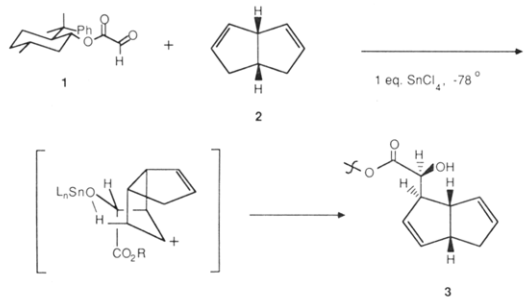


Figure 1.

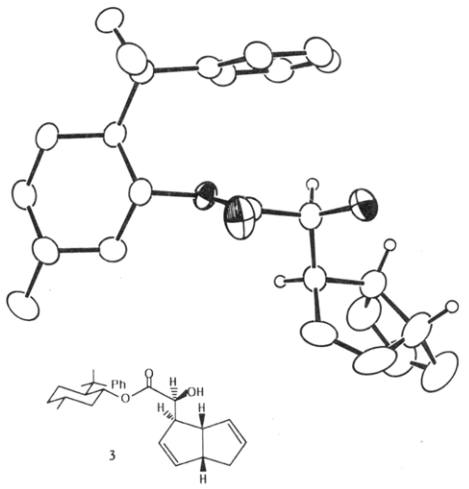


Figure 2.

spectra of the product both before and after purification were consistent with the presence of only one diastereomer.[6] The relative and absolute stereochemical relationships were determined by a single-crystal, X-ray analysis (Figure 2).[7] In accord with our previous observations of high levels of asymmetric induction with **1**, the reaction occurred on only one face of the aldehyde and, in addition, had been limited to the exo face of the bicyclo[3.3.0]octadiene. In addition, only one of the two enantiotopically related rings of diene **2** underwent reaction, the result of the combination of the two face selectivities operating in concert on the transition state.[8]

To our knowledge this is the first practical example of a nonenzymatic reaction that shows selective breaking of molecular symmetry. We anticipate that this concept will find application in the synthesis of a range of natural products and ourselves are pursuing its use in the synthesis of iridoid terpenes.

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(6) The $^{13}C$ spectrum of the crude reaction product showed the largest impurity peaks to be less than 5% of those for **3**.

(7) We have accumulated a large body of experimental observations for the ene reactions of glyoxylate **1** which is consistent with a two-step mechanism where the stereochemical outcome is controlled in the second or a proton-transfer step leading from an intermediate carbocation to product.

(8) We are grateful to Dr. Steven Larsen of the University of Texas at Austin for this analysis. Full details will appear in the near future in a complete accounting of our research involving asymmetric induction in the ene reactions of **1**.

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## Synthesis of Dichlorocyclobuta[*b*]benzofuran-2a-carboxylic Derivatives and 3-(Trichlorovinyl)coumarin through the Cross Photocycloadduct of Coumarin and Tetrachloroethylene

*Summary:* Treatment of the cross photocycloadduct of coumarin and tetrachloroethylene with nucleophiles gives dichlorocyclobuta[*b*]benzofuran-2a-carboxylic derivatives in excellent yields via lactone-opening, cyclobutene formation and intramolecular $S_N2'$ displacement or affords 3-(trichlorovinyl)coumarin in a high yield via cyclobutene formation followed by [2 + 2] cycloreversion.

*Sir:* Photochemical cyclobutanation of a heterocyclic ring system often brings about highly enhanced reactivity in the heterocyclic ring as observed in the reaction of coumarin dimers and their derivatives.[1] Our continuing studies on this subject have led us to examine a cross photocycloaddition of coumarin and tetrachloroethylene to prepare 1,1,2,2-tetrachloro-1$\alpha$,2$\alpha$,2a$\alpha$,8b$\alpha$-tetrahydro-3*H*-cyclobuta[*c*]chromen-3-one (**1**), with an expectation that cyclobutane-fused pyrone compounds would undergo some attractive reactions such as ring-expansion or rearrangement.[2]

In this communication we wish to report the reaction of **1** with nucleophiles, resulting in a ring contraction to 1,2-dichloro-2a$\alpha$,7b$\alpha$-dihydrocyclobuta[*b*]benzofuran-2a-carboxylic derivatives (**4**) or in a cycloreversion via cyclobutene formation to give 3-(trichlorovinyl)coumarin (**7**).

The typical procedure for the preparation of the cross photocycloadduct is as follows: 14.54 g (0.10 mol) of coumarin and 3.14 g (0.017 mol) of benzophenone were dissolved in a mixture of tetrachloroethylene (633.6 g, 3.82 mol) and benzene (36.0 g). The solution was irradiated with 500-W high-pressure mercury lamp through Pyrex filter for 28.5 h. After concentration of the reaction mixture under reduced pressure, silica gel column chromatographic separation gave 9.52 g (30.5%) of **1**.[3]

Treatment of **1** with butylamine or alkali smoothly gave two compounds in a ratio depending on the basicity and/or the amount of the nucleophile used, but neither of them was the simple lactone-opened derivative (**2a,b**). By spectroscopic analysis the compounds were revealed to be **3**[4] and 4.[5] The result means that dehydrochlorination causing cyclobutene formation took place immediately after lactone-opening reaction of **1**. The formation of **4** proceeds through the ring closure of **3** via intramolecular $S_N2'$ displacement by the attack of the phenoxy anion on the $sp^2$ carbon in the cyclobutene ring. This ring-closure step was more influenced by the basicity of the nucleophile than the cyclobutene formation step (runs 2–8, Table I).

(1) (a) Yonezawa, N.; Hasegawa, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 367. (b) Hasegawa, M.; Saigo, K.; Katsuki, H.; Yonezawa, N.; Kanoe, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2345. (c) Saigo, K.; Yonezawa, N.; Sekimoto, K.; Hasegawa, M.; Ueno, K.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1000. (d) Yonezawa, N.; Yoshida, T.; Hasegawa, M. *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1083.

(2) (a) Hanifin, J. W.; Cohen, E. *J. Org. Chem.* **1968**, *33*, 2811. (b) Hanifin, J. W.; Cohen, E. *J. Org. Chem.* **1971**, *36*, 910. (c) Haywood, D. J.; Hunt, R. G.; Potter, C. J.; Reid, S. T. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2458. (d) Shimo, T.; Somekawa, K.; Kuwakino, S.; Tsuge, O.; Kanemasa, S. *Chem. Lett.* **1984**, 1503.

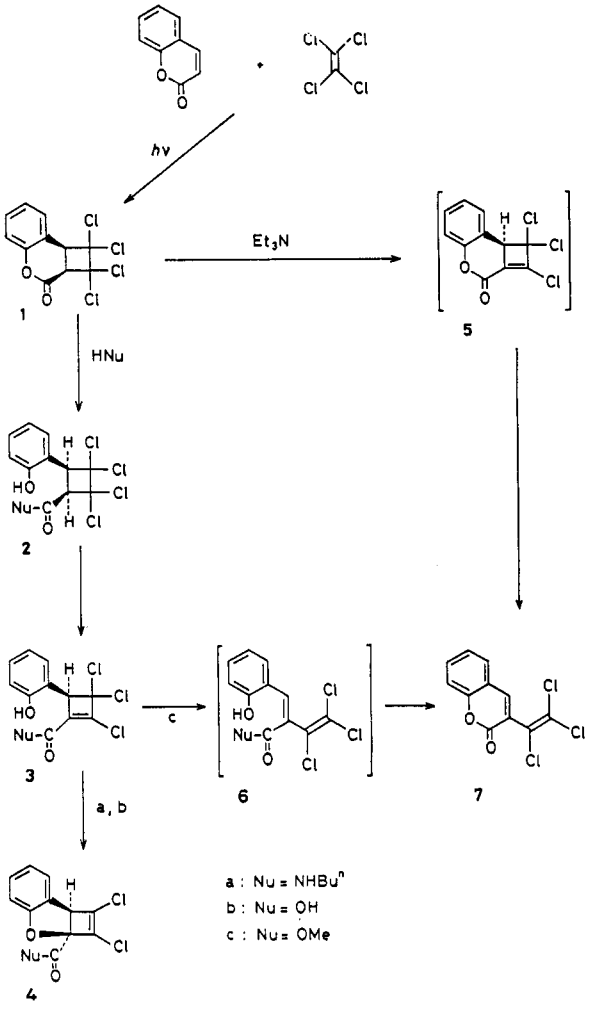
(3) **1**: mp 144–145 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 4.22 (d, 1 H, $J$ = 10 Hz), 4.59 (d, 1 H, $J$ = 10 Hz), 7.07–7.43 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 50.7 (d), 50.8 (d), 89.8 (s), 93.9 (s), 114.3 (s), 117.5 (d), 125.2 (d), 129.5 (s), 131.0 (d), 151.6 (s), 158.9 (s); IR (KBr) $\nu$ 1770, 930, 820, 805, 775, 745, 700 $cm^{-1}$. Anal. Calcd for $C_{11}H_6Cl_4O_2$: C, 42.35; H, 1.93; Cl, 45.46. Found: C, 42.23; H, 2.06; Cl, 45.04. On the basis of $^1H$ NMR spectrum of the reaction mixture, it was confirmed that 42% of coumarin converted to **1**, 13% to anti head-to-head coumarin dimer, and trace amount (less than 0.5%) to syn head-to-head and anti head-to-tail coumarin dimers. No other products could be detected.

0022-3263/85/1950-3026$01.50/0 

**Table I. Reaction of 1**

| run | base | equiv | solvent | time/h | temp[b]/°C | % conversion[a] (isolated yield) 2 | 3 | 4 | 7 | % recovery[a] of 1 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $BuNH_2$ | 1 | acetone | 1 | rt | 0 | 48 | 0 | 0 | 52 |
| 2 | $BuNH_2$ | 2 | acetone | 1 | rt | 0 | 100 (67) | 0 | 0 | 0 |
| 3 | $BuNH_2$ | 4 | dioxane | 1 | rt | 0 | 40 | 60 | 0 | 0 |
| 4 | $BuNH_2$ | 10 | acetone | 1.5 | rt | 0 | 0 | 100 (96) | 0 | 0 |
| 5 | $NaHCO_3$ | 10 | $H_2O$–acetone | 42 | rt | 0 | 90 (31) | 10 | 0 | 0 |
| 6 | $Na_2CO_3$ | 30 | $H_2O$–MeOH | 97 | rt | 0 | 0 | 100 | 0 | 0 |
| 7 | NaOH | 1 | $H_2O$–acetone | 4 | rt | 0 | 28 | 12 | 0 | 60 |
| 8 | NaOH | 10 | $H_2O$–acetone | 1 | 60 | 0 | 0 | 100 (90) | 0 | 0 |
| 9 | MeOH | excess | MeOH–acetone | 240 | rt | 52 | 0 | 0 | 0 | 48 |
| 10 | MeOH | excess | MeOH–acetone | 60 | rflx | 40 | 3 | 0 | 11 | 46 |
| 11 | MeOH | excess | MeOH | 60 | rflx | 21 | 12 | 0 | 19 | 48 |
| 12 | $Et_3N$ | 45 | benzene | 0.25 | rt | 0 | 0 | 0 | 100 (82) | 0 |

[a] Conversion and recovery were determined on the basis of the $^1H$ NMR spectra of the crude products. [b] rt = room temperature; rflx = reflux temperature.




The reactions mentioned above resulted finally in an almost quantitative contraction to the cyclobutene-fused benzofuran system (runs 4, 6, and 8).

However, when methanol was used as a nucleophile at room temperature, the simple lactone-opened cyclobutane compound **2c** was formed as a sole product[6] (run 9). Along with relactonization to **1**, **2c** was easily transformed to dehydrochlorination product **3c**[4] and **7**[7] on heating (runs 10 and 11) or under acidic conditions such as treatment with silica gel. As methanol cannot produce phenoxy anion from the phenolic hydroxy group of **3c**, the cycloreversion of **3c** occurred instead of the intramolecular $S_N2'$ displacement. The plausible intermediate, methyl 2-(trichlorovinyl)coumarate (**6c**), would gradually form and smoothly undergo thermal or acid-catalyzed relactonization to **7**.[1d]

The exclusive formation of **7** was performed in the reaction of **1** with triethylamine. The dehydrochlorination of **1**, giving intermediate **5**, is considered to be the sole reaction route with such a nonnucleophilic base. In a similar manner to the dehydrochlorination and cyclocleavage reactions of the photocycloadduct of cyclohexanone and dichloroethylene,[8] smooth cycloreversion of the cyclobutene ring in the unstable intermediate (**5**) would proceed easily to give **7** exclusively.

The syntheses of cyclobutene-fused benzofuran systems by [2 + 2] photocycloaddition were reported by Tinnemans and Neckers[9] along with a large number of reports about the 4,5,6-fused ring systems of nitrogen and sulfur ana-

(4) **3a**: glass; $^1H$ NMR ($CDCl_3$) $\delta$ 0.95 (t, 3 H, $J$ = 7.3 Hz), 1.20–1.80 (m, 4 H), 3.29–3.50 (m, 2 H), 5.15 (s, 1 H), 6.14 (br s, 1 H), 6.60–7.25 (m, 4 H), 7.96 (br s, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.7 (q), 20.0 (t), 31.3 (t), 39.5 (t), 59.3 (d), 84.5 (s), 115.3 (d), 119.6 (d), 120.5 (s), 128.3 (d), 129.8 (d), 134.3 (s), 134.8 (s), 155.2 (s), 160.0 (s); IR (KBr) $\nu$ 1655, 1530, 760, 595 $cm^{-1}$. **3b**: mp 132 °C dec; $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 4.97 (s 1 H), 6.67–6.90 (m, 3 H), 7.15–7.20 (m, 1 H), 9.89 (s, 1 H), 13.8 (br s, 1 H); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 60.8 (d), 85.9 (s), 115.9 (d), 120.2 (d), 122.1 (s), 129.6 (d), 130.5 (d), 133.8 (s), 140.3 (s), 156.9 (s), 161.2 (s); IR (KBr) $\nu$ 1705, 885, 740, 600 $cm^{-1}$. **3c**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.81 (s, 3 H), 5.07 (s, 1 H), 6.75–6.95 (m, 4 H).

(5) **4a**: mp 94–95 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.94 (t, 3 H, $J$ = 7.3 Hz), 1.31–1.41 (m, 2 H), 1.50–1.60 (m, 2 H), 3.26–3.36 (m, 1 H), 3.38–3.48 (m, 1 H), 4.62 (s, 1 H), 6.68 (br s, 1 H), 6.96–7.06 (m, 2 H), 7.26–7.34 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.7 (q), 20.0 (t), 31.5 (t), 39.4 (t), 58.9 (d), 91.4 (s), 112.3 (d), 122.4 (d), 124.4 (s), 124.6 (s), 125.2 (d), 129.8 (d), 136.7 (s), 161.1 (s), 165.1 (s); IR (KBr) $\nu$ 1665, 1555, 1230, 875, 740, 635 $cm^{-1}$. Anal. Calcd for $C_{15}H_{15}Cl_2NO_2$: C, 57.71; H, 4.84; N, 4.49; Cl, 22.71. Found: C, 57.43; H, 4.74; N, 4.53; Cl, 22.71. **4b**: mp 144 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 4.66 (s, 1 H), 6.98–7.04 (m, 2 H), 7.24–7.30 (m, 2 H), 9.46 (s, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 60.27 (d), 89.8 (s), 113.3 (d), 122.3 (d), 124.2 (s), 125.0 (s), 125.8 (d), 130.9 (d), 138.3 (s), 140.3 (s), 156.9 (s), 161.2 (s); IR (KBr) $\nu$ 1730, 1700, 1230, 940 $cm^{-1}$. Anal. Calcd for $C_{11}H_6Cl_2O_3$: C, 51.39; H, 2.35; Cl, 27.58. Found: C, 51.53; H, 2.50; Cl, 26.99.

(6) Isolation of **2c** was unsuccessful since relactonization took place easily on the silica gel column. The formation of **2c** was ascertained by the $^1H$ and $^{13}C$ NMR spectra of the reaction mixture, which show two doublets of cyclobutane ring protons ($\delta$ 4.49 and 4.89 ($J$ = 10.1 Hz), $CDCl_3$) and four peaks of cyclobutane ring carbons ($\delta$ 51.9 (d), 59.0 (d), 89.2 (s), and 93.0 (s), $CDCl_3$), respectively. Other peaks appeared in the reasonable regions for **2c**.

(7) **7**: mp 129–130 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.32–7.40 (m, 2 H), 7.54–7.65 (m, 2 H), 7.87 (s, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 117.6 (d), 118.9 (s), 124.2 (s), 124.6 (s), 124.7 (s), 125.6 (d), 129.3 (d), 133.9 (d), 145.4 (d), 154.8 (s), 158.0 (s); IR (KBr) $\nu$ 1725, 1700, 1600, 1200, 890, 815, 770 $cm^{-1}$. Anal. Calcd for $C_{11}H_5Cl_3O_2$: C, 47.95; H, 1.83; Cl, 38.60. Found: C, 47.78; H, 1.98; Cl, 38.64.

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logues.[10] According to their method the cyclobutene-fused benzofuran was synthesized by the cross photocycloaddition of benzofurans and an alkyne, but initial photoadduct easily underwent photoisomerization, resulting in the formation of a complicated mixture of the rearranged isomers. By contrast, for the reaction described here, **4a** and **4b** were formed exclusively from **1**, which is readily prepared as a pure material in an adequate yield. In addition, compared to the related nucleophilic and/or thermal ring transformation reactions of pyrone derivatives to give furans,[11] the ring contraction from **1** proceeds under mild conditions even when butylamine was used as a nucleophile at room temperature. For the occurrence of this ring contraction, the ring-opening reaction must occur before dehydrochlorination, and the $S_N2'$ displacement must proceed much faster than the [2 + 2] cycloreversion. If either reaction is slow, a considerable amount of **7** would form. Thus, this result clearly shows the highly enhanced ring-opening tendency of the lactone ring of **1**. This high reactivity is considered to be attributable to the strain of the lactone rings which was brought about by cyclobutanation. Although under such weakly basic conditions, the equilibrium between the phenolic hydroxyl group and the phenolic anion does not favor the phenoxy anion; the neighboring group effect permits the nucleophilic attack of the phenoxy anion to proceed so rapidly that it competes effectively with the thermal cycloreversion.

**Registry No.** 1, 96964-81-7; **2**, 96964-82-8; **3a**, 96964-83-9; **3b**, 96964-86-2; **3c**, 96964-87-3; **4a**, 96964-84-0; **4b**, 96964-88-4; **7**, 96964-85-1; coumarin, 91-64-5; tetrachloroethylene, 127-18-4.

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