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# Synthesis of Dichlorocyclobuta[*b*]benzofuran-2a-carboxylic Derivatives and 3-(Trichloroethenyl)coumarin through Cross Photocycloadduct of Coumarin and Tetrachloroethylene[1)]

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Photoirradiation of coumarin and tetrachloroethylene with a high-pressure mercury lamp through Pyrex filter in the presence of benzene and benzophenone gave cross cycloadduct (**3**) in a moderate yield. By treatment with bases or nucleophiles at room temperature, **3** underwent ring-contraction reaction through lactone-opening, cyclobutene formation, and intramolecular $S_N2'$ displacement to yield dichlorocyclobuta[*b*]-benzofurancarboxylic derivatives exclusively. By use of a non-nucleophilic base, 3-(trichloroethenyl)coumarin was alternatively obtained through [2+2] cycloreversion of cyclobutene intermediate in a good yield.

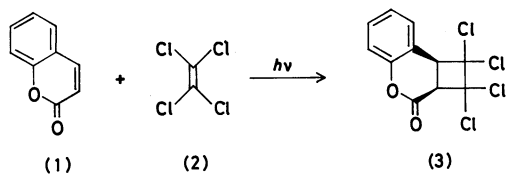
[2+2] Photocycloadducts of olefins occasionally have particular reactivities based on their strain arisen from the highly restricted geometry. For example, we have reported the highly enhanced reactivities of coumarin dimers and their lactone-opened derivatives,[2)] and their application to polymer synthesis and polymer reaction.[3)] Our continuing studies on [2+2] photocycloadducts led us to investigate the reaction of the compounds having dissymmetrical structures. Recently, we carried out cross photocycloaddition reaction of coumarin (**1**) and tetrachloroethylene (**2**) with an expectation that cyclobutane-fused pyrone compounds would undergo easily lactone-opening reaction to lead some attractive reactions such as ring-expansion and rearrangement.[4)] The reaction of the obtained cross photocycloadduct, 1,1,2,2-tetrachloro-1$\alpha$,2$\alpha$,2a$\alpha$,8b$\alpha$-tetrahydro-3*H*-cyclobuta[*c*][1]benzopyran-3-one (**3**), with nucleophiles or bases resulted in the ring-contraction or cycloreversion to give two types of compounds. One is dichlorocyclobuta[*b*]benzofuran-2a-carboxylic derivatives (**6**), which would be yielded via lactone-opening, cyclobutene formation, and intramolecular $S_N2'$ displacement. The other is 3-(trichloroethenyl)coumarin (**9**) obtained by cycloreversion of the cyclobutene intermediate.

In this paper, we wish to report these reactions in detail with the X-ray structural analysis of the new type of compound having 4,5,6-fused ring system.

## Results and Discussion

The cross photocycloaddition between coumarin (**1**) and tetrachloroethylene (**2**) was undertaken by irradiation with the light of a high-pressure mercury lamp. When the irradiation was carried out in the absence of benzene, the photoreaction did not proceed at all. Moreover, when benzophenone was not present, the formation of homodimers of coumarin, anti head-to-head, anti head-to-tail, and syn head-to-head coumarin dimers, overcame the production of cross cycloadduct (**3**). Accordingly, for the synthesis of **3** in a high yield, presence of both benzene and benzophenone was proved to be essential. Under the optimum conditions, 52% conversion to **3** and 39% isolated yield were achieved (Scheme 1).

Treatment of **3** with methanol at room temperature gave simply lactone-opened derivative **4a** as a sole product (Run 1), which would be obtained in analogy with the lactone-opening reaction of coumarin dimers.[2a)] When the reaction was undertaken at reflux temperature, cyclobutene compound **5a** and 3-(trichloroethenyl)coumarin (**9**) were formed (Runs 2 and 3). Though easy relactonization of cyclobutanecarboxylate **4a** to lactone **3** on heating or under acidic conditions such as contact with silica gel disturbed the isolation, the formation of **4a** was ascertained by $^1$H and $^{13}$C NMR spectra of the reaction mixture, which showed two doublets of cyclobutane ring protons [$\delta$=4.49 and 4.89 ($J$=10 Hz), in $CDCl_3$] and four peaks of cyclobutane ring carbons [$\delta$=51.9 (d), 59.0 (d), 89.2 (s), and 93.0 (s), in $CDCl_3$], together with other peaks appearing in the reasonable regions for **4a**. Isolation of cyclobutenecarboxylate **5a** was also unsuccessful, because of the spontaneous transformation to trichloroethenylcoumarin (**9**). The formation of **5a** was also confirmed by the $^1$H NMR spectrum of the reaction mixture, which showed singlet for methoxyl protons (3H) at $\delta$=3.81, singlet for cyclobutene ring proton (1H) at $\delta$=5.07, and multiplet for aromatic protons



(1) (2) (3)

Scheme 1.

(4H) at $\delta$=6.75—6.95.

However, when butylamine or an alkali was used, two types of compounds (**5** and **6**) were obtained in the ratio depending on the basicity and/or the amount of the nucleophile used. Simply lactone-opened derivatives **4b**, **4c** were not detected. This result indicates that in the reaction of **3** with butylamine or an alkali, lactone-opening reaction initially took place to produce cyclobutanecarboxylic derivatives **4**, followed by immediate dehydrochlorination reaction yielding cyclobutenes **5**, and finally intramolecular $S_N2'$ displacement occurred by the attack of the phenolate anion on the $sp^2$ carbon of the cyclobutene ring.

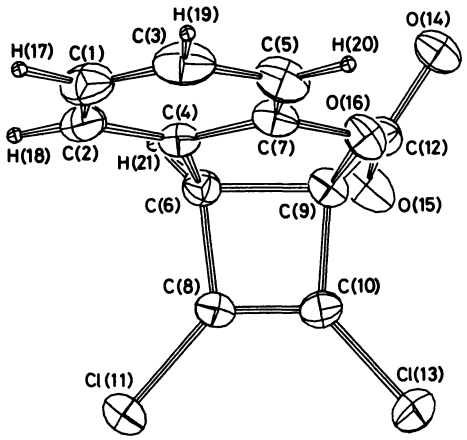



Fig. 1. Perspective view of cyclobutabenzofurancarboxylic acid (**6c**) drawn by ORTEP[12] program. Atoms (except hydrogen) are shown by ellipsoids of 30% probability.

The intramolecular $S_N2'$ displacement for ring closure was more influenced by the basicity of the nucleophile than the cyclobutene formation (Runs 5—11). The reaction mentioned above resulted finally in an almost quantitative contraction of the cyclobutenefused benzofuran systems (Runs 7, 9, and 11).

Reactions of **3** with nucleophiles or bases are summarized in Table 1.

The structures of these compounds were determined by $^1H$ and $^{13}C$ NMR spectra, IR spectra, and elemental analyses. The structure of cyclobutabenzofurancarboxylic acid (**6c**) was confirmed by X-ray analysis. The perspective view is shown in Fig. 1, and the atomic coordinates, the bond lengths, and the bond angles are shown in Tables 2—4.

As methanol has not enough basicity, in the reaction with **3** at room temperature methanol did not act other than a weak nucleophile and there existed an equilibrium between lactone-opened and -closed compounds. Then a mixture of lactone **3** and ester **4a** was obtained. But when the reaction mixture was heated at methanol reflux temperature, thermal dehydrochlorination of cyclobutanecarboxylate **4a** would occur to give cyclobutenecarboxylate **5a**. At such high temperature, by further [2+2] cycloreversion the plausible intermediate, methyl *cis*-3-(2-hydroxyphenyl)-2-(trichloroethenyl)-2-propenoate (**7a**), would be gradually formed from **5a**. Then, **7a** should smoothly undergo thermal or acid-catalyzed relactonization to give trichloroethenylcoumarin (**9**) without formation of cyclobutabenzofuran **6a**, because methanol cannot produce phenolate anion from

Table 1. Reaction of Cross Cycloadduct **3**

| Run | Base | Equiv | Solvent | Time / h | Temp[b] | Conversion[a] (Isolated Yield) % | | | | Recovery[a] % |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **4** | **5** | **6** | **9** | **3** |
| 1 | MeOH | 1250 | MeOH-Acetone (5:1) | 240 | r.t. | 52 | 0 | 0 | 0 | 48 |
| 2 | MeOH | 1000 | MeOH-Acetone (2:3) | 60 | reflux | 40 | 3 | 0 | 11 | 46 |
| 3 | MeOH | 12000 | MeOH | 60 | reflux | 21 | 12 | 0 | 19 | 48 |
| 4 | $BuNH_2$ | 1 | Acetone | 1 | r.t. | 0 | 48 | 0 | 0 | 52 |
| 5 | $BuNH_2$ | 2 | Acetone | 1 | r.t. | 0 | 100 (67) | 0 | 0 | 0 |
| 6 | $BuNH_2$ | 4 | Dioxane | 1 | r.t. | 0 | 40 | 60 | 0 | 0 |
| 7 | $BuNH_2$ | 10 | Acetone | 1.5 | r.t. | 0 | 0 | 100 (96) | 0 | 0 |
| 8 | $NaHCO_3$ | 10 | $H_2O$-Acetone (1:1) | 42 | r.t. | 0 | 90 (31) | 10 | 0 | 0 |
| 9 | $Na_2CO_3$ | 30 | $H_2O$-MeOH (3:2) | 97 | r.t. | 0 | 0 | 100 | 0 | 0 |
| 10 | NaOH | 1 | $H_2O$-Acetone (1:10) | 4 | r.t. | 0 | 28 | 12 | 0 | 60 |
| 11 | NaOH | 10 | $H_2O$-MeOH (5:1) | 1 | r.t. | 0 | 0 | 100 (90) | 0 | 0 |
| 12 | $Et_3N$ | 45 | Benzene | 0.25 | r.t. | 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) r.t. means room temperature.

phenolic hydroxyl group.

The exclusive formation of **9** was performed by treatment of **3** with triethylamine. As triethylamine has not nucleophilicity, the six-membered lactone-ring should be maintained all over the reaction steps. Then, by dehydrochlorination plausible 6,6,4-fused ring intermediate **8**, which is considered to be very unstable because of its highly restricted structure, would be formed, and immediate cycloreversion to **9** should exclusively proceed in a similar manner to the dehydrochlorination and cyclocleavage reactions of the photoadduct of cyclohexanone and dichloroethylene.[5]

On the contrary, the reaction path from cyclobutenecarboxylate **5a** to **9** via cyclobutene **8** seems unsuitable, since heating *N*-butylcyclobutenecarboxamide (**5b**) in benzene afforded **9** exclusively. The spontaneous lactonization of *cis*-cinnamamide derivative **7b** is reasonable, but the formation of very unstable 6,6,4-fused ring compound (**8**) together with cleavage of amide linkage looks very disadvantageous, and under such drastic conditions [2+2] cycloreversion of cyclobutene **5b** to diene **7** must proceed far rapidly.

The overall feature of these reactions is summarized in Scheme 2.

By the reactions mentioned above, cyclobutenecarboxylic derivatives fused benzofuran ring (**6**) were readily obtained through three sequential stepwise

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors for Cyclobutabenzofurancarboxylic Acid (**6c**) with Standard Deviations in Parentheses

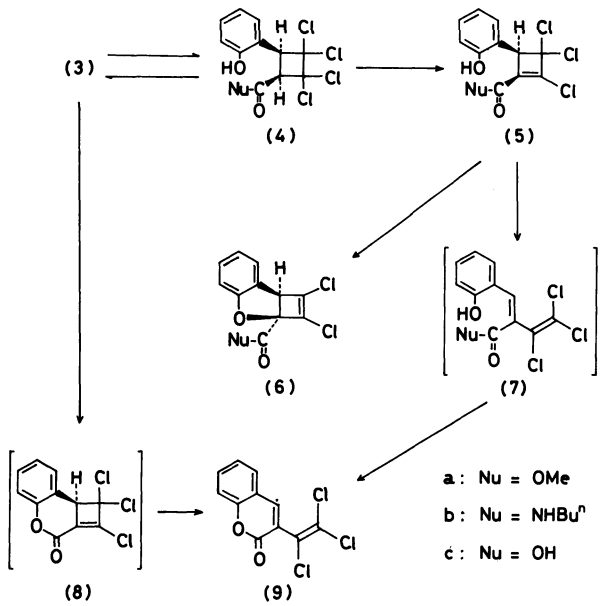
| No | Atom | $x$ $10^4$ | $y$ $10^4$ | $z$ $10^4$ | $B_{eq}$ Å$^2$ |
|---|---|---|---|---|---|
| 1 | C(1) | 973(3) | 1782(10) | 3501(6) | 4.95(0.10) |
| 2 | C(2) | 810(3) | 2007(9) | 5020(6) | 3.86(0.08) |
| 3 | C(3) | 1222(3) | −26(11) | 2978(6) | 5.33(0.10) |
| 4 | C(4) | 906(2) | 368(8) | 5963(5) | 3.09(0.07) |
| 5 | C(5) | 1318(3) | −1700(10) | 3910(6) | 4.61(0.09) |
| 6 | C(6) | 827(2) | 179(7) | 7646(5) | 2.94(0.06) |
| 7 | C(7) | 1146(2) | −1433(8) | 5422(5) | 3.44(0.07) |
| 8 | C(8) | 1481(2) | 634(7) | 8612(5) | 2.89(0.06) |
| 9 | C(9) | 1070(2) | −2069(7) | 7907(5) | 2.91(0.06) |
| 10 | C(10) | 1694(2) | −1241(8) | 8788(5) | 3.05(0.06) |
| 11 | Cl(11) | 1838(1) | 2853(2) | 9230(2) | 4.46(0.02) |
| 12 | C(12) | 573(2) | −3403(7) | 8786(5) | 3.12(0.07) |
| 13 | Cl(13) | 2403(1) | −2312(2) | 9703(2) | 4.64(0.02) |
| 14 | O(14) | 278(2) | −4860(5) | 8151(4) | 3.89(0.05) |
| 15 | O(15) | 500(2) | −2888(6) | 10149(4) | 5.16(0.07) |
| 16 | O(16) | 1205(2) | −2948(5) | 6479(4) | 3.57(0.05) |
| No | Atom | $x$ $10^3$ | $y$ $10^3$ | $z$ $10^3$ | $B_{eq}$ Å$^2$ |
| 17 | H(17) | 90(3) | 293(10) | 278(7) | 7(2) |
| 18 | H(18) | 63(3) | 327(9) | 536(6) | 6(1) |
| 19 | H(19) | 132(4) | −20(11) | 189(8) | 9(2) |
| 20 | H(20) | 149(3) | −294(10) | 348(7) | 7(2) |
| 21 | H(21) | 30(3) | 71(11) | 791(7) | 8(2) |

Table 3. Bond Lengths of Cyclobutabenzofurancarboxylic Acid (**6c**) with Standard Deviations in Parentheses

| | |
|---|---|
| C(1)-C(2) | 1.396(7) Å |
| C(1)-C(3) | 1.383(10) |
| C(2)-C(4) | 1.384(7) |
| C(3)-C(5) | 1.396(9) |
| C(4)-C(6) | 1.504(6) |
| C(4)-C(7) | 1.379(7) |
| C(5)-C(7) | 1.397(7) |
| C(6)-C(8) | 1.500(6) |
| C(6)-C(9) | 1.586(7) |
| C(7)-O(16) | 1.378(6) |
| C(8)-C(10) | 1.323(7) |
| C(8)-Cl(11) | 1.709(5) |
| C(9)-C(10) | 1.488(6) |
| C(9)-C(12) | 1.527(7) |
| C(9)-O(16) | 1.424(5) |
| C(10)-Cl(13) | 1.690(5) |
| C(12)-O(14) | 1.243(6) |
| C(12)-O(15) | 1.264(6) |

Table 4. Bond Angles of Cyclobutabenzofurancarboxylic Acid (**6c**) with Standard Deviations in Paretheses

| | |
|---|---|
| C(2)-C(1)-C(3) | 120.4(5)° |
| C(4)-C(2)-C(1) | 117.6(5) |
| C(5)-C(3)-C(1) | 122.8(6) |
| C(6)-C(4)-C(2) | 130.1(4) |
| C(6)-C(4)-C(7) | 108.4(4) |
| C(2)-C(4)-C(7) | 121.3(4) |
| C(7)-C(5)-C(3) | 115.5(5) |
| C(8)-C(6)-C(4) | 115.6(4) |
| C(8)-C(6)-C(9) | 83.4(3) |
| C(4)-C(6)-C(9) | 100.6(3) |
| O(16)-C(7)-C(4) | 115.2(4) |
| O(16)-C(7)-C(5) | 122.5(4) |
| C(4)-C(7)-C(5) | 122.3(5) |
| C(10)-C(8)-C(6) | 96.4(4) |
| C(10)-C(8)-Cl(11) | 132.3(4) |
| C(6)-C(8)-Cl(11) | 131.3(3) |
| C(10)-C(9)-C(6) | 86.5(3) |
| C(10)-C(9)-C(12) | 116.0(4) |
| C(10)-C(9)-O(16) | 116.8(4) |
| C(6)-C(9)-C(12) | 116.7(4) |
| C(6)-C(9)-O(16) | 108.9(3) |
| C(12)-C(9)-O(16) | 110.1(4) |
| Cl(13)-C(10)-C(8) | 133.3(4) |
| Cl(13)-C(10)-C(9) | 133.0(4) |
| C(8)-C(10)-C(9) | 93.7(4) |
| O(14)-C(12)-C(9) | 120.0(4) |
| O(14)-C(12)-O(15) | 125.4(4) |
| C(9)-C(12)-O(15) | 114.6(4) |
| C(7)-O(16)-C(9) | 106.5(3) |




Scheme 2.

reactions, and trichloroethenyl lactone (**9**) was easily prepared by dehydrochlorination and cycloreversion. In addition, both of these reactions proceeded under very mild conditions with high yields. The syntheses of cyclobutene-fused benzofuran systems were reported by Tinnemans and Neckers[6] along with a large number of reports about the 4,5,6-fused ring systems of nitrogen and sulfur analogues.[7] According to their method the cyclobutene-fused benzofurans were synthesized by the cross photocycloaddition between benzofurans and an alkyne, but initial photoadducts easily underwent photoisomerization, resulting in the formation of complicated mixtures of the rearranged isomers. By contrast, cyclobutabenzofurans **6b**, **6c** were formed exclusively from cyclobuta[1]benzopyran-3-one **3**, which was 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,[8] the ring contraction of **3** proceeded 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 trichloroethenylcoumarin (**9**) would be formed. Thus, this result clearly shows the highly enhanced ring-opening tendency of the lactone ring of cross cycloadduct **3**. This high reactivity is considered to be attributed to the strain of the lactone rings which is brought about by cyclobutanation. Although under such weakly basic conditions, the equilibrium between the phenolic hydroxyl group and the phenolate anion does not favor the phenolate anion; the neighboring group effect. should permit the nucleophilic attack of the phenolate anion to proceed so rapid that it competes effectively with the thermal cycloreversion.

## Experimental

All melting points were measured on a MELTEMP micro melting point apparatus and are uncorrected. IR and NMR spectra were recorded on a JASCO IR-810 spectrophotometer and JEOL GX-400 nuclear magnetic spectrometric instrument, respectively. Photoirradiation was undertaken with an Eiko-sha EHB-WI(F)-500 high-pressure mercury lamp (500 W).

All the reagents and solvents were purified by the methods described in the literature.[9] Anti head-to-head, anti head-to-tail, and syn head-to-head coumarin dimers were prepared according to the methods described in the literature,[10] and used as authentic samples for the identification and the quantification of the photoproducts by $^1$H NMR spectroscopy.

Unless specified otherwise, the following experimental conditions were used. The reactions were carried out under an argon atmosphere. The extracts were washed with saturated aqueous sodium chloride before drying. The solution was dried overnight and the desciccant was removed by filtration. The solvents were taken off on a flash evaporator at the temperature below 10 °C. The conversions were determined by $^1$H NMR spectrum of the reaction mixture in $CDCl_3$. Separations of the products by column chromatography were carried out using silica gel (Wako-gel C-200, 100—200 mesh). The chemical shifts in $^1$H and $^{13}$C NMR spectra were referred to tetramethylsilane (TMS) signals.

**Synthesis of 1,1,2,2-Tetrachloro-1α,2α,2aα,8bβ-tetrahydro-3*H*-cyclobuta[*c*][1]benzopyran-3-one (3):** 14.54 g (0.10 mol) of coumarin (**1**) and 3.14 g (0.017 mol) of benzophenone were dissolved in a mixture of tetrachloroethylene (**2**) (633.6 g, 3.82 mol) and benzene (36.0 g). The solution was irradiated with the 500 W high-pressure mercury lamp through Pyrex filter for 28.5 h. On the basis of $^1$H NMR spectrum of the reaction mixture, 42% of **1** was found to convert to **3**, accompanying 13% of anti head-to-head coumarin dimer and a trace amount (less than 0.5%) of syn head-to-head coumarin dimer. No other product could be detected. After concentration of the reaction mixture under reduced pressure, silica-gel column chromatographic separation using benzene as an eluant gave 9.52 g (30.5%) of **3**: Mp 144—145 °C; IR (KBr) 1770 (C=O), 930 (cyclobutane), 820, 805, 775, 745, 700 cm$^{-1}$; $^1$H NMR (400 MHz $CDCl_3$) $\delta$=4.22 (1H, d, $J$=10 Hz, cyclobutane ring proton), 4.59 (1H, d, $J$=10 Hz, cyclobutane ring proton), 7.07—7.43 (4H, m, aromatic protons); $^{13}$C NMR (100 MHz $CDCl_3$) $\delta$=50.7 (d), 50.8 (d), 89.8 (s), 93.9 (s), 114.3 (s), 117.5 (d), 125.2 (d), 129.5 (d), 131.0 (d), 151.6 (s), 158.9 (s); Found: C, 42.23; H, 2.06; Cl, 45.04%. Calcd for $C_{11}H_6Cl_4O_2$: C, 42.35; H, 1.93; Cl, 45.46%.

When 7.27 g (50 mmol) of coumarin (**1**) was irradiated for 141 h under same conditions described above, 39% (5.97 g) of **3** was obtained (conversion was 52%).

**Reaction of Cross Adduct (3) with Methanol at Room Temperature:** A solution of **3** (156 mg, 0.5 mmol) in methanol (100 ml) was stirred for 240 h at room temperature,

followed by evaporation of excess methanol. The $^1$H NMR spectrum of the residue thus obtained in $CDCl_3$ showed a singlet of methoxyl protons ($\delta$=3.83, 3H), two doublets of cyclobutane ring protons ($\delta$=4.49 and 4.89, each 1H, $J$=10 Hz), and a multiplet for aromatic ring protons ($\delta$=6.70—7.30, 4H) together with the peaks of **3**. In its $^{13}$C NMR spectrum in $CDCl_3$, four carbons of cyclobutane ring [$\delta$=51.9 (d), 59.0 (d), 89.2 (s), and 93.0 (s)], a methoxyl carbon [$\delta$=51.8 (q)], aromatic carbons [$\delta$=115.1 (d), 119.9 (s), 120.2 (d), 128.7 (d), 128.8 (d), and 153.5 (s)], and a carbonyl carbon [166.6 (s)] were observed. These NMR data were consistent with the structure of methyl 2,2,3,3-tetrachloro-*c*-4-(2-hydroxyphenyl)-*r*-1-cyclobutanecarboxylate (**4a**). Based on the integration intensities in the $^1$H NMR spectrum, content of ester **4a** was calculated to be 52% and that of **3** to be 48%. But isolation of **4a** was unsuccessful since relactonization took place easily on silica-gel column or on standing at room temperature.

**Reaction of Cross Cycloadduct (3) with Methanol at Reflux Temperature:** **3** (156 mg, 0.5 mmol) was dissolved in methanol (70 ml) at room temperature, and the solution was stirred for 60 h at reflux temperature. The solution was concentrated under reduced pressure to yield a solid. On the basis of the $^1$H NMR spectrum of the solid thus obtained, it was confirmed that 21% of **3** converted to cyclobutanecarboxylate **4a**, 12% to cyclobutenecarboxylate **5a**, and 19% to trichloroethenylcoumarin (**9**). Chromatography on silica gel using benzene as an eluant afforded **5a** (20 mg, 14%), along with a mixture of starting material (**3**) and **9**. Data for cyclobutene **5a**; $^1$H NMR ($CDCl_3$) $\delta$=3.81 (3H, s, OMe), 5.07 (1H, s, cyclobutene ring proton), and 6.75—6.95 (4H, m, aromatic protons). On silica-gel column, **4a** was considered to be decomposed to **5a** or lactone **3**, and resulted cyclobutenecarboxylate **5a** was also very unstable and spontaneously decomposed to **9** on standing at room temperature. So elemental analysis and measurement of mp were unsuccessful.

***N*-Butyl-2,3,3-trichloro-4-(2-hydroxyphenyl)-1-cyclobutenecarboxamide (5b):** Butylamine (73 mg, 1.0 mmol) was added to a stirred acetone solution (10 ml) of **3** (156 mg, 0.5 mmol) at room temperature. After stirring for 1 h, the solution was poured into 1 M† HCl (20 ml), and extracted with benzene (50 ml×3). The extracts were combined, dried ($MgSO_4$), and concentrated to leave viscous liquid, which was washed with chloroform (10 ml×3) to give cyclobutenecarboxamide **5b** (116 mg, 67%): glass; IR (KBr) 1655 (amide I), 1530 (amide II), 760, 595 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.95 [3H, t, $J$=7.5 Hz, $(CH_2)_3\underline{CH_3}$], 1.20—1.80 (4H, m, $CH_2\underline{CH_2}\underline{CH_2}CH_3$), 3.29—3.50 [2H, m, $NC\underline{H_2}(CH_2)_2CH_3$], 5.15 (s, 1H, cyclobutene ring proton), 6.14 (1H, br s, NH), 6.60—7.25 (4H, m, aromatic protons), 7.96 (1H, br s, ArOH); $^{13}$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); Elemental analysis was unsuccessful since cyclobutene **5b** was transformed to trichloroethenylcoumarin (**9**) on a silica-gel column.

**2,3,3-Trichloro-4-(2-hydroxyphenyl)-1-cyclobutenecarboxylic Acid (5c):** To a stirred solution of **3** (156 mg, 0.5 mmol) in acetone (10 ml), 10 ml of sodium hydrogencarbonate (1 M) was added at room temperature. After stirring at room temperature for 42 h, the reaction mixture was poured into 15 ml of 1 M HCl and extracted with benzene (50 ml×3). The extracts were combined, dried ($MgSO_4$), and concentrated to yield a white powder, which was washed with chloroform (10 ml×3) to give cyclobutenecarboxylic acid (**5c**) (46 mg, 31%): mp 132°C (decomp.); IR (KBr) 1705 (C=O), 885, 740, 600 cm$^{-1}$; $^1$H NMR [$(CD_3)_2SO$] $\delta$=4.97 (1H, s, cyclobutene ring proton), 6.67—6.90 (3H, m, aromatic protons), 7.15—7.20 (1H, m, aromatic proton), 9.89 (1H, s, NH), 13.8 (1H, br s, $CO_2H$); $^{13}$C NMR [$(CD_3)_2CO$] $\delta$=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), and 161.2 (s); Elemental analysis was unsuccessful because cyclobutenecarboxylic acid (**5c**) was transformed to **9** on a silica-gel column.

***N*-Butyl-1,2-Dichloro-2a$\alpha$,7b$\alpha$-dihydrocyclobuta[*b*]benzofuran-2a-carboxamide (6b):** Butylamine (365 mg, 5.0 mmol) was added to a stirred acetone solution (10 ml) of **3** (156 mg, 0.5 mmol) at room temperature. After stirring for 1.5 h, the solution was poured into 1 M HCl (7.5 ml), and extracted with benzene (50 ml×3). The extracts were combined, dried ($MgSO_4$), and concentrated to give a white solid. The crude product was recrystallized from hexane to give cyclobutabenzofurancarboxamide (**6b**) as needles (150 mg, 96%): Mp 94—95°C; IR (KBr) 1665 (amide I), 1555 (amide II), 875, 740, 635 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.94 (3H, t, $J$=7.5 Hz, $(CH_2)_3\underline{CH_3}$), 1.31—1.41 (2H, m, $CH_2\underline{CH_2}\underline{CH_2}CH_3$), 1.50—1.60 (2H, m, $CH_2\underline{CH_2}CH_2CH_3$), 3.26—3.36 (1H, m, $C\underline{H_2}CH_2CH_2CH_3$), 3.38—3.48 (1H, m, $C\underline{H_2}CH_2CH_2CH_3$), 4.62 (1H, s, cyclobutene ring proton), 6.68 (1H, br s, NH), 6.96—7.06 (2H, m, aromatic protons), 7.26—7.34 (2H, m, aromatic protons); $^{13}$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); Found: C, 57.43; H, 4.74; N, 4.53; Cl, 22.71%. Calcd for $C_{15}H_{15}Cl_2NO_2$: C, 57.71; H, 4.84; N, 4.49; Cl, 22.71%.

**1,2-Dichloro-2a$\alpha$,7a$\alpha$-dihydrocyclobuta[*b*]benzofuran-2a-carboxylic Acid (6c):** To a stirred methanol solution (50 ml) of **3** (189 mg, 0.61 mmol) aqueous sodium hydroxide (1 M, 6.1 ml) was added at room temperature. After stirring for 1 h at room temperature, the solution was poured into 1 M HCl (20 ml), and extracted with benzene (50 ml×3). The extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure, and the residue was recrystallized from benzene–hexane to afford white blocks of cyclobutabenzofurancarboxylic acid (**6c**) (140 mg, 90%): Mp 144°C (decomp); IR (KBr) 1730, 1700 (C=O and cyclobutene), 750 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=4.66 (1H, s, cyclobutene ring proton), 6.98—7.04 (2H, m, aromatic protons), 7.24—7.30 (2H, m, aromatic protons), 9.46 (1H, s, $CO_2H$); $^{13}$C NMR ($CDCl_3$) $\delta$=60.27 (d), 89.8 (s), 113.3 (d), 123.0 (d), 124.7 (s), 125.0 (s), 125.8 (d), 130.9 (d), 138.3 (s), 162.1 (s), 172.5 (s); Found: C, 51.53; H, 2.50; Cl, 26.99%. Calcd for $C_{11}H_6O_3Cl_2$: C, 51.39; H, 2.35; Cl, 27.58%.

**3-(Trichloroethenyl)coumarin (9):** Triethylamine (730 mg, 7.2 mmol) was added to a stirred benzene solution (20 ml) of **3** (50 mg, 0.16 mmol) at room temperature. After stirring at room temperature for 15 min, reaction mixture was poured into 1 M HCl (40 ml) and extracted with benzene (50 ml×3). The extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure to leave a white solid (39.4 mg), which was purified on a silica-gel column using

† 1 M=1 mol dm$^{-3}$.

benzene as an eluant to give pure **9** as white powder (36.2 mg, 82%). Recrystallization from hexane gave needles: Mp 129—130 °C; IR (KBr) 1725, 1700 (pyrone ring), 890, 815, 770 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=7.32—7.40 (2H, m, aromatic protons), 7.54—7.65 (2H, m, aromatic protons), 7.87 (1H, s, olefinic proton); $^{13}C$ 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); Found: C, 47.78; H, 1.98; Cl, 38.64%. Calcd for $C_{11}H_5Cl_3O_2$: C, 47.95; H, 1.83; Cl, 38.60%.

**Crystallographic Measurement of Cyclobutabenzofurancarboxylic Acid (6c): Crystal Data.** $C_{11}H_6Cl_2O_3$, $M$=257.1. Monoclinic, $a$=18.814(10), $b$=6.688(5), $c$=8.825(5) Å, $\beta$=92.38(5)°, $V$=1109 Å$^3$, space group $P2_1/n$, $Z$=4, $D_x$=1.538 g $cm^{-3}$, $\mu$ for Cu $K\alpha$=52.9 $cm^{-1}$.

The crystal of approximate dimensions 0.25×0.20×0.35 mm was mounted on a Philips PW1100 diffractometer and the integrated intensities were measured by a $2\theta$—$\theta$ scan method using graphite monochromated Cu $K\alpha$ radiation. 2042 Independent reflections were measured as above the $2\sigma$(I) level out of 2542 theoretically possible ones in the $2\theta$ range 6° through 156°. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The crystal structure was determined by the direct method[11] and refined by the block-diagonal-matrix least-squares calculations. The $R$ value was reduced to 0.067 for 2042 observed structure factors including 5 hydrogen atoms which were located on a difference electron-density map and assessed isotropic temperature factors. The carboxyl group may be protonated at O(15) since C(12)-O(15) is longer than C(12)-O(14) and C(9)-C(12)-O(15) is quite smaller than C(9)-C(12)-O(14), but this hydrogen atom was not found in the difference map.

The complete $F_o$—$F_c$ data are deposited as Document No. 8715 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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