Chemistry of α-Haloaldehyde. VI.* Reaction of 2-Chloro-2-methylpropanal with Benzoylacetonitrile in the Presence of Potassium Carbonate

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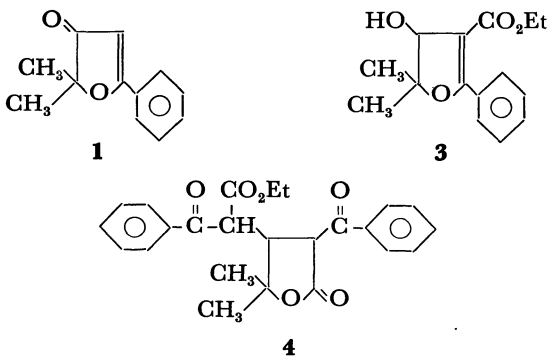
The reaction of 2-chloro-2-methylpropanal with benzoylacetonitrile in aqueous K_2CO_3 has been studied. When 2-chloro-2-methylpropanal was added to a stirred suspension of benzoylacetonitrile in aqueous K_2CO_3, 2-hydroxy-3,3-dimethyl-4-cyano-5-phenyl-2,3-dihydrofuran (**7**) was obtained. The oxidation of **7** with CrO_3 gave α,α-dimethyl-β-cyano-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (**8**). When benzoylacetonitrile was added to a suspension of 2-chloro-2-methylpropanal in aqueous K_2CO_3 stirred beforehand for 60 min, the reaction proceeded in a different manner to give the enol tautomer (**9b**) of 2,4-dibenzoyl-3-(α-hydroxyisopropyl)glutaronitrile (**9a**) at room temperature, and 2,2-dimethyl-3-(α-carbaminophenacyl)-4-cyano-5-phenyl-2,3-dihydrofuran (**11**) at 80—90 °C. The alkaline hydrolysis of the nitrile **9** conducted at 70 °C also afforded the amide **11**. The nitrile **9** eliminated one mol of benzoylacetonitrile on treatment with H_2SO_4 to afford 2,2-dimethyl-3-hydroxy-4-cyano-5-phenyl-2,3-dihydrofuran (**12**). Chromic acid oxidation of **12** gave 2,2-dimethyl-3-oxo-4-cyano-5-phenyl-2,3-dihydrofuran (**14**), which can be derived from bullatenone in two steps. Structures of compounds **11**, **12**, and **14**, which all possess 2,2-dimethyl-4-cyano-5-phenyl-2,3-dihydrofuran ring, have been confirmed and well correlated by both chemical transformations and spectral data.

The synthesis of bullatenone (2,2-dimethyl-3-oxo-5-phenyl-2,3-dihydrofuran) (**1**) has been carried out.[1,2] Studies on the reaction of 2-halo-2-methylpropanal (**2**)[3,4] with active methylene compounds show that in contrast to reactions under nonaqueous conditions, undergoing S_N2-type substitution at the α carbon of **2**, the enolate anion attacks the carbonyl carbon of **2** in aqueous media. It was thought that the base-catalyzed condensation of **2** with ethyl benzoylacetate in an aqueous solution of K_2CO_3 might turn out to be a new route for obtaining 3-hydroxydihydrofuran **3**, which is expected to be readily oxidized to bullatenone. However, it gave only α-benzoyl-β-benzoylethoxycarbonylmethyl-γ-butyrolactone (**4**).[4] It appears that the extraordinarily facile lactonization of the aldol-type product interrupted the formation of **3**. Such a breakdown could be evaded by starting from benzoylacetonitrile (**5**) in place of ester, since the aldol-type product in this case is incapable of lactonization. We report the result of the title reaction conducted under several basic conditions in aqueous media. Structural assignments were made based on spectral data and microanalysis.

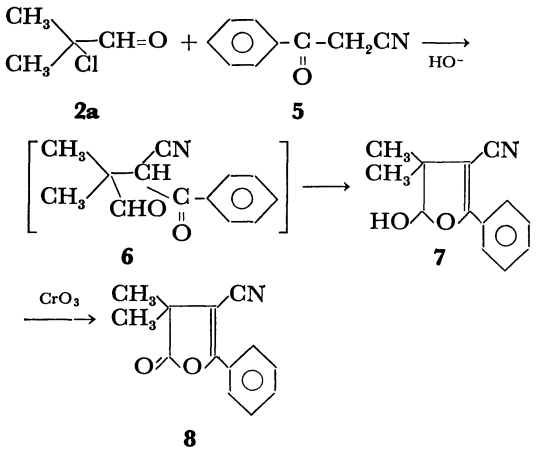


1 **3** **4**

Results and Discussion

When 2-chloro-2-methylpropanal (**2a**) was added to a stirred suspension of benzoylacetonitrile (**5**) in an aqueous solution of K_2CO_3, 2-hydroxy-3,3-dimethyl-4-cyano-5-phenyl-2,3-dihydrofuran (**7**) was obtained in a 72% yield. This indicates that a nucleophilic substitution occurred at the α carbon of **2a** to give the 1,4-dioxo compound **6** as an intermediate, which immediately tautomerized to the cyclic hemiacetal **7**. Compound **7** is more stable against heating as compared with the corresponding ester and resists ring-opening on distillation.[5] The oxidation of **7** with CrO_3 gave α,α-dimethyl-β-cyano-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (**8**) in an 81% yield. NMR spectrum ($CDCl_3$) of **8** showed a simple pattern exhibiting a singlet at δ 1.55 ppm due to α,α-dimethyl protons and a multiplet (5H) at δ 7.2—8.0 ppm due to phenyl protons. Its IR spectrum showed characteristic bands at 2240 and 1830 cm^{-1} due to β-cyano-$\Delta^{\beta,\gamma}$-butenolide structure. The reaction sequence of the formation of compounds **7** and **8** is shown in Scheme 1.

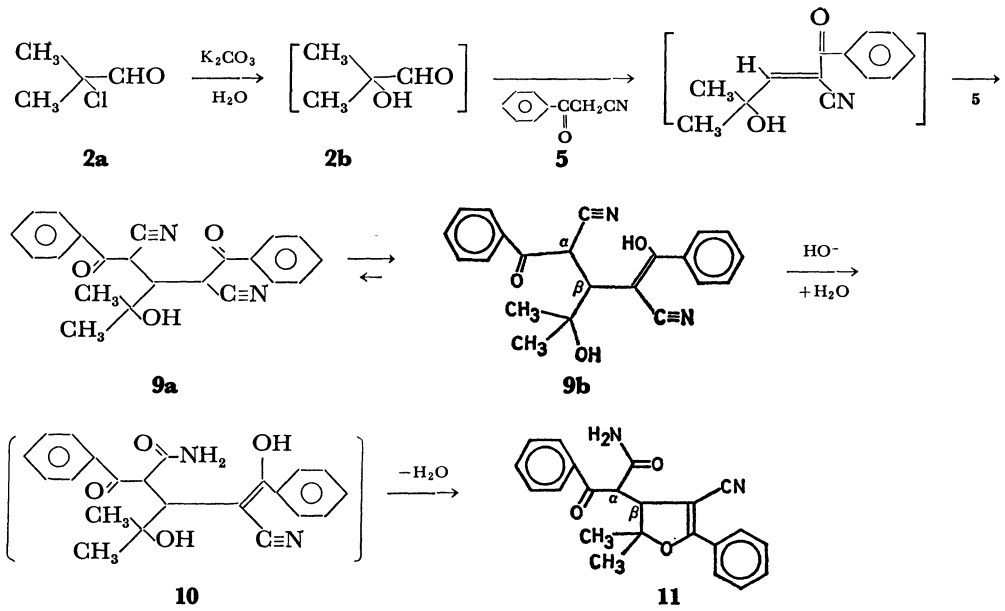
The reaction proceeded quite differently when nitrile **5** was added to a suspension of **2a** in an aqueous solution of K_2CO_3, which was stirred beforehand for at least 60 min (Scheme 2). The reaction carried out in this way at room temperature gave the enol tautomer of 2,4-dibenzoyl-3-(α-hydroxyisopropyl)glutaro-



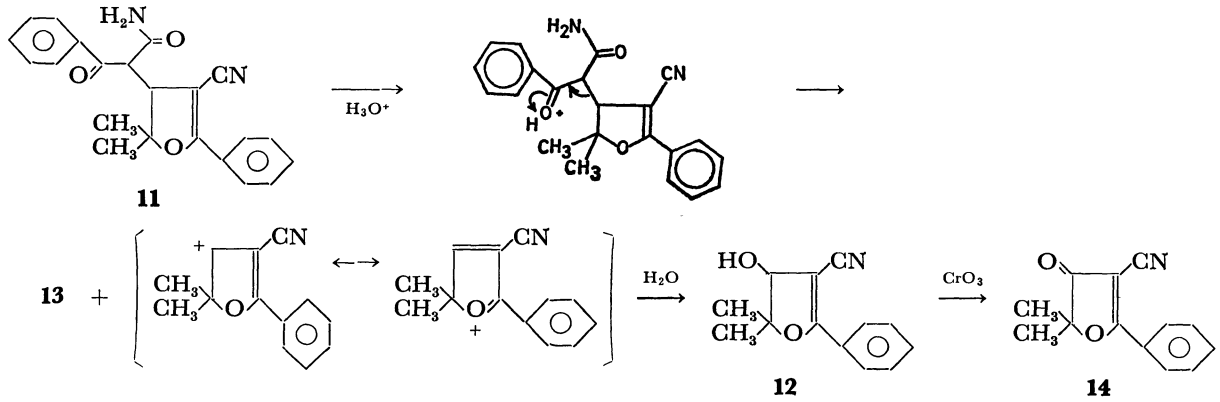
2a **5** **6** **7** **8**

Scheme 1.

* Presented at the 30th Annual Meeting of the Chemical Society of Japan, Higashi-Osaka, April 1, 1974.



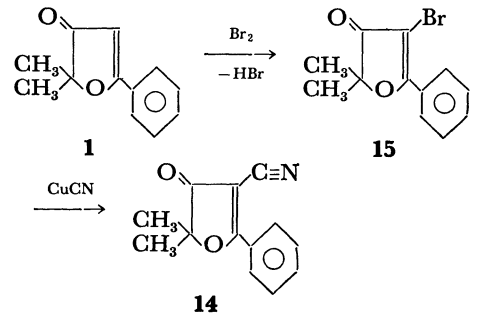
Scheme 2.



Scheme 3.

nitrile (**9**) in an 81% yield, whereas a similar reaction conducted at 80—90 °C afforded 2,2-dimethyl-3-(α-carbaminophenacyl)-4-cyano-5-phenyl-2,3-dihydrofuran (**11**) in a 48% yield together with a small amount of α-benzoyl-γ,γ-dimethyl-$\Delta^{\alpha,\beta}$-butenolide (11%).[5] NMR spectrum [$(CD_3)_2SO$] of the nitrile **9** exhibited two doublets at δ 3.11 and 4.21 ppm (1H each, J= 13 Hz, β-methine proton and α-methine proton), and singlets at 3.20 and 11.8 ppm (1H each, 2 OH), respectively. These signals indicate that one of two benzoyl groups of **9** has been enolized, since otherwise a more complex pattern due to three methine protons coupled to each other should be observed. On the other hand, NMR spectrum [$(CD_3)_2SO$] of the amide **11** showed two singlets at δ 1.01 and 1.40 ppm due to 2,2-dimethyl protons, and one singlet at δ 3.30 ppm due to amide protons. Signals due to two methine protons of this compound appeared at δ 5.02 ppm (d, 1H, J=11 Hz, β-methine proton) and 5.38 ppm (d, 1H, J=11 Hz, α-methine proton), respectively. The amide **11** can be prepared also by treating **9** with an aqueous solution of K_2CO_3 at 70 °C in an 88% yield. Since **9** does not show any tendency to cyclize to dihydrofuran structure, compound **11** is thought to be derived from amide **10**, which was produced from **9** by the saponification of its cyano group.

Treatment of **9** with concentrated H_2SO_4 caused elimination to yield 2,2-dimethyl-3-hydroxy-4-cyano-5-phenyl-2,3-dihydrofuran (**12**) and benzoylacetamide (**13**) in 69% and 78% yields, respectively. A probable mechanism of this acid-catalyzed elimination is given in Scheme 3. The chromic acid oxidation of **12** afforded 2,2-dimethyl-3-oxo-4-cyano-5-phenyl-2,3-dihydrofuran (**14**). This ketone has been prepared by an alternative way starting from bullatenone (**1**). The direct bromination of **1** gave 2,2-dimethyl-3-oxo-4-bromo-5-phenyl-2,3-dihydrofuran (**15**) in good yield (91%). The treatment of **15** with CuCN afforded **14** in a 24% yield.



It is assumed that 2-hydroxy-2-methylpropanal (**2b**) acts as the real substrate of the reaction when nitrile **5** was added to **2a** treated beforehand with an aqueous solution of K_2CO_3, since 2-halo-2-methylpropanal promptly undergoes displacement of halogen to give **2b**.[6] The fact that the reaction of **2b** and **5** carried out at 60 °C in an aqueous solution of K_2CO_3 also gave **11** in a 55% yield supports the assumption.

Experimental

General. Melting points and boiling points are uncorrected. The infrared spectra were recorded on a Hitachi EPI-S2 model spectrophotometer. NMR spectra (60 MHz) were taken on a Hitachi R-24 model spectrometer, and MS spectra were obtained on a Hitachi RMS-4 model mass spectrometer. Analytical thin layer chromatography (tlc) was carried out using silica gel GF_{254} (E. Merck AG, Darmstadt). Preparative tlc was carried out on silica gel PF_{254} (E. Merck AG). Microanalyses were carried out by Mr. Eiichiro Amano of our laboratory. Starting materials such as 2-chloro-2-methylpropanal (**2a**),[7] 2-hydroxy-2-methylpropanal (**2b**)[8] were prepared by the procedures in literature.

*2-Hydroxy-3,3-dimethyl-4-cyano-5-phenyl-2,3-dihydrofuran (**7**).* To a solution of 4.8 g (0.0345 mol) of potassium carbonate in 12 ml of water was added 5 g (0.035 mol) of **5** at room temperature. To the resulting mixture was added 3.3 g (0.031 mol) of **2a** with ice bath cooling. The mixture was stirred at room temperature for 2 hr, and then at 60 °C for 3 hr. It was poured into a large amount of water and extracted with ether. The ethereal extract was washed several times with water and dried over Na_2SO_4. Removal of the solvent left 7 g of a brown oil which, on distillation, gave 4.8 g (72%) of **7**: bp 144—148 °C/0.16 mmHg; mp 75—76 °C (petroleum ether-benzene-ethanol); IR (nujol) 3420 (OH), 2200 (CN), 1615 (C=C), 1600 and 1575 cm^{-1} (benzene C=C); NMR ($CDCl_3$) δ 1.30 (s, 6H, $2CH_3$), 4.35 (broad s, 1H, OH), 5.60 (s, 1H, >CH(OH)), 7.26—8.02 (m, 5H, C_6H_5); MS (70 eV) *m/e* (rel. intensity) 215 (14, M^+), 200 (8, M^+-CH_3), 186 (43), 172 (9), 154 (14), 105 (100, PhCO), 77 (74, C_6H_5). Found: C, 72.59; H, 6.05; N, 6.81%. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51%.

*α,α-Dimethyl-β-cyano-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (**8**).* To a mixed solution of 0.62 g (0.0029 mol) of **7** in 5 ml of aqueous 50% acetic acid was added 0.32 g (0.0032 mol) of chromium trioxide in several portions, with moderate cooling. The mixture was stirred for 2.5 hr at room temperature. The reaction mixture was diluted with 5 ml of water and then extracted with ether. The ethereal extract was washed with water and dried over Na_2SO_4. Removal of the solvent left 0.50 g (81%) of **8**: mp 95—95.5 °C (petroleum ether-benzene); IR (neat) 2240 (CN), 1830 (lactone C=O), 1640 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.55 (s, 6H, $2CH_3$), 7.20—8.00 (m, 5H, C_6H_5); MS (70 eV) *m/e* (rel. intensity) 213 (50, M^+), 198 (85, M^+-CH_3), 184 (40, $M^+-C_2H_5$), 171 (34), 157 (8), 143 (8), 122 (31), 105 (100, PhCO), 77 (87, C_6H_5).

Found: C, 73.41; H, 5.08; N, 6.61%. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%.

*Enol Tautomer (**9b**) of 2,4-Dibenzoyl-3-(α-hydroxyisopropyl)-glutaronitrile (**9a**).* To a solution of 2.5 g (0.017 mol) of potassium carbonate in 10 ml of water was added 1.85 g (0.017 mol) of **2a**. After the mixture was stirred for 1 hr at room temperature, 4.0 g (0.028 mol) of **5** was added and the stirring was continued for 17 hr. The semisolid material separated was collected by filtration and washed with 10% HCl and with ether successively to give 2.4 g (81%) of **9b**, white crystal: mp 178—178.5 °C (acetone); IR (KBr) 3300 (broad, OH), 2980, 2200 (CN), 1700 (m, C=O), 1630 (s, C=C, C=O), 1600 (w), 1350, 1240, 1050, 765, 700 cm^{-1}; NMR [$(CD_3)_2SO$] δ 1.33 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 3.11 (d, 1H, J=13 Hz, β-methine proton), 3.20 (broad s, 1H, OH), 4.21 (d, 1H, J=13 Hz, α-methine proton), 7.10—7.83 (m, 10H, $2C_6H_5$), 11.80 (broad s, 1H, enolic OH); MS (70 eV) *m/e* (rel. intensity) 343 (0.1), 342 (0.1). 317 (0.2), 302 (0.2), 198 (3), 197 (2.6), 172 (4.4), 149 (9), 145 (5), 122 (4), 105 (100, PhCO), 77 (79, C_6H_5).

Found: C, 73.39; H, 5.88; N, 7.47%. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77%.

*2,2-Dimethyl-3-(α-carbaminophenacyl)-4-cyano-5-phenyl-2,3-dihydrofuran (**11**). (a) From **2a** and **5**.* A mixed solution of **2a** (0.107 g, 0.001 mol) and potassium carbonate (0.138 g, 0.001 mol) in 1 ml of water was stirred for 30 min at room temperature. To the resulting suspension was added 0.145 g (0.001 mol) of benzoylacetonitrile. After being stirred at room temperature for 2 hr and at 80—90 °C for an additional 3 hr, the mixture was acidified with 10% HCl. After addition of a small amount of ether, the precipitated crystals of **11** (0.0445 g, 25%) were collected by filtration: mp 230 °C (THF); IR (KBr) 3450 (sharp, NH_2), 2230 (w, CN), 1685 (s, C=O), 1640 (m, C=C), 1604 and 1584 (benzene ring), 780, 700 cm^{-1}; NMR [$(CD_3)_2SO$] δ 1.01 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 3.30 (s, 2H, $CONH_2$), 5.02 (d, 1H, J=11 Hz, β-methine proton), 5.38 (d, 1H, J=11 Hz, α-methine proton), 7.30—8.30 (m, 10H, $2C_6H_5$); MS (70 eV) *m/e* (rel. intensity) 343 (0.2), 317 (3), 302 (8), 197 (3), 195 (6), 122 (33), 105 (100, C_6H_5CO), 77 (67, C_6H_5).

Found: C, 73.50; H, 5.63; N, 7.67%. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77%.

Tlc analysis (*n*-hexane : acetone, 1 : 1) of the residue (0.077 g) recovered from the filtrate showed three spots at R_f values 0.48, 0.57, and 0.66 (content ratio in wt, 12 : 42 : 23). Component with R_f value 0.57 and that with R_f value 0.66 were identified as **11** (23%)[9] and α-benzoyl-γ,γ-dimethyl-$\Delta^{\alpha,\beta}$-butenolide[5] (11% yield), respectively, by the identities of the spectral data with those of authentic samples.

*(b) From **9b**.* A mixed solution of **9b** (0.067 g, 0.19 mmol) and potassium carbonate (0.068 g, 0.49 mmol) in water (1 ml) was stirred for 3 hr at 70 °C. After being acidified with 10% HCl, the mixture was extracted with ether. White crystals (0.031 g) precipitated were collected and identified as **11** by comparison of its IR spectrum with that of an authentic sample. From the ethereal layer, additional amount (0.040 g) of crude product with 70% purity by tlc analysis (*n*-hexane : acetone, 1 : 1) was obtained, total yield 88%.

*(c) From **2b** and **5**.* To a solution of 0.106 g (0.76 mmol) of potassium carbonate in 0.45 ml of water was added 0.11 g (0.76 mmol) of **5**. After the mixture was stirred for 1 hr, 0.081 g (0.76 mmol) of **2b** was added. It was stirred at room temperature for 2 hr, and at 60—65 °C for 3 hr, and then acidified with dilute HCl. The crude product was collected and washed with ether to give 0.15 g (55%) of **11**: mp 230 °C (acetone).

*2,2-Dimethyl-3-hydroxy-4-cyano-5-phenyl-2,3-dihydrofuran (**12**).* The nitrile **9** (0.24 g, 0.67 mmol) was dissolved in 6 ml of concd H_2SO_4. After being allowed to stand for one day at room temperature, the solution was poured into 50 ml of ice-water. The organic layer was extracted with ether and dried over $MgSO_4$. After removal of the solvent, residual semisolid (0.018 g) was obtained. Tlc analysis (*n*-hexane : acetone, 2 : 1) of this solid showed two spots at R_f values 0.07 and 0.26 (content ratio in wt, 44 : 56). Component with R_f value 0.07 was collected by preparative tlc and iden-

tified as benzoylacetamide (**13**), 78% recovery: mp 111—112 °C (acetone) (lit,[10] mp 112—113 °C). IR and NMR spectra were identical with those of the authentic sample obtained by the treatment of benzoylacetonitrile with concd H_2SO_4: IR (KBr) 3400 and 3170 (NH and enolic OH), 1670 and 1630 (C=O), 1595 and 1575 (benzene C=C), 1390, 800, 760, 690 cm^{-1}: NMR[11] [$(CD_3)_2SO$] δ 2.85 (broad s, NH_2), 3.99 (s, $-CH_2CO$), 5.88 (s, enolic >C=CH–), 7.30—8.18 (m, C_6H_5), 15.10 (broad s, enolic OH).

Component with R_f value 0.26 collected by preparative tlc was microdistilled at 150 °C under 0.05 mmHg with a bath, and identified as **12**, yield 69%: IR (neat) 3450 (OH), 2200 (CN), 1625 (C=C), 1575 (benzene C=C), 1495, 1115, 1070, 875, 820, 780, 695 cm^{-1}; NMR [$(CD_3)_2C=O$] δ 1.43 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 4.71 (d, 1H, J=8 Hz, OH), 4.85 (d, 1H, J=8 Hz, >CHOH), 7.40—8.10 (m, 5H, C_6H_5); MS (70 eV) *m/e* (rel. intensity) 215 (40, M^+), 188 (34), 156 (26), 141 (40), 128 (50), 105 (100), 77 (78), 59 (68).

Found: C, 72.70; H, 6.33; N, 6.31%. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51%.

*2,2-Dimethyl-3-oxo-4-cyano-5-phenyl-2,3-dihydrofuran (**14**).* *(a) From **12**.* To a mixture of 0.1 ml of 70% acetic acid and 0.04 g (0.4 mmol) of chromium trioxide was added 0.042 g (0.2 mmol) of **12** in several portions at 0 °C. The mixture was stirred for 2 hr at room temperature and then for 1 hr at 60 °C. The mixture was poured into 1 ml of water and the organic layer was extracted with ether, washed with water, and dried over $MgSO_4$. After removal of the solvent, 0.022 g of the residual oil was obtained. Tlc analysis (*n*-hexane : acetone, 2 : 1) of this oil showed two spots at R_f values 0.3 and 0.5 (content ratio in wt, 1 : 3). The component of R_f value 0.5 collected by preparative tlc was recrystallized from the mixed solvent of *n*-hexane and ether to give 0.017 g (40%) of **14**: mp 122—124 °C; IR (KBr) 2200 (CN), 1705 (C=O), 1590 (benzene ring), 1560 (C=C), 1395, 1215, 900 (C–O), 765 and 695 cm^{-1} (monosubstituted benzene); NMR ($CDCl_3$) δ 1.57 (s, 6H, $2CH_3$), 7.40—8.45 (m, 5H, C_6H_5); MS (70 eV) *m/e* (rel. intensity) 213 (22, M^+), 149 (10), 127 (100), 105 (11, C_6H_5CO), 77 (11, C_6H_5).

Found: C, 72.85; H, 5.28; N, 6.86%. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%.

*(b) Synthesis from 2,2-Dimethyl-3-oxo-4-bromo-5-phenyl-2,3-dihydrofuran (**15**).* In a hood, a stirred suspension of 0.18 g (0.66 mmol) of **15** and 0.069 g (0.76 mmol) of cuprous cyanide in 1 ml of dry DMF was heated at 80 °C for 4 hr, and finally at 150 °C for 20 min. A solution of 2 g of ferric chloride in 4 ml of 5% HCl was added to the reaction mixture, which was then stirred for 20 min at 60 °C to decompose the complex. Ethereal extract of the organic layer was washed with water and dried over $MgSO_4$. After removal of the solvent, 0.146 g of a solid was obtained. Tlc analysis (*n*-hexane : acetone, 2 : 1) of this solid showed the presence of two spots at R_f values 0.42 and 0.49. Preparative tlc of the component with the R_f value 0.42 gave 0.034 g (24%) of a crystal, which was identified as **14** by comparison of IR spectrum with that of the authentic sample. The component with the R_f value 0.49 was collected similarly and identified as **15**.

*2,2-Dimethyl-3-oxo-4-bromo-5-phenyl-2,3-dihydrofuran (**15**).* To a stirred suspension of 0.38 g (2 mmol) of **1**[1] in 2 ml of water was added 0.51 g (3.2 mmol) of bromine dropwise at 80 °C. The mixture was stirred for 15 min at 90 °C. Removal of the solvent left 0.49 g (91%) of **15**: mp 66—67 °C (*n*-hexane): IR (KBr) 1700 (C=O), 1602 and 1583 (benzene ring), 1559 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.51 (s, 6H, $2CH_3$), 7.40—8.30 (m, 5H, C_6H_5); MS (70 eV) *m/e* (rel. intensity) 266 (68, M^+, 1Br), 187 (8, M^+-Br), 180 (22, $C_6H_5C{\equiv}CBr$, 1Br), 129 (100, $C_6H_5C=C=C=O$).

Found: C, 53.97; H, 3.96%. Calcd for $C_{12}H_{11}O_2Br$: C, 53.95; H, 4.31%.

References and Notes

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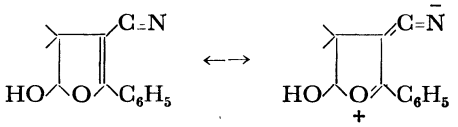
5) A. Takeda, S. Tsuboi, and T. Sakai, *J. Org. Chem.*, (*in press*): "Chemistry of α-Haloaldehydes. IV. Reaction of 2-Halo-2-methylpropanal with Acylacetates in the Presence of Base." Ethyl 2-hydroxy-3,3-dimethyl-5-phenyl-2,3-dihydrofuran-4-carboxylate, a cyclic hemiacetal related to the nitrile **7**, can be converted into 2,2-dimethyl-3-(ethoxycarbonyl)-4-phenyl-4-oxobutanal by distillation (bp 130 °C/0.1 mmHg). The latter compound, when kept at room temperature for several days, tautomerized to the cyclic hemiacetal. The stability of **7** is partly attributable to the conjugation of cyano group with the ring system.



The butyrolactone **4**, on distillation, eliminates one mol of ethyl benzoylacetate releasing α-benzoyl-γ,γ-dimethyl-$\Delta^{\alpha,\beta}$-butenolide quantitatively: mp 65—66 °C; IR (nujol) 1750—1780 (lactone C=O), 1650 (benzoyl C=O), 1630 (C=C), 1598 and 1580 cm^{-1} (benzene C=C); NMR ($CDCl_3$) δ 1.58 (s, 6H, $2CH_3$), 7.70 (s, 1H, =C–H), 7.40—7.90 (m, 5H, C_6H_5).

6) The percentage of **2a** transformed into **2b** was found to be 90% in 15 min, 95% in 30 min, and 97% in 60 min.

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9) Additional yield of **11**.

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11) This spectrum showed the existence of a mixture of keto and enol forms (1 : 1).