Table II. Synthesis of Quinoline Carboxylic Acids from α-Keto Amide 2 and $R^1CH_2COR^2$

run	R^1	R^2		reacn conditions	yield, %
1	H	Me	7	8% NaOH (H_2O), 8 h reflux	75[a]
2	H	Ph	8	18% NaOH (H_2O), 18 h reflux	72
3	Ph	Ph	9	33% KOH (EtOH–H_2O), 25 h reflux	81
4	H	COOH	10	33% KOH (H_2O), 16 h at room temperature and 2 h reflux	74

[a] Isolated as immonium salt.

o-holoacetanilides and identified by means of IR spectroscopy and elemental analysis.

Double Carbonylation of *o*-Haloacetanilide. Typical procedure is as follows: *o*-Iodoacetanilide (**1a**, 1.57 g, 6.0 mmol) and Et_2NH (6.0 mL, 58 mmol) were added to a 100-mL stainless steel pressure bottle containing $PdCl_2(PMePh_2)_2$ (0.071 g, 0.12 mmol) under argon. After evacuating the system, 52 atm of CO gas was introduced at room temperature, and the mixture was stirred at 40 °C for 40 h. After purging the CO gas, the mixture was extracted with Et_2O (10 mL × 2). GLC analysis (Silicone OV-1, 2-m column; *o*-terphenyl as internal reference) revealed a mixture of 82% of *N,N*-diethyl-*o*-acetamidophenylglyoxylamide (**2**) and 18% of *N,N*-diethyl-*o*-acetamidobenzamide (**3**).

Compounds **2** and **3** were isolated as white crystals by column chromatography (silica, hexane–Et_2O). **2**: mp 76–77 °C; IR (KBr) 3270, 1720, 1670, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 and 1.30 (each t, 3 H, J = 7 Hz, NCH_2CH_3), 2.25 (s, 3 H, $COCH_3$), 3.29 and 3.60 (each q, 2 H, J = 7 Hz, NCH_2), 7.13, 7.66, and 8.80 (total 4 H, Ar), 11.32 (s, 1 H, NH); MS, *m/e* 262 (M^+). Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.11; H, 6.92; N, 10.68. Found: C, 64.13; H, 6.99; N, 10.69. **3**: mp 127–128 °C; IR (KBr) 3270, 1700, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (t, 6 H, J = 7 Hz, NCH_2CH_3), 2.12 (s, 3 H, $COCH_3$), 3.44 (q, 4 H, J = 7 Hz, NCH_2), 6.9–7.6 and 8.08 (total 4 H, Ar), 8.71 (s, 1 H, NH); MS, *m/e* 234 (M^+). Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.48; H, 7.78; N, 11.90.

Preparation of Isatin. Compound **2** (390 mg, 1.5 mmol) was hydrolyzed in 3 N HCl aqueous solution (5 mL) under reflux. The initially heterogeneous reaction mixturee turned into a reddish orange homogeneous solution after 30 min. On further reflux, reddish orange crystals of isatin gradually precipitated. After 2 h, the system was cooled to room temperature, and the crystals were collected by filtration, washed with water, and dried in vacuo (170 mg). The filtrate was extracted with ethyl acetate (20 mL × 5) until the aqueous solution became colorless. The extract was evaporated to dryness to give isatin (54 mg) as an orange solid. Sublimation afforded pure isatin (204 mg, 93%), with the mp and IR spectrum identical with those of an authentic sample.

Preparation of 2-Methylquinoline-4-carboxylic Acid Immonium Salt (7). A heterogeneous mixture of **2** (262 mg, 1.0 mmol) and NaOH (250 mg, 6.3 mmol) in water (3 mL) was heated under reflux. After 1 h, the system turned into a yellow homogeneous solution (**2** absent by TLC). Acetone (2 mL) was added to the solution, and the system was refluxed for 8 h. After removal of unreacted acetone by distillation and cooling to 0 °C, the solution was made acidic (pH 2) with 3 N HCl, to yield yellow-brown crystals. Concentration of the solution yielded additional crystals. The crystals were collected by filtration, washed with cold water, EtOH, and $CHCl_3$, and dried in vacuo (176 mg). Sublimation yielded yellow crystals of **7** (167 mg, 89%): mp 257–259 °C dec; IR (KBr) 3400–2600, 1730, 1670, 1260, 1230 cm^{-1}; MS, *m/e* 187 (M^+ – HCl). Anal. Calcd for $C_{11}H_{10}NO_2Cl$: C, 59.36; H, 4.51; N, 6.26; Cl, 15.85. Found: C, 59.36; H, 5.06; N, 5.94; Cl, 15.58.

Compounds **8**, **9**, and **10** were similarly obtained as yellow crystals. The reaction conditions are listed in Table II. **8**: mp 227–228 °C (lit.[8] mp 212–213 °C); IR (KBr) 3400–2450, 1720, 1600, 1550, 1260 cm^{-1}; MS, *m/e* 249 (M^+). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 76.91; H, 4.37; N, 5.54. **9**: mp 298 °C dec (lit.[9] mp 295 °C); IR (KBr) 3400–2400, 1690, 1650, 1610, 1590, 1280, 1250; MS, *m/e* 325 (M^+). Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found: C, 81.43; H, 4.38; N, 4.41. **10**: mp 257 °C dec (lit.[9] mp 245 °C); IR (KBr) 3500–2300, 1720, 1650, 1620, 1580, 1300, 1260, 1240; MS, *m/e* 217 (M^+). Anal. Calcd for $C_{11}H_7NO_4$: C, 60.84; H, 3.25; N, 6.45. Found: C, 60.26; H, 3.44; N, 6.13.

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Registry No. **1a**, 19591-17-4; **1b**, 614-76-6; **2**, 99686-93-8; **3**, 99686-94-9; **4**, 99686-95-0; **5**, 99686-96-1; **6**, 99686-97-2; **7**, 634-38-8; **8**, 132-60-5; **9**, 99686-98-3; **10**, 5323-57-9; $PdCl_2(PMePh_2)_2$, 52611-08-2; $PdCl_2(Ph_2P(CH_2)_4PPh_2)$, 29964-62-3; $PhCH_2COPh$, 451-40-1; CH_3COCO_2H, 127-17-3; Et_2NH, 109-89-7; CH_3COCH_3, 67-64-1; CH_3COPh, 98-86-2; isatin, 91-56-5.

(8) Boehm, R.; Bournot, K. *Chem. Ber.* **1915**, *48*, 1570.
(9) Pfitzinger, W. *J. Prakt. Chem.* **1877**, *56*, 283.

Reaction of Cycloaliphatic Carbodiimides with Oxalyl Chloride

R. Richter* and E. A. Barsa

Dow Chemical USA, North Haven Laboratories, North Haven, Connecticut 06473

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The addition of oxalyl chloride to the cumulated CN double bonds of carbodiimides has been reported to afford 1,3-disubstituted 2,2-dichloroimidazolidine-4,5-diones in high yields.[1] Similarly, methyloxalyl chloride reacts with *N,N'*-dialkyl- as well as *N,N'*-diarylcarbodiimides across both CN double bonds in a stepwise fashion and with elimination of methyl chloride to ultimately yield 1,3-disubstituted imidazolidine-2,4,5-triones.[2] We recently found that oxalyl chloride adds to isothiocyanates also across both double bonds of the heterocumulene; alkyl and aryl isocyanates, on the other hand, underwent a different type of addition which involved only the CN double bond and afforded 3-substituted 5,5-dichlorooxazolidine-2,4-diones.[2]

In this context it was of interest to study the behavior of aliphatic cyclic carbodiimides[3] toward oxalyl chloride and methyloxalyl chloride and see whether steric restrictions have any influence on the course of the reactions.

1,3-Diazacyclotetradeca-1,2-diene (**1c**) reacts instantaneously with equimolar amounts of oxalyl chloride at room temperature to produce a moisture-sensitive adduct that we believe to have the bicyclic structure **2**. A ^{13}C NMR spectrum of the crude product shows a signal at 103.0 ppm belonging to the orthocarbonic acid carbon bearing two chlorines and two nitrogens while the carbonyl carbons appear at 155.6 ppm downfield from M_4Si. Both chemical shift values compare well with those of other 1,3-disubstituted 2,2-dichloroimidazolidine-4,5-diones. The 1,3-diphenyl derivative has corresponding signals at 102.3 and

(1) Zinner, G.; Vollrath, R. *Chem. Ber.* **1970**, *103*, 766. Gross, H.; Zinner, G. *Chem. Ber.* **1973**, *106*, 2315. Stachel, H. D. *Angew. Chem.* **1959**, *71*, 246. Ulrich, H.; Sayigh, A. A. R. *J. Org. Chem.* **1965**, *30*, 2781.
(2) Richter, R.; Stuber, F. A.; Tucker, B. *J. Org. Chem.* **1984**, *49*, 3675.
(3) All aliphatic cyclic carbodiimides described herein have been synthesized by ring expansion from the corresponding lactam oxime *O*-mesylates in presence of base or by dehydrosulfuration of thioureas as reported: Richter, R.; Tucker, B.; Ulrich, H. *J. Org. Chem.* **1983**, *48*, 1694.

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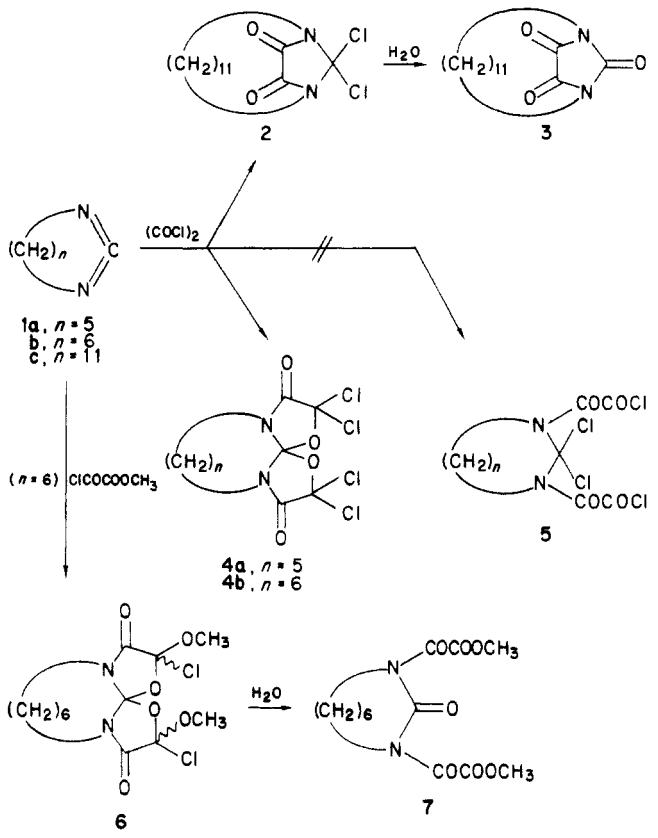
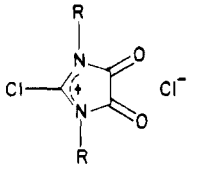


154.1 ppm, while those of 2,2-dichloro-1,3-dicyclohexylimidazolidin-4,5-dione are found at 103.2 and 154.3 ppm. Both chlorines in **2** are very labile and easily hydrolyzed on treating the crude product with aqueous acetone to give the 1,3-alkylene-bridged imidazolidine-2,4,5-trione (**3**) in high yield. This hydrolytic instability is also the reason that we were not able to obtain an analytically pure sample of **2**.

Decreasing the number of methylene groups in the cyclic carbodiimide to five (1,3-diazacyclocta-1,2-diene; **1a**, n = 5) and six (1,3-diazacyclonona-1,2-diene; **1b**, n = 6) leads to formation of a new type of cycloadduct for which we propose structure **4**. Each CN double bond of the heterocumulene adds one molecule of oxalyl chloride to form quantitatively the novel *N,N'*-alkylene-bridged spirobi[oxazolidine]diones **4a,b**. Both adducts are much less sensitive to hydrolysis and can be isolated in pure form. This relative stability of **4** in contrast to **2** most certainly rules out a structure **5** for the bis(oxalyl chloride) adducts in which both chlorooxalyl groups as well as the geminal chlorines are vulnerable to hydrolytic degradation. The novel cycloadducts have ^{13}C NMR spectra consistent with the proposed symmetric structures. The signals for the orthocarbonic acid carbons appear at 117 ppm and the chlorine and oxygen bearing ring carbon in position 5 appear at 100 ppm downfield from Me_4Si. These chemical shift values are consistent with reported values of related compounds. Thus, the ring carbon in position 2 of 3-substituted 2,2-dimethoxythiazolidine-4,5-diones are found at 118 ppm while the CCl_2 carbons of 3-substituted 5,5-dichlorooxazolidine-2,4-diones appear at approximately 98.5–99.1 ppm.[2] Only one carbonyl carbon at 162 ppm can be seen in the spectra of both **4a** (n = 5) and **4b** (n = 6); this also rules out an acyclic oxalyl chloride adduct **5**.

The reaction of carbodiimide **1b** (n = 6) with methyloxalyl chloride at room temperature leads also to formation of a bis adduct, believed to be the alkylene-bridged spirobi[oxazolidine] **6** in which one chlorine each in position 5 and 5' is replaced by a methoxy group. A ^{13}C NMR spectrum of the crude reaction product clearly shows split signals at 116.2/115.2 and 111.6/111.3 ppm, indicating the presence of stereoisomers. This cycloadduct is less stable than the structurally related adducts **4** as indicated by its ready hydrolysis with ring opening on treatment with aqueous potassium bicarbonate to yield the bisacylated cyclic urea **7**. The carbodiimide **1c** (n = 11), however, reacted with methyloxalyl chloride in the same manner as the acyclic carbodiimides[2] to form the bicyclic 1,3-undecamethyleneimidazolidine-2,4,5-trione (**3**).

The observed difference in the formation of cycloadducts from oxalyl chloride and cycloaliphatic carbodiimides must be caused by the varying ring size of the latter. It is believed that in forming the imidazolidine-4,5-dione ring, a structure similar to a planar 2-chloroimidazolidine-4,5-dione cation **8** is formed in the transition state. A small



ring bridge forces the nitrogen lone pairs to twist out of conjugation with the positive charge and also with the neighboring carbonyls. To avoid this, both **1a** and **1b** react with oxalyl chloride as if the heterocumulene consists of two isolated C=N bonds. The observed ring closure to oxazolidines, accompanied by chlorine migration to an adjacent carbon, is reminiscent of cycloadduct formation between oxalyl chloride and isocyanates which involves only the CN double bond of the heterocumulene.[2] The formation of 2,2-dichloro-2,3-dihydro-4,5-bis(trimethylsilyl)-3-furanone from bis(trimethylsilyl)acetylene is an example involving a carbon–carbon multiple bond–oxalyl chloride cycloaddition with a similar cyclization step.[4]

Experimental Section

Infrared spectra were recorded on a Beckman Acculab 4 spectrophotometer with chloroform or dichloromethane as medium; ^1H NMR spectra were determined on a Varian 360 spectrophotometer and the ^{13}C NMR spectra on a Varian CFT-20 spectrophotmeter with $CDCl_3$ as solvent and Me_4Si as internal standard (values are given in ppm); elemental analyses were performed by Galbraith Laboratories, Knoxville, TN; melting points are uncorrected.

5,5,5',5'-Tetrachloro-3,3'-pentamethylene-2,2'-spirobi[oxazolidine]-4,4'-dione (4a). 1,3-Diazacycloocta-1,2-diene (**1a**) was prepared by stirring a dichloromethane solution of pentamethylenethiourea[5] (1.44 g, 0.01 mol) with excess yellow mercury(II) oxide (9.5 g) and anhydrous magnesium sulfate (5 g) for 30 min at ambient temperature. The filtered reaction solution was added dropwise to 5.1 g (0.04 mol) of oxalyl chloride, dissolved in 20 mL of dichloromethane, at 0 °C. A precipitate or emulsion formed and slowly disappeared on stirring the reaction mixture for 2 h at room temperature. Excess oxalyl chloride was then removed together with solvent by vacuum distillation. Redissolving the residue in dichloromethane and washing the solution with aqueous sodium bicarbonate solution followed by drying with sodium sulfate and evaporation of solvent left crude **4a** as a colorless solid, which was further purified by column chromatography on silica gel (Bio-Sil A, 100–200 mesh, 1,2-dichloroethane as eluent) and recrystallized from hexane to yield 1.6 g (44%) of colorless crystals: mp 107–108 °C; IR ($CHCl_3$) 1755 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 161.7, 117.2, 100.8, 40.8, 25.4, 23.1. Anal. Calcd for $C_{10}H_{10}Cl_4N_2O_4$: C, 32.99; H, 2.77; N, 7.70; Cl, 38.96. Found:

(4) Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45.
(5) Behringer, H.; Meier, H. *Justus Liebigs. Ann. Chem.* **1957**, *607*, 68.

C, 33.27; H, 2.71; N, 7.67; Cl, 38.68.

5,5,5′,5′-Tetrachloro-3,3′-hexamethylene-2,2′-spirobi[oxazolidine]-4,4′-dione (4b). A solution of 2.5 g (0.02 mol) of 1,3-diazacyclonona-1,2-diene (**1b**)[3] in 20 mL of $CHCl_3$ was added dropwise to 5.1 g (0.04 mol) of oxalyl chloride in 30 mL of $CHCl_3$ at 0 °C and brought to room temperature over a 30-min period. Removal of solvent left crude **4b** as colorless solid in virtually quantitative yield. Removal of traces of acid was best achieved by treating a chloroform solution of the product with aqueous sodium bicarbonate; further purification was by column chromatography on silica gel (Bio-Sil A, 100–200 mesh, 1,2-dichloroethane as eluent) and recrystallization from cyclohexane: mp 150–152 °C; IR ($CHCl_3$) 1750 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 162.2, 117.9, 100.5, 41.4, 23.4, 23.0. Anal. Calcd for $C_{11}H_{12}Cl_4N_2O_4$: C, 34.94; H, 3.20; N, 7.41; Cl, 37.52. Found: C, 34.98; H, 3.45; N, 7.39; Cl, 37.45.

1,13-Diaza-16,16-dichlorobicyclo[11.2.1]hexadecane-14,15-dione (2) and 1,13-Diazabicyclo[11.2.1]hexadecane-14,15,16-trione (3). A solution of 2.36 g (0.012 mol) of 1,3-diazacyclotetradeca-1,2-diene (**1c**) in 20 mL of chloroform was slowly added with stirring to an ice-cold solution of 1.7 g (0.013 mol) of oxalyl chloride in 30 mL of chloroform. After the mixture was allowed to warm to room temperature over a 30-min period, the solvent was removed under vacuum to give a solid reaction product **2**, which showed the following spectra: IR ($CHCl_3$) 1755 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 4.25–3.40 (m, 4 H), 2.2–1.7 (complex m, 4 H), 1.6–1.0 (complex m, 14 H); ^{13}C NMR ($CDCl_3$) 155.6 (C-14, C-15), 103.0 (C-16), 42.6 (C-2, C-12), 28.2, 27.4, 26.3, 25.3, 25.0.

Due to the moisture sensitivity of **2**, an analytically pure sample was not obtained. Treatment of the crude reaction product with 5% aqueous acetone (60 mL) lead to its immediate and complete hydrolysis producing **3**. Filtration and drying left 3.0 g (94%) of **3**, mp 187–188 °C (toluene), colorless crystals. Anal. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52. Found: C, 62.94; H, 8.26; N, 10.45.

3,3′-Hexamethylene-5,5′-dimethoxy-5,5′-dichloro-2,2′-spirobi[oxazolidine]-4,4′-dione (6) and 1,3-Diaza-1,3-bis-(methyloxalyl)cyclononan-2-one (7). Solutions of 2.44 g (0.02 mol) of methyloxalyl chloride and 1.24 g (0.01 mol) of **1b** in 20 mL of dichloromethane each were combined with stirring at 0 °C. The reaction mixture was allowed to warm to room temperature (30 min.) and was concentrated in vacuum to leave a virtually quantitative yield of **6** as a colorless solid; crude mp 90–120 °C. Crude **6** shows the following spectra: IR ($CHCl_3$) 1750 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 162.0 (C-4, C-4′), 116.2/115.9 (C-5, C-5′), 111.6/113 (C-2), 53.6/53.3 (C[N]), 40.4/40.3, 23.5, 23.0, and 22.7 (signal splitting due to stereoisomerism). The bis cycloadduct **6** is readily hydrolyzed on stirring a dichloromethane solution with a saturated solution of potassium bicarbonate for 2 h. Drying the organic phase ($MgSO_4$), concentrating in vacuo, and recrystallization (CCl_4) gave 1.2 g (36%) of **7**: colorless crystals, mp 93–96 °C (CCl_4); IR ($CHCl_3$) 1760–1680 cm^{-1} (br m, C=O); ^{13}C NMR ($CDCl_3$) 161.5, 160.8, 159.6, 53.5, 44.5, 25.5, 21.0. Anal. Calcd for $C_{13}H_{18}N_2O_7$: C, 49.68; H, 5.77; N, 8.92. Found: C, 49.66; H, 5.61; N, 8.72.

Registry No. **1a**, 85237-12-3; **1b**, 6248-74-4; **1c**, 72995-04-1; **2**, 99798-85-3; **3**, 99798-86-4; **4a**, 99798-87-5; **4b**, 99808-62-5; **6**, 99798-88-6; **7**, 99798-89-7; $(COCl)_2$, 79-37-8; $ClCOCOOCH_3$, 5781-53-3; pentamethylenethiourea, 5269-85-2.

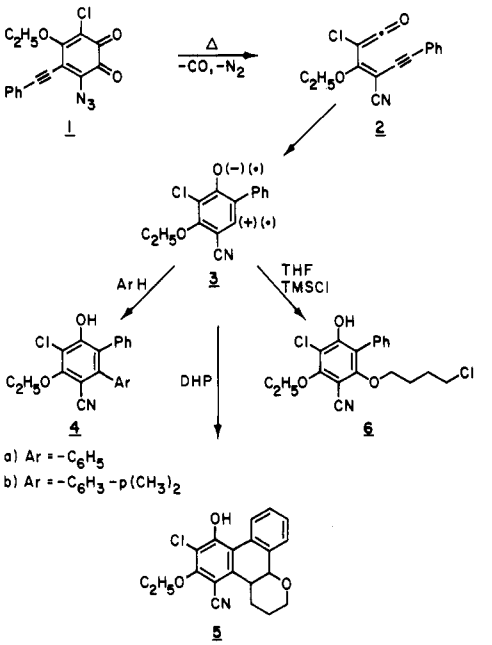
Communications

Chemistry of Azidoquinones. Conversion of 3-Azido-4-alkynyl-1,2-benzoquinones to Cyanophenols via (2-Alkynylethenyl)ketenes

Summary: Thermolysis of 4-alkynyl-3-azido-1,2-benzoquinones in refluxing benzene results in their conversion to (2-alkynylethenyl)ketenes. These, in turn, cyclize to dipolar or diradical intermediates, which proceed to products via intra- or intermolecular trapping. This provides a very unusual entry to highly substituted cyanophenols.

Sir: Reported here is a unique thermally induced rearrangement of 4-alkynyl-3-azido-1,2-benzoquinones to cyanophenols. This transformation is outlined in Scheme I and is envisaged to involve the following steps: (1) thermal fragmentation of the previously unknown azidoquinones **1** and **7** to dinitrogen, carbon monoxide, and (2-alkynylethenyl)ketenes, e.g., **2**;[1,2] (2) ring closure of the respective ketenes to the dipolar or diradical intermediates **3** and **8**; (3) intra- or intermolecular trapping of these intermediates to give the observed products.

Scheme I



Thermolysis of **1** (mp, 100 °C dec) in benzene or *p*-xylene gave respectively **4a** (84%, mp 201–202 °C) and **4b** (56%, mp 184–185 °C).[3,4] A particularly interesting

(1) For analogies to this fragmentation, see: Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

(2) We have recently shown that (2-alkynylethenyl)ketenes can also be generated upon thermolysis of 4-alkynyl-4-(trimethylsiloxy)cyclobutenones. However, here the products are trimethylsilylquinones. See: Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392.

(3) The structure of **4a** was established by single-crystal X-ray data. We acknowledge Professor Robert Doedens for this work.

0022-3263/86/1951-0419$01.50/0