The solvent was removed from the eluate under reduced pressure, and the residual matter was triturated with ethanol. Crystallization from benzene–ethanol gave 1.9 g (36% yield) of 2,2,4,5-tetraphenyl-3-oxazoline[7] (**3a**): mp 193–195 °C dec; IR ($CHCl_3$) 1625 (s, C=N) cm^{-1}; NMR ($CDCl_3$) δ 6.20–7.60 (m, 19 H),[8] 7.80–8.20 (m, 2 H);[9] UV (MeOH) max 248 nm; mass spectrum, m/e (relative intensity) 375 (M^+, 33), 374 (M^+ – 1, 100), 270 (M^+ – PhCO, 36), 269 (60), 167 (11), 166 (Ph_2C, 53), 165 (91), 105 (PhCO, 42), 77 (Ph, 53), 63 (15), 51 (37), 50 (12).

Similar reaction of 1 with **2b** gave 2,2-di-p-tolyl-4,5-diphenyl-3-oxazoline[7] (**3b**; 23% yield): mp 194–196 °C dec; IR ($CHCl_3$) 1625 (s, C=N) cm^{-1}; NMR ($CDCl_3$) δ 2.17 (s, 6 H), 6.40–7.70 (m, 17 H),[8] 7.90–8.20 (m, 2 H);[9] UV (MeOH) max 249 nm; mass spectrum, m/e (relative intensity) 403 (M^+, 35), 402 (M^+ – 1, 100), 401 (M^+ – 2, 15), 386 (15), 299 (18), 298 (M^+ – PhCO, 80), 297 (60), 296 (20), 195 (11), 194 [(p-Me-C_6H_4)$_2$C, 22], 193 (13), 179 [(p-Me-C_6H_4)$_2$C – 15, 35], 178 (20), 166 (12), 165 (28), 105 (PhCO, 78), 91 (p-Me-C_6H_4, 22), 89 (10), 78 (14), 77 (Ph, 72), 68 (10), 65 (10), 51 (10), 50 (20).

The reaction of 1 with **2c** gave 2-(p-chlorophenyl)-2,4,5-triphenyl-3-oxazoline[7] (**3c**; 20% yield): mp 183–184 °C dec; IR ($CHCl_3$) 1622 (s) (C=N) cm^{-1}; NMR ($CDCl_3$) δ 6.30–6.70 (m, 18 H),[8] 7.90–8.19 (m, 2 H);[9] UV (MeOH) max 248 nm; mass spectrum, m/e (relative intensity) 410 (27), 409 (30), 408 (100), 304 (21), 303 (13), 200 (13), 166 (19), 165 (85), 163 (10), 105 (PhCO, 56), 78 (14), 77 (Ph, 50), 51 (23).

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Registry No. 1, 3469-17-8; **2a**, 1013-88-3; **2b**, 16620-75-0; **2c**, 41839-60-5; **3a**, 81315-68-6; **3b**, 81315-69-7; **3c**, 81724-87-0.

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