(b) From 2-Benzoyl-1-chloro-2-propene (2a). A 2.3-g (0.012 mol) sample of **2a** was dissolved in 20 mL of dry benzene and added dropwise to an ethereal solution of *tert*-butylamine (0.876 g, 0.012 mol) and triethylamine (1.21 g, 0.012 mol) dissolved in ether. The mixture was allowed to react at 20 °C for an additional 4 h. The triethylamine salt was filtered and the residue concentrated and extracted with 200 mL of ether. The ether solution was filtered to remove traces of salt and concentrated to give a white solid (0.5 g) which was found to be identical with **3a** as described above.

Synthesis of Bis(2-methylene-3-oxo-3-phenylpropyl)(1,1-dimethylethyl)amine (4a). The filtrate from the above reaction was concentrated to afford a yellow oil which upon standing in the cold gave a pale yellow solid. Recrystallization of this material several times from hexane gave 3.5 g (light yellow crystals): mp 76–77 °C; IR (CCl_4) 1660 cm^{-1} (carbonyl); NMR ($CDCl_3$) δ 7.2–7.9 (m, 10 H, aromatic) 5.5, 6.05 (2 s, 2 H, both vinyl), 3.65 (s, 4 H, methylene), 3.15 (s, 9 H, *tert*-butyl); mass spectrum, *m/e* 361 (parent).

Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.88. Found: C, 79.87; H, 7.60; N, 3.81.

Synthesis of 1,3-Bis(*tert*-butylamino)-2-benzoylpropane (5a). A solution of *tert*-butylamine (18 g, 0.246 mol) and triethylamine (5.0 g, 0.024 mol) in benzene was added dropwise to a solution of **1a** (5.0 g, 0.024 mol) in benzene–ether over a 1-h period. The reaction was stirred for 24 h, the amine salt was filtered, and filtrate was evaporated. The yellow oil obtained solidified to a pale yellow solid. Recrystallization gave colorless crystals: 6.0 g (88% yield); mp 65–66 °C; IR ($CHCl_3$) 1680 cm^{-1} (carbonyl); NMR ($CDCl_3$) δ 7.2–7.8 (m, 5 H, aromatic), 3.65 (m, 1 H), 2.95 (d, 4 H, methylene, J = 6.7 Hz), 1.6 (s, 1 H, NH), 1.15 (s, 18 H, *tert*-butyl); mass spectrum, *m/e* 290.1 (parent). Anal. Calcd for $C_{18}H_{30}ON_2$ 0.5 H_2O: C, 72.24; H, 10.36; N, 9.36. Found: C, 72.59; H, 10.25; N, 9.30.

Synthesis of Bis(2-methylene-3-oxo-3-phenylpropyl)-cyclohexylamine (4b). A 5.0-g sample of **1a** (0.024 mol) was dissolved in dry benzene and added dropwise to an ethereal solution of cyclohexylamine (2.23 g, 0.023 mol) and triethylamine (0.046 mol). The mixture was allowed to stir for 4 h. Filtration of the salt and evaporation of the solvent gave a viscous yellow oil which could not be crystallized; yield 8.3 g (89%) of **4b**. TLC, with several solvent combinations, indicated one component: IR ($CDCl_3$) 1660 cm^{-1} (carbonyl); NMR ($CDCl_3$) δ 7.2–7.9 (m, 10 H, aromatic), 5.4, 6.1 (2 s, 2 H, both vinyl), 3.8 (s, 4 H, methylene), 1.1–1.9 (br m, 11 H, cyclohexyl); high-resolution mass spectrum, calcd for $C_{26}H_{29}O_2N$ *m/e* 387.2198, found *m/e* 387.2198.

Synthesis of 2-Benzoyl-1-morpholino-2-propene (3b). A 5.0-g sample of **1a** was dissolved in benzene and added dropwise to an ethereal solution of morpholine (2.0 g, 0.023 mol) and triethylamine (4.6 g, 0.046 mol), and the solution was stirred for 4 h. Filtration of the salt and evaporation of the solvent yielded a white solid. Recrystallization from 95% ethanol–ether yielded 3.4 g of **3b**: mp 65–66 °C; IR ($CHCl_3$) 1660 cm^{-1} (carbonyl); NMR ($CDCl_3$) δ 2.5 (q, 4 H, morpholine ring protons α to N), 3.3 (s, 1 H, methylene), 3.68 (m, 4 H, morpholine ring protons β to N), 5.7, 5.9 (2 s, 2 H, vinyl), 7.3–7.8 (m, 5 H, aromatic); mass spectrum, *m/e* 231 (parent).

Anal. Calcd for $C_{14}H_{17}O_2N$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.99; H, 7.40; N, 5.91.

Synthesis of 1-Morpholino-3-(*tert*-butylamino)-2-benzoylpropane (5b). A 10.0-g sample (0.043 mol) of **3b** was dissolved in ether. To this solution was added 0.43 mol of *tert*-butylamine (31.3 g), dissolved in ether, in a dropwise manner. The solution was stirred for 24 h. At the end of this time the solution was evaporated, yielding a white solid. Recrystallization from petroleum ether several times gave **5b**, the mixed amine: mp 62–63 °C; 10.2 g (75% yield); IR ($CHCl_3$) 1680 cm^{-1} (carbonyl); NMR ($CDCl_3$) δ 0.9 (s, 9 H, *tert*-butyl), 1.9–2.0 (br s, NH, 1 H), 2.3 (apparent q, 4 H, morpholine), 2.7–3.0 (m, 4 H, methylene), 3.5 (apparent q, 4 H, morpholine ring protons), 3.8 (m, 1 H, methine), 7.2–7.9 (m, 5 H, aromatic); mass spectrum, *m/e* calcd 305.222 90, found *m/e* 305.222 41.

Anal. Calcd for $C_{18}H_{28}N_2O_2$: C, 71.01; H, 9.27; N, 9.20. Found: C, 71.03; H, 9.28; N, 9.14.

Synthesis of 2-Benzoyl-1-(diisopropylamino)-2-propene (3c). To a solution of **1a** in ether was added 1 molar equiv of diisopropylamine and 2 molar equiv of triethylamine dissolved in benzene. Stirring for 4 h and filtration of the salt gave a green colored solution. Distillation of the oil [bp 116 °C (0.1 mm)] gave a green-yellow oil which quickly crystallized. Recrystallization from petroleum ether yielded green crystals: mp 31 °C; IR ($CHCl_3$) 1660 cm^{-1} (carbonyl); NMR ($CDCl_3$) δ 0.6 (d, 12 H, isopropyl methyl), 2.8 (m, 1 H, isopropyl methine), 3.1 (s, 2 H, methylene), 5.7, 5.9 (2 s, 2 H, both vinyl), 7.1–7.8 (m, 5 H, aromatic).

Anal. Calcd for $C_{16}H_{23}ON$: C, 78.33; H, 9.45; N, 5.71. Found: C, 78.37; H, 9.53; N, 5.65.

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Registry No. 1a, 39192-57-9; **1b**, 75030-60-3; **2a**, 58703-02-9; **3a**, 75030-61-4; **3a**·HCl, 75030-62-5; **3b**, 2845-45-6; **3c**, 75030-63-6; **4a**, 75030-64-7; **4b**, 75030-65-8; **5a**, 75030-66-9; **5b**, 75030-67-0; formaldehyde, 50-00-0; acetophenone, 98-86-2; formaldehyde 2-benzoyltrimethylene acetal, 21769-22-2; *tert*-butylamine, 75-64-9; cyclohexylamine, 108-91-8; morpholine, 110-91-8; diisopropylamine, 108-18-9.

Mesoionic Compounds. 52. Attempted Synthesis of the Anhydro-2-hydroxyoxazolo[2,3-*b*]oxazolium Hydroxide System[1]

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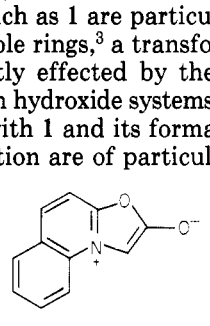
Several recent publications[2] describe a study of the factors controlling the stability of ortho-fused mesoionic ring systems and their ability to undergo cycloaddition reactions, these reactions being particularly useful for ring annelations. In this publication we describe attempts to generate the ortho-fused anhydro-2-hydroxyoxazolo[2,3-*b*]oxazolium hydroxide system **2** and the corresponding benzoxazole system **3** by cyclodehydration of their respective precursors, **4** and **5**. Ortho-fused oxazolium hydroxide systems such as **1** are particularly useful for the annelation of pyrrole rings,[3] a transformation which can also be conveniently effected by the use of the corresponding thiazolium hydroxide systems.[4] The ring system **3** is isoelectronic with **1** and its formation and ability to undergo cycloaddition are of particular interest.



1

Reaction of 2-oxazolidone with ethyl bromoacetate after treatment with NaH/benzene gave the ester **4** (R = COOEt) as a colorless oil (91%). This was hydrolyzed with concentrated HCl at room temperature to the corresponding acid **4** (R = H), obtained as water-soluble, col-

(1) (a) Partial support of this work by U.S. Public Health Service Research Grant CA08495, National Cancer Institute, is gratefully acknowledged. (b) On leave from Yamaguchi University, Japan.

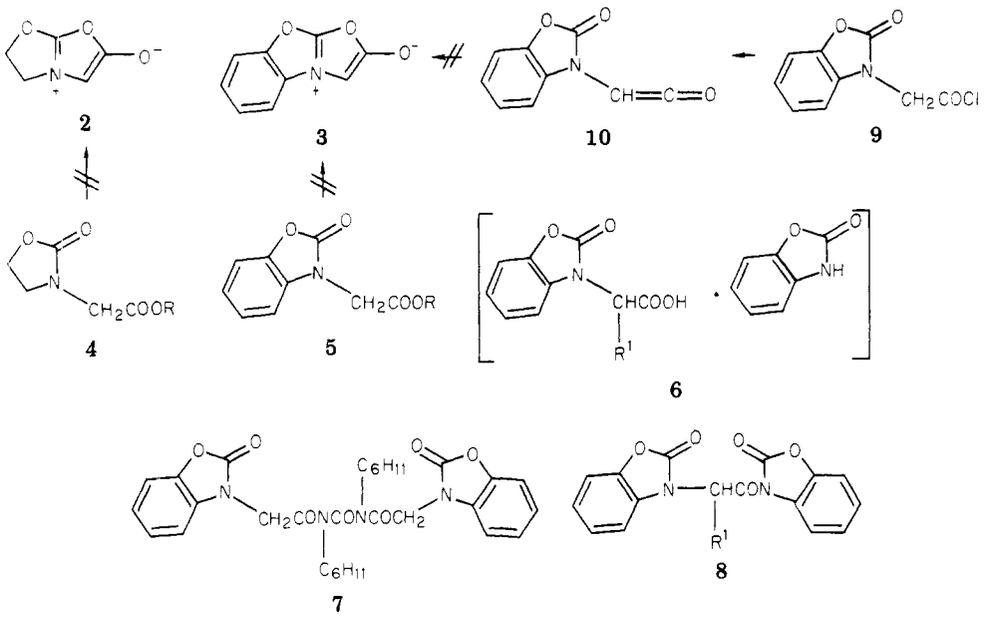
(2) Potts, K. T.; Kanemasa, S. *J. Org. Chem.* **1979**, *44*, 3803, 3806.

(3) Potts, K. T.; Yao, S. *J. Org. Chem.* **1979**, *44*, 977. Potts, K. T.; Chen, S. C.; Szmuszkovicz, J. *Ibid.* **1977**, *42*, 2525.

(4) Potts, K. T.; Choudhury, D. R. *J. Org. Chem.* **1978**, *43*, 2697.

0022-3263/80/1945-4985$01.00/0

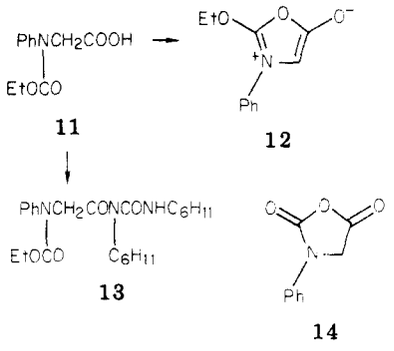
Scheme I



orless plates (see the Experimental Section). Attempts to cyclize this acid 4 (R = H) with *N,N'*-dicyclohexylcarbodiimide to 2 were unsuccessful (Scheme I), the acid being recovered unchanged. Reaction of the acid undoubtedly occurred with the carbodiimide, and failure to obtain 2 (or trap it in situ with dimethyl acetylenedicarboxylate) is most likely the result of the poor nucleophilicity of the carbonyl oxygen atom in what is essentially a carbamic ester environment.

We were also unsuccessful in converting the benzoxazole derivative 5 (R = H) into 3 with a variety of cyclodehydration agents including DCC. This reaction gave[5] the condensation product of 5 (R = H) with DCC and identified as 7, rather than the ring closed product 3. That this dicondensation was preferred over ring closure may again be attributed to the poor nucleophilic character of the 2-carbonyl oxygen atom. Oxazolium salts are frequently readily formed[6] by ring closure of 2-(acylamino)-acetic acid derivatives with perchloric acid in acetic anhydride–acetic acid or tetrafluoroboric acid in acetic anhydride. Neither set of reaction conditions was successful in converting 5 (R = H) into 3. Thionyl chloride has also frequently been used in cyclizations of this type and on reaction of 5 (R = H) with $SOCl_2$, the corresponding acid chloride 9 was obtained in excellent yield. However, attempts to form 3 by treatment of the acid chloride 9 with triethylamine were also unsuccessful. When this reaction was carried out in the presence of reactive dipolarophiles such as *N*-phenylmaleimide or dibenzoylacetylene, the dipolarophile was recovered. That the intermediate ketene 10 was formed was shown by treatment of 9 with triethylamine in the presence of C_2H_5OD. The corresponding ester incorporating deuterium at the methylene carbon of the acetic acid residue was obtained in 100% yield.

An attempt was made to prepare anhydro-2-ethoxy-5-hydroxy-3-phenyloxazolium hydroxide (12) by cyclization of *N*-(ethoxycarbonyl)-*N*-phenylglycine[7] (11) to test the hypothesis that the carbonyl group of the oxazolone was not sufficiently nucleophilic for ring closure to occur. In this case, delocalization of the ester oxygen lone pair over the aromatic ring cannot occur. Reaction of 11 with DCC under reaction conditions similar to those utilized above gave the condensation product 13. Acetic anhydride likewise did not effect ring closure but reaction with thionyl chloride gave 14, ethyl chloride being evolved from the reaction.[7] This suggests that ring closure to 12 actually occurred and that it underwent rapid deethylation under the more vigorous reaction conditions.



In attempts to prepare 5 (R = H) by reaction of 2-benzoxazolinone with bromoacetic acid/NaH/DMF, a 1:1 complex of 5 (R = H) and 2-benzoxazolinone was obtained. This well-crystalline complex could not be separated into its component parts by recrystallization and is represented by 6 (R^1 = H). A similar complex 6 (R^1 = Ph) was obtained when α-bromophenylacetic acid was used in the condensation. Spectral and analytical data used in establishing these structures are described in the Experimental Section. When these complexes were treated with DCC, amide formation occurred with formation of 8 (R^1 = H and Ph, respectively), no evidence for ring closure to 3 being obtained.

Experimental Section[8]

(2-Oxooxazolidin-3-yl)acetic Acid (4, R = H). 2-Oxazolidone (4.4 g, 0.05 mol) was added to a suspension of NaH (2.9 g, 0.06 mol; 50% in oil) in anhydrous benzene (50 mL). After 1 h of reflux and cooling to room temperature, this reaction mixture was treated dropwise with ethyl bromoacetate (8.4 g, 0.05 mol)

(5) Hegarty, S. F.; McCormack, M. T.; Ferguson, G.; Roberts, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 2015.
(6) Boyd, G. V. *Chem. Commun.* **1968**, 1410.
(7) Leuchs, H.; Manasse, W. *Chem. Ber.* **1927**, *40*, 3235.

(8) Spectral characterizations and reaction workup procedures were as described in previous papers in this series. Microanalyses were by Instranal Laboratories, Rensselaer, NY.

and the resulting mixture was then heated under reflux for 2 h. The solid precipitate was collected, the benzene layer was evaporated, and the resulting oil was distilled in vacuo, giving a colorless oil: 7.9 g (91%); bp 129–131 °C (0.02 mm); IR (film) ν_{CO} 1750 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (t, 3, J = 7.8 Hz, CH_2CH_3), 3.72 (br t, 2, C_4-CH_2), 4.03 (s, 2, NCH_2), 4.23 (q, 2, J = 7.8 Hz, CH_2CH_3), 4.42 (br t, 2, C_5-CH_2).

The above oil (14.8 g) was stirred at room temperature in concentrated HCl (40 mL) for 18 h. After evaporation of the HCl in vacuo, the remaining colorless, viscous oil was dissolved in acetone and dried (anhydrous $MgSO_4$), and the acetone was evaporated to give a viscous material which crystallized on standing. The acid **4** (R = H), 7.3 g (59%), crystallized from 2-propanol as colorless plates: mp 114–115 °C; IR (KBr) 3400–2500 (OH), 1700 (CO) cm^{-1}; NMR (CF_3COOH) δ 3.87 (br t, 4, C_4-CH_2), 4.23 (s, 2, NCH_2COO), 4.57 (br t, 3, C_5-CH_2); mass spectrum, m/e (relative intensity) 101 ($M^{+\cdot}$ – CO_2, 39), 100 ($M^{+\cdot}$ – COOH, 31), 56 (100).

Anal. Calcd for $C_5H_7NO_4$: C, 41.38; H, 4.86; N, 9.65. Found: C, 41.52; H, 4.86; N, 9.61.

Ethyl (2-Oxobenzoxazol-3-yl)acetate (5, R = Et). 2-(3*H*)-Benzoxazolinone (13.5 g, 0.1 mol) was added to a suspension of NaH (5.8 g, 0.12 mol; 50% in oil) in anhydrous benzene (100 mL) and the reaction heated under reflux for 1 h. After cooling in ice–water, this reaction mixture was treated with ethyl bromoacetate (16.7 g, 0.1 mol) added dropwise and the resulting mixture then refluxed for an additional 2 h. Water, followed by $CHCl_3$, was added to the cooled reaction mixture, the organic layer was separated, dried ($MgSO_4$), and finally evaporated to leave a colorless, crystalline product. It crystallized from benzene as colorless needles: 16.4 g (75%); mp 66–67 °C; IR (KBr) 1770 (CO) cm^{-1}; NMR ($CDCl_3$) δ 1.28 (t, 3, J = 7.0 Hz, CH_2CH_3), 4.23 (q, 2, J = 7.0 Hz, CH_2CH_3), 4.55 (s, 2, NCH_2COO), 7.15–6.80 (m, 4, aromatic); mass spectrum, m/e (relative intensity) 221 ($M^{+\cdot}$, 57), 148 ($M^{+\cdot}$ – CO_2Et, 100).

Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.01; N, 6.33. Found: C, 60.08; H, 4.81; N, 6.40.

Use of NaOEt/EtOH to generate the anion from 2(3*H*)-benzoxazolinone and reaction as above gave a 50% yield of **5** (R = Et).

(2-Oxobenzoxazol-3-yl)acetic Acid (5, R = H). The above ester **5** (R = Et; 2.2 g, 0.01 mol) was heated under reflux for 2 h in a mixture of concentrated HCl (10 mL) and dioxane (10 mL). The reaction mixture was then evaporated to dryness, giving a colorless product which, after washing with ether, was recrystallized from H_2O to form colorless prisms: 1.8 g (93%); mp 176–178 °C; IR (KBr) 3600–2850 (br OH), 1750 (CO) cm^{-1}; NMR (CF_3COOH) δ 4.87 (s, 2, NCH_2COO), 7.00–7.50 (m, 4, aromatic); mass spectrum, m/e (relative intensity) 193 ($M^{+\cdot}$, 47), 149 ($M^{+\cdot}$ – CO_2, 38), 148 ($M^{+\cdot}$ – CO_2H, 92).

Anal. Calcd for $C_9H_7NO_4$: C, 55.96; N, 3.65; N, 7.25. Found: C, 55.89; H, 3.60; N, 7.20.

(2-Oxobenzoxazol-3-yl)acetyl Chloride (9). The carboxylic acid (**5**, R = H; 1.93 g, 0.01 mol) in $CHCl_3$ (10 mL) was heated under reflux with $SOCl_2$ (2 mL) for 4 h. The reaction mixture was evaporated to dryness in vacuo, giving a colorless, crystalline product which formed colorless needles from benzene–petroleum ether (bp 40–60 °C): 2.1 g (99%); mp 112–113 °C; IR (KBr) 1770, 1620 (CO) cm^{-1}; NMR ($CDCl_3$) δ 4.90 (s, 2, NCH_2COO), 6.8–7.3 (m, 4, aromatic); mass spectrum, m/e (relative intensity) 211 ($M^{+\cdot}$, 10), 148 ($M^{+\cdot}$ – COCl, 100).

Anal. Calcd for $C_9H_6ClNO_3$: C, 51.08; H, 2.86; N, 6.62. Found: C, 51.36; H, 2.86; N, 6.48.

Formation of (2-Oxobenzoxazol-3-yl)acetic Acid. 2-(3*H*)-Benzoxazolinone 1:1 Complex (6, R = H). 2(3*H*)-Benzoxazolinone (13.5 g, 0.1 mol) was added portionwise to a suspension of NaH (12 g, 0.25 mol; 50% in oil) in dry DMF (50 mL). The resulting dark-blue solution was stirred at room temperature for 30 min and then cooled with ice–water. Bromoacetic acid (13.9 g, 0.1 mol) was added at such a rate that the reaction temperature did not exceed 30 °C (about 30 min). After it was cooled to room temperature and poured onto crushed ice, and the resulting solution made slightly acid with concentrated HCl, the beige colored precipitate was collected and recrystallized from water, forming colorless prisms of **6** (R^1 = H): 16.0 g (97%); mp 149 °C; IR (KBr) 3500–3200 (br, OH, NH), 1760, 1710, 1610 (br, CO) cm^{-1}; NMR (CF_3COOH) δ 4.87 (s, 2, CH_2), 7.20 (s, 8, aromatic); mass spectrum, m/e (relative intensity), 193 ($M^{+\cdot}$ of **5** (R = H), 20), 149 ($M^{+\cdot}$ of **5** (R = H) – CO_2, 14), 148 [$M^{+\cdot}$ of **5** (R^1 = H) – COOH, 26), 135 [$M^{+\cdot}$ of 2(3*H*)-benzoxazolinone, 100).

Anal. Calcd for $C_{16}H_{12}N_2O_6$: C, 58.54; H, 3.68; N, 8.53. Found: C, 58.69; H, 3.91; N, 8.65.

1,2-Bis(2-oxobenzoxazol-3-yl)-2-oxoethane (8, R^1 = H). The above 1:1 complex (**6**, R^1 = H; 0.39 g, 1.1 mmol), *N,N'*-dicyclohexylcarbodiimide (0.51 g, 2.5 mmol) and dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) were heated under reflux in dry CH_2Cl_2 (5 mL) for 2 h. After the solution was cooled with ice, the colorless precipitate was filtered and washed several times with CH_3OH to remove *N,N'*-dicyclohexylurea. The product (**8**, R^1 = H) crystallized from $CHCl_3$ as colorless needles: 0.22 g (67%); mp 260–261 °C; IR (KBr) 1770, 1720 (CO) cm^{-1}; mass spectrum, m/e 310 ($M^{+\cdot}$, 15).

Anal. Calcd for $C_{16}H_{10}N_2O_5$: C, 61.94; H, 3.25; N, 9.03. Found: C, 62.34; H, 3.12; N, 9.32.

The same amide was also obtained in the absence of dimethyl acetylenedicarboxylate.

Formation of (2-Oxobenzoxazol-3-yl)phenylacetic Acid. 2(3*H*)-Benzoxazolinone 1:1 Complex (6, R^1 = Ph). Reaction of 2(3*H*)-benzoxazolinone (5.4 g, 0.04 mol), NaH (3.8 g, 0.08 mol; 50% in oil) in DMF (50 mL) and α-bromophenylacetic acid (8.6 g, 0.04 mol) as described above gave finally a colorless product which crystallized as colorless plates from water or benzene: 4.5 g (56%); mp 149–150 °C; IR (KBr) 3600–3200 (very strong and broad), 3050–2500 (br, OH, NH), 1750, 1700 (br, CO) cm^{-1}; NMR ($CDCl_3$) δ 6.35 (s, 1, CHCOO), 7.3 (br s, 8, aromatic), 7.50 (s, 5, phenyl).

Anal. Calcd for $C_{22}H_{16}N_2O_6$: C, 65.34; H, 3.99; N, 6.93. Found: C, 65.94; H, 4.00; N, 6.94.

1,2-Bis(2-oxobenzoxazol-3-yl)-1-phenyl-2-oxoethane (8, R^1 = Ph). The above 1:1 complex (**6**, R^1 = Ph; 0.27 g) and *N,N'*-dicyclohexylcarbodiimide (0.21 g, 1 mmol) were heated under reflux for 17 h in anhydrous CS_2 (10 mL). After the mixture was cooled, the colorless precipitate of *N,N'*-dicyclohexylurea was filtered off and the filtrate evaporated in vacuo to give an oily residue. After trituration with Et_2O, colorless crystals were obtained which separated from benzene as colorless prisms: 0.07 g (27%); mp 210 °C; IR (KBr) 1780, 1720, 1610 (CO) cm^{-1}; mass spectrum, 386 ($M^{+\cdot}$, 19).

Anal. Calcd for $C_{22}H_{14}N_2O_5$: C, 68.39; H, 3.65; N, 7.25. Found: C, 68.17; H, 3.62; N, 7.13.

Attempted Reaction of (2-Oxobenzoxazol-3-yl)acetic Acid with Dimethyl Acetylenedicarboxylate. Formation of (7). The carboxylic acid (**5**, R = H; 0.39 g, 2 mmol), dimethyl acetylenedicarboxylate (0.3 g slight excess), and *N,N'*-dicyclohexylcarbodiimide (0.51 g, 2.5 mmol) in anhydrous benzene (5 mL) were heated under reflux for 3 h. The separated *N,N'*-dicyclohexylurea was filtered off and the benzene evaporated. The oily residue was treated successively with ether and 2-propanol, giving colorless crystals which were finally washed with methanol. Crystallization from benzene afforded colorless needles of **7**: 0.31 g (54%); mp 205 °C dec; IR (KBr) 1770, 1710, 1690 (CO) cm^{-1}; NMR ($CDCl_3$), δ 1.5–2.5 (br m, 20, cyclohexyl CH_2), 3.7 (br m, 2, cyclohexyl CH), 4.75 (s, 4, NCH_2), 6.8–7.2 (m, 8, aromatic).

Anal. Calcd for $C_{31}H_{34}N_4O_7$: C, 64.79; H, 5.96; N, 9.75. Found: C, 65.24; H, 5.93: N, 9.71.

***N*-(Ethoxycarbonyl)-*N*-phenylglycine (11).** Purification of a sample prepared according to published procedures[7] was most efficiently achieved through the ammonium salt. The crude acid was treated with a cold, saturated solution of ammonia in ethanol. The colorless salt was collected and washed with ether followed by a small amount of cold EtOH, mp 150–151 °C. Treatment of this salt with dilute HCl (10%), followed by Et_2O extraction and washing and drying of the Et_2O extract, gave, after evaporation of the Et_2O, a colorless oil: 78%; NMR (Me_2SO-d_6) δ 7.37 (s, 5, Ph), 5.60 (br, 1, COOH), 4.28 (s, 2, NCH_2), 4.10 (q, 2, CH_2CH_3), 1.13 (t, 3, CH_2CH_3).

Attempted Reaction of *N*-(Ethoxycarbonyl)-*N*-phenylglycine with *N,N'*-Dicyclohexylcarbodiimide. Purified *N*-(ethoxycarbonyl)-*N*-phenylglycine (11; 2.23 g, 0.01 mol) in dry benzene (30 mL) was treated with DCC (2.06 g, 0.01 mol) and dimethyl acetylenedicarboxylate (1.56 g, 0.011 mol) was then added. After 12 h of reflux the precipitated material was removed

from the cooled reaction mixture and washed with benzene to give 1.4 g. The combined benzene solutions were evaporated to dryness and the residue was chromatographed over silica gel, using petroleum ether (bp 40–60 °C)–ether (9:1) as eluant. The initial fraction, on trituration with petroleum ether–ether formed colorless needles, 1.3 g. The filtrate essentially contained dimethylacetylenedicarboxylate. Further recrystallization from hexane afforded **13** as colorless needles, mp 125–126 °C. Additional quantities (0.76 g) of **13** were eluted from the column by increasing the amount of Et_2O in the elution mixture. Unreacted **11** was the last product eluted from the column. **13**: IR (KBr) ν_{CO} 1695, 1655 cm^{-1}; NMR ($CDCl_3$) δ 7.37 (s, 5, Ph), 4.43 (s, 2 NCH_2CO), 4.17 (q, 2, J = 7.0 Hz, $COOCH_2CH_3$), 3.67 (br, 1, NH), 1.86–1.07 (m, 25, aliphatic and $COOCH_2CH_3$); mass spectrum, m/e (relative intensity) 429 ($M^{+\cdot}$, 22).

Anal. Calcd for $C_{24}H_{35}N_3O_4$: C, 67.10; H, 8.21; N, 9.78. Found: C, 67.12; H, 8.20; N, 9.73.

Registry No. **4** (R = H), 75125-23-4; **4** (R = COOEt), 75125-24-5; **5** (R = H), 13610-49-6; **5** (R = Et), 13610-51-0; **6** (R′ = H), 75125-25-6; **6** (R′ = Ph), 75125-27-8; **7**, 75125-28-9; **8** (R′ = H), 75125-29-0; **8** (R′ = Ph), 75125-30-3; **9**, 74527-22-3; **11**, 75125-31-4; **11** ammonium salt, 75125-32-5; **13**, 75125-33-6; 2-oxazolidone, 497-25-6; ethyl bromoacetate, 105-36-2; 2(3*H*)-benzoxazolinone, 59-49-4; α-bromophenylacetic acid, 4870-65-9; *N*,*N*′-dicyclohexylcarbodiimide, 13488-09-0.

Synthesis and Characterization of [Methoxy(tosyloxy)iodo]benzene, an Acyclic Monoalkoxyiodinane

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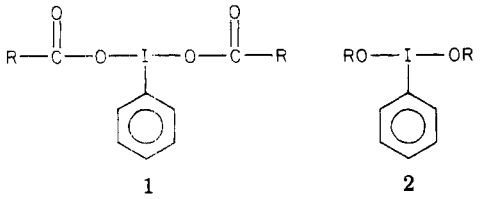
Organoiodine(III) compounds with iodine-bound alkoxy groups are rare. Indeed, while the aryliodosodicarboxylates **1** are well-known and moderately stable[1] to thermal decomposition, the analogous aryliodosodialkoxides **2** have



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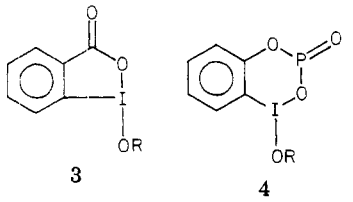
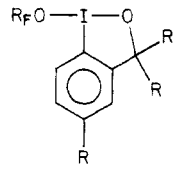


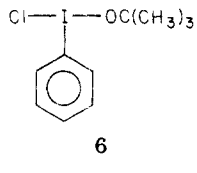
3

4

not been prepared. The inclusion of iodine into five- and six-membered rings stabilizes its hypervalent states, and cyclic alkoxyiodinanes are known. Structures **3** and **4** have been assigned to the esters of *o*-iodosobenzoic acid[2] and *o*-iodosophenylphosphoric acid.[3] Recently, Martin and Amey utilized the stabilizing capacity of electronegative ligands in conjunction with that of cyclic structures to synthesize the first dialkoxyiodinanes; these are of general structure **5**.[4,5] They also prepared several related mono-



5, R_F = $Ph(CF_3)_2$



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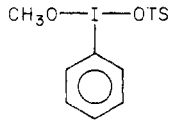

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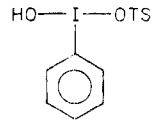

8

alkoxyiodinanes, among them being the first isolated bromoiodinanes. To our knowledge, [chloro(*tert*-butoxy)iodo]benzene (**6**), reported by Tanner and Gidley in 1968, is the only known example of an isolated acyclic alkoxyiodianane.[6] In this note, we detail the synthesis and characterization of [methoxy(tosyloxy)iodo]benzene (**7**), a crystalline, acyclic monoalkoxyiodinane in which two ligands are bonded to iodine(III) through oxygen.

[Hydroxy(tosyloxy)iodo]benzene (**8**), first reported by Neiland and Karele in 1970,[7] is a rather versatile reagent. We have recently found that it will undergo ligand-transfer reactions with a variety of aryl iodides[8] and that it, and some of its analogues, will react with aryltrimethylsilanes in CH_3CN, thus affording a regiospecific synthesis of iodonium salts.[9] We have also discovered a facile one-step α-tosyloxylation reaction of mono- and diketones with (**8**).[10]

[Hydroxy(tosyloxy)iodo]benzene (**8**) serves as a precursor of **7**. An example preparation of **7** follows. [Hydroxy(tosyloxy)iodo]benzene (**8**, 2.00 g) was added to trimethyl orthoformate (~2 mL), and the reaction mixture was flushed with nitrogen. After 10 min, the white crystals of **8** had dissolved to give a clear yellow solution. After a time, large glassy plates of **7** crystallized from the liquid and were subsequently isolated by decantation and blown dry with nitrogen (yield 1.79 g, mp 88–92 °C).

The structure of **7** was assigned on the basis of its elemental composition (C, H, I) and by NMR analysis. The ^1H NMR spectrum (CD_3CN, Me_4Si) exhibits singlets at δ 2.28 [(tosyloxy)methyl] and 3.92 (OCH_3) and a complex aromatic multiplet. Confusion reigned in our initial attempts to characterize **7** owing to crystal-surface hydrolysis by atmospheric moisture; in the presence of water, it hydrolyzes rapidly and efficiently back to [hydroxy(tosyloxy)iodo]benzene. In one experiment, **7** (0.90 g) was dissolved in dry acetonitrile (2 mL; **7** is quite soluble in CH_3CN). Upon treatment with 0.1 g of water, the solution immediately became filled with white crystals of insoluble **8** (0.72 g, 83%).

We considered two plausible mechanisms for the hydrolysis reaction, one involving nucleophilic displacement of $PhI(OTS)O^-$ from the methyl carbon of the methoxyl group by H_2O and another involving formal displacement of methanol from iodine after initial nucleophilic attack of water at the iodine atom; both are illustrated in Scheme I.

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