# Studies on Keten and Its Derivatives. Part 86.[1] Photoreaction of Diketen with Dimedone and Isophorone

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Photoreaction of diketen with dimedone (1) gave 1-hydroxy-4,4-dimethyl-2,6-dioxocyclo-octan-1-ylacetic acid β-lactone (2) and 4,4-dimethyl-2,6-dioxobicyclo[5.1.0]octan-1-ylacetic acid (3). A similar reaction of isophorone (6) gave 8-hydroxy-4,4,6-trimethyl-2-oxo-*cis*-bicyclo[4.2.0]octan-8-ylacetic acid β-lactone (7a, b), and an oil, which, on treatment with aniline, gave 7-hydroxy-4,4,6-trimethyl-2-oxo-*cis*-bicyclo[4.2.0]octan-7-ylacetanilide (11a, b). Reaction of compounds (7a) and (7b) with aniline gave 3-anilino-1-hydroxy-5,7,7-trimethylbicyclo[3.3.1]non-2-ene-2-carboxanilide (9).

PREVIOUSLY we have reported that diketen (4-methyleneoxetan-2-one) reacted with dimedone (5,5-dimethylcyclohexane-1,3-dione) (1) in the presence of a basic catalyst to give 2-acetoacetyl-5,5-dimethylcyclohexane-1,3-dione, which, on treatment with acid, was cyclized to 2,7,7-trimethyl-5,6,7,8-tetrahydro-4*H*-1-benzopyran-4,5-dione.[2] In contrast, it is reported that the photoreaction of dimedone (1) with an olefin such as acrolein results in [2 + 2] cycloaddition followed by ring-expansion to give 3-formyl-7,7-dimethylcyclo-octane-1,5-dione.[3,4] The object of the present paper is to describe the reaction of diketen with dimedone (1) and isophorone (6) when irradiated.

*Reaction of Dimedone* (1) *with Diketen.*—Irradiation of dimedone (1) and diketen in ethanol afforded crystalline products of m.p. 147—148.5 and 180—181.5 °C, to which, on the basis of their elemental analyses and spectroscopic data, we assigned the cyclo-octane structures (2) and (3), respectively. Thus, the i.r. spectrum of compound (2) showed β-lactone carbonyl absorption at 1 825 $cm^{-1}$ besides two ketone carbonyl absorptions at 1 705 and 1 682 $cm^{-1}$ and its n.m.r. spectrum showed 2 × $CH_3$ (δ 1.16, s), 2 × $CH_2$ (δ 2.08—3.17, ABq, and 3.03—3.86, ABq), and 3 × $CH_2$ (δ 2.16—2.95, m) signals.

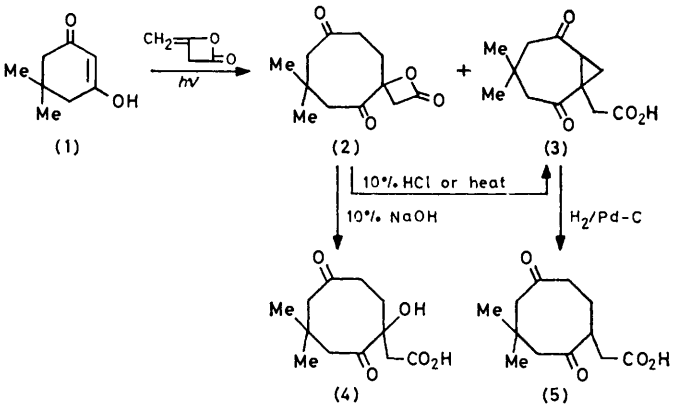
Hydrolysis of the β-lactone (2) with sodium hydroxide afforded compound (4) which was soluble in 5% sodium hydrogen carbonate. The i.r. spectrum (KBr) of compound (4) indicated the absence of the β-lactone carbonyl function and the presence of hydroxy (3 560 $cm^{-1}$) and carboxylic acid (3 000—2 560 and 1 705 $cm^{-1}$) groups. From these data the structure of the acid (4) was assigned as 1-hydroxy-4,4-dimethyl-2,6-dioxocyclo-octan-1-ylacetic acid †. Treatment of this acid (4) with diazomethane easily afforded the methyl ester.

Compound (3) was also obtained when the lactone (2) was heated or treated with 10% hydrochloric acid. The i.r. spectrum of compound (3) showed carboxylic acid absorptions at 3 140—2 560 and 1 710 $cm^{-1}$ besides two ketone carbonyl absorptions at 1 675 and 1 670 $cm^{-1}$. The n.m.r. spectrum showed signals due to 2 × $CH_3$ (δ 0.94, s, and 1.00, s), 3 × $CH_2$ (δ 2.88, s, 2.27—3.05, ABq, and 2.27—3.17, ABq), and the cyclopropane ring protons [δ 1.55—1.92 (1 H) and 2.23—2.72 (2 H)].

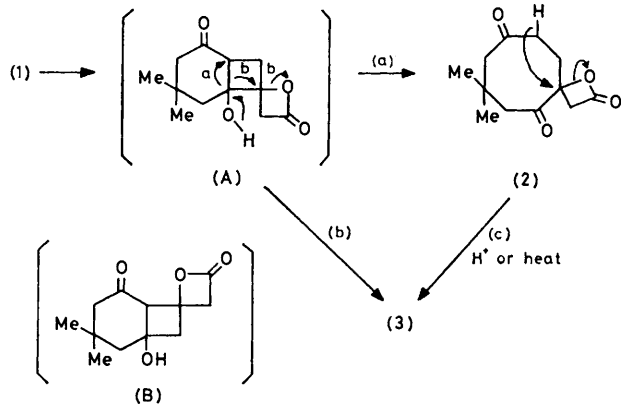
† An n.m.r. spectroscopic study suggested that the acid (4) and its methyl ester existed partially as intramolecular hemiacetals. This work is currently in progress and will form the subject of future reports.

Treatment of compound (3) with diazomethane gave the methyl ester. Mass and $^{13}C$ n.m.r. spectra were consistent with this structure (see Table).

Catalytic hydrogenolysis of compound (3) with palladium–carbon resulted in the fission of the cyclopropane ring to give the cyclo-octanylacetic acid (5), which was,




SCHEME 1




SCHEME 2

on treatment with diazomethane, converted into the methyl ester.

[1] Part 85, T. Kato and H. Kimura, *Chem. and Pharm. Bull. (Japan)*, in the press.
[2] T. Kato and T. Hozumi, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 1840.
[3] H. Hikino and P. de Mayo, *J. Amer. Chem. Soc.*, 1964, **86**, 3582.
[4] I. Agata, K. Kawashima, and T. Aono, *Yakugaku Zasshi*, 1975, **95**, 1013.

The formation of compounds (2) and (3) can be explained in terms of a [2 + 2] cycloaddition of the *exo*-methylene of diketen to the enolic C=C double bond of dimedone (1) which gives rise to the spirobicyclo-intermediate (A) (see Scheme 2). Ring expansion of this intermediate by path (a) gives rise to the lactone (2), which when heated or treated with acid gives the bicyclo-octanedione derivative (3) by path (c). Since compound (3) was not obtained by photolysis of the lactone (2), the formation of compound (3) may plausibly be explained by ring transformation of the intermediate (A) along path (b).

No product arising from the isomeric intermediate (B) was detected.

*Reaction of Isophorone* (3,5,5-*Trimethylcyclohex*-2-*enone*) (6) *with Diketen*.—Since it has been reported that the photoreaction of isophorone (6) with an olefin undergoes [2 + 2] cycloaddition to give a bicyclo[4.2.0]-octane derivative [5,6] the photoreaction of isophorone (6) with diketen was also investigated.

Thus irradiation of a solution of isophorone (6) and diketen in acetonitrile gave crystalline products [m.p. 96—97 °C (7a) and m.p. 86.5—87.5 °C (7b)] and an oily mixture [(8a) and (8b)]. On the basis of spectroscopic evidence (see below) it was inferred that both (7a) and (7b) have the 8-hydroxy-4,4,6-trimethyl-2-oxo-*cis*-bicyclo[4.2.0]octan-8-ylacetic acid β-lactone structure, the junction of C(8)–O and C(1)–H of compound (7a) being in the *cis*-configuration and that of (7b) in the *trans*-configuration. The oily product was presumed to be a stereomixture of the 7-hydroxy-*cis*-bicyclo-octan-7-ylacetic acid β-lactones (8a, b).

The i.r. spectra of compounds (7a) and (7b) showed both β-lactone carbonyl (1 835 and 1 830 $cm^{-1}$) and ketone carbonyl peaks (1 695 and 1 687 $cm^{-1}$) whilst their n.m.r. spectra were closely similar [3 × $CH_3$ (s), 4 × $CH_2$ (s, ABq), and CH (s) signals].

The above spectroscopic data are consistent with the bicyclo[4.2.0]octanone structure, and the C(1)-proton appeared as a singlet, evidence for attachment of the oxetan moiety to the 8-position of the bicyclo-octane moiety.

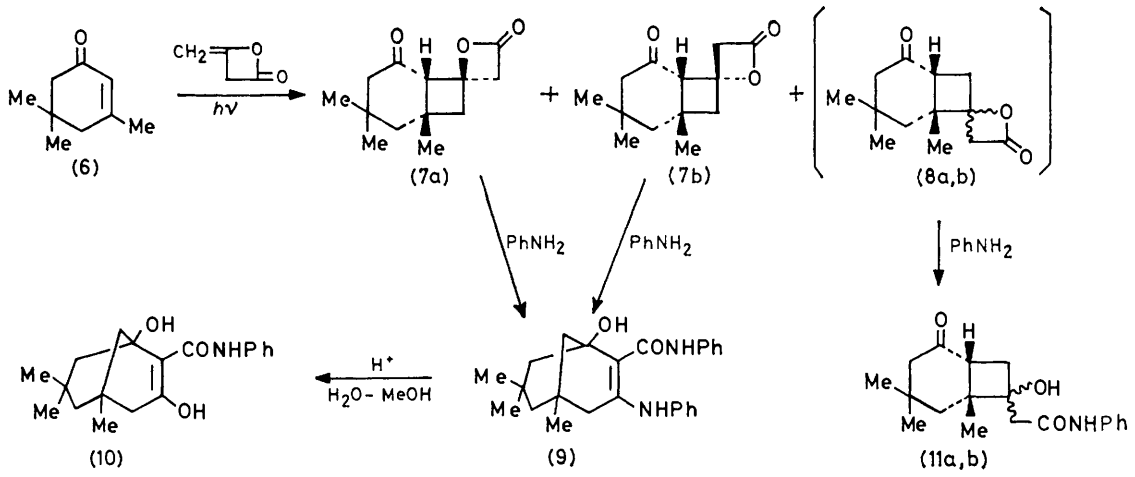
Cantrell *et al.*[7] reported that photoreactions of 3-methylcyclohex-2-enone with olefins gave *cis*- and *trans*-6-methylbicyclo[4.2.0]octan-2-one derivatives, the n.m.r. spectra of which showed that the angular methyl of the *cis*-compounds appears at δ <1.2 while that of the *trans*-isomers is at δ >1.

$^{13}C$ N.m.r. data (δ from $SiMe_4$) for the lactone (2) and the ester (3; Me ester)

| | $CH_3$ | $CH_2$ | CH | C | C=O |
|---|---|---|---|---|---|
| (2) [a] | 29.5, 29.8 | 31.3, 40.4, 46.1, 47.7, 51.4 | | 37.5, 82.5 | 166.3, 205.1, 209.1 |
| (3; Me ester) [b] | 24.8, 32.8, 51.7 | 23.8, 39.7, 53.2, 54.1 | 39.0 | 34.2, 37.4 | 171.0, 205.0, 205.5 |

[a] In [$^2H_5$]pyridine. [b] In $CDCl_3$.

Since the lactones (7a) and (7b) show chemical shifts of δ 1.45 and 1.31, respectively for the C(6)-methyl either could exist in the *cis*-configuration. Similarly a n.m.r. study using europium shift reagent showed that both C(1)-protons had greater downfield shifts than the corresponding C(3) protons (see Figure), again indicating that either (7a) or (7b) might have a *cis*-configuration.




SCHEME 3

A distinction was observed however in the behaviour of the oxetan methylene proton (3′-proton) when that for (7a) showed a remarkable downfield shift whilst that of (7b) was virtually unchanged. On the basis of this evidence the oxetan oxygen of the lactone (7a) was assigned the *cis*- and that of (7b) the *trans*-configuration.

Reaction of both lactones (7a) and (7b) with aniline gave rise to a single product, the bicyclo[3.3.1]nonene

[5] D. C. Owsley and J. J. Bloomfield, *J. Chem. Soc.* (*C*), 1971, 3445.

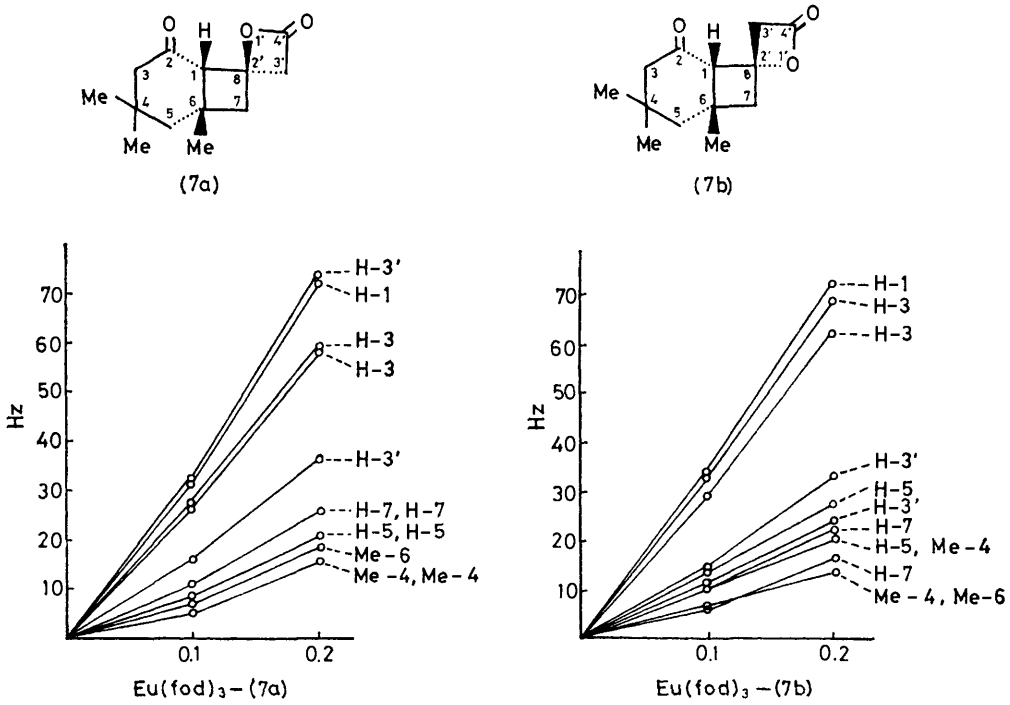
[6] H. J. Liu and T. Ogino, *Tetrahedron Letters*, 1973, 4937.

[7] T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, 1969, **34**, 509.

derivative (9), which when hydrolysed with hydrochloric acid gave compound (10). Compounds (9) and (10) were assigned structures on the basis of elemental analyses and spectroscopic data (see Experimental section).

The oily product (8a, b) was difficult to purify, but its i.r. spectrum showed the presence of the β-lactone moiety (1 835 $cm^{-1}$). Treatment of the oily product with aniline afforded crystalline products, m.p. 244 °C (decomp.) (11a) and m.p. 159—160 °C (11b). Elemental analyses and i.r. spectra of these were consistent with the anilide structures (11a) and (11b), the n.m.r. spectra showed C(1)-proton and C(8)-methylene protons as multiplets [(11a) δ 2.52—3.08, (11b) 2.32—2.72]. This indicates that the acetanilide moiety attaches to the 7-position of the bicyclo-octanone moiety. Furthermore, signals for the C(6)-methyl protons of compounds (11a) and (11b) appeared at δ 1.57 and 1.20, respectively, indicating that the bicyclo[4.2.0]octanone junction had a *cis*-configuration.[7]

In the light of the above evidence it is reasonable to assume that compounds (11a) and (11b) are C-7 epimers of the *cis*-bicyclo[4.2.0]octan-2-one moiety. The stereochemistry, at the 7-junction of neither could, however, be determined.




The relationship between paramagnetic shifts and the molar ratio of $Eu(fod)_3$–substrate (7a,b)

## EXPERIMENTAL

I.r. spectra were taken with a JASCO IR–S spectrophotometer. N.m.r. spectra were measured with a Hitachi R-20 instrument and a JEOL-JNM-PS-100 instrument (tetramethylsilane as an internal standard). $^{13}C$ N.m.r. spectra were measured with a JEOL-JNM-PS-100 instrument (tetramethylsilane as an internal standard). Mass spectra were obtained with a Hitachi double-focusing spectrometer RMU-7L. M.p.s. were uncorrected. The u.v. light source was a RIKO UVL-100HA water-cooled, high-pressure mercury lamp (Pyrex filter).

*Reaction of Dimedone* (1) *with Diketen to give* 1-*Hydroxy*-4,4-*dimethyl*-2,6-*dioxocyclo-octan*-1-*ylacetic Acid* β-*Lactone* (2) *and* 4,4-*Dimethyl*-2,6-*dioxobicyclo*[5.1.0]*octan*-1-*ylacetic Acid* (3).—A solution of dimedone (1) (2.8 g, 0.02 mol) and diketen (17 g, 0.2 mol) in ethanol (25 ml) was photolysed with ice-cooling for 12 h, during which time nitrogen was bubbled through the solution. Removal of the solvent and an excess of diketen gave a semicrystalline residue, which was washed with a small amount of ethanol and ethyl acetate. The resulting crystalline residue was recrystallized from ethanol to give needles of compound (2), m.p. 147—148.5 °C. The liquors were concentrated and chromatographed on a silica gel (Wakogel C-200, 60 g) column. Elution with chloroform gave a further quantity of the lactone (2); total yield 0.5 g (23%) (Found: C, 64.0; H, 7.45. $C_{12}H_{16}O_4$ requires C, 64.25; H, 7.2%), $\nu_{max.}$ (KBr) 1 825, 1 705, and 1 682 $cm^{-1}$; δ($CDCl_3$) 1.16 (6 H, s, 2 × $CH_3$), 2.08—3.17 (2 H, ABq, *J* 13 Hz, $CH_2$), 2.16—2.95 (6 H, m), and 3.03—3.86 (2 H, ABq, *J* 16 Hz, $CH_2$); *m/e* 224 ($M^+$), 196, 154, 140 ($M^+ - C_4H_4O_2$), 98 ($M^+ - C_6H_6O_3$), and 83. Further elution with chloroform gave the starting dimedone (0.3 g). Elution was continued with ethyl acetate to afford the acid (3) as needles (0.7 g, 32%), m.p. 180—181.5 °C (from ethyl acetate) (Found: C, 64.5; H, 7.25. $C_{12}H_{16}O_4$ requires C, 64.25; H, 7.2%), $\nu_{max.}$ (KBr) 3 140—2 560, 1 710, 1 675sh, and 1 670 $cm^{-1}$; δ(pyridine) 0.94 (3 H, s, $CH_3$), 1.00 (3 H, s, $CH_3$), 1.55—1.92 (1 H, m), 2.23—2.72 (2 H, m), 2.27—3.05 (2 H, ABq, *J* 12.5 Hz, $CH_2$), 2.27—3.17 (2 H, ABq, *J* 12.5 Hz, $CH_2$), and 2.88 (2 H, s).

*Isomerization of the β-Lactone* (2) *to the Acid* (3).—(1) A suspension of the lactone (2) (112 mg) in 10% hydrochloric acid (2 ml) was heated at 90 °C for 30 min. After cooling, crystals (3) (71 mg) separated and these were collected. The filtrate was extracted with ethyl acetate. The organic layer was concentrated, and the residue was recrystallized from ethyl acetate to give the acid (3) as needles (25 mg), m.p. 180 °C, undepressed on admixture with a sample obtained in the above run; total yield, 96 mg (86%).

(2) Heating of the lactone (2) (50 mg) at 190—200 °C for 15 min gave a crystalline substance, recrystallization of which from ethyl acetate gave the acid (3) (30 mg, 60%).

*Methyl* 4,4-*Dimethyl*-2,6-*dioxobicyclo*[5.1.0]*octan*-1-*ylacetate* (3; Me ester).—To a solution of the acid (3) (224 mg) in ethyl acetate (20 ml), was added a solution of an excess of diazomethane in ether and the mixture was set aside overnight; the mixture was concentrated and the residue was crystallized from ethyl acetate to give needles of the methyl ester of (3) (218 mg, 91%), m.p. 139—140 °C (Found: C, 65.9; H, 7.65. $C_{13}H_{18}O_4$ requires C, 65.55; H, 7.6%), $\nu_{max.}$ ($CHCl_3$) 1 730, 1 685sh and 1 675 $cm^{-1}$; δ($CDCl_3$) 0.88 (3 H, s, $CH_3$), 1.07 (3 H, s, $CH_3$), 1.47—1.85 (1 H, m), 2.10—2.96 (8 H, m), and 3.67 (3 H, s, $OCH_3$); *m/e* 238 ($M^+$), 154 ($M^+ - C_4H_4O_2$), 123 ($M^+ - C_5H_7O_3$), 122, 112, 95, 94, 83, and 81.

1-*Hydroxy*-4,4-*dimethyl*-2,6-*dioxocyclo-octan*-1-*ylacetic Acid* (4).—A suspension of the lactone (2) (55 mg) in 10% sodium hydroxide (1 ml) was stirred at room temperature for 1 h. The mixture was then acidified with concentrated hydrochloric acid and extracted with ethyl acetate. The ethyl acetate extract gave compound (4) as needles (40 mg, 68%), m.p. 180—181 °C (from ethyl acetate–cyclohexane) (Found: C, 59.4; H, 7.3. $C_{12}H_{18}O_5$ requires C, 59.5; H, 7.5%), $\nu_{max.}$ (KBr) 3 560, 3 000—2 560, 1 705, and 1 677 $cm^{-1}$.

*Methyl* 1-*Hydroxy*-4,4-*dimethyl*-2,6-*dioxocyclo-octan*-1-*ylacetate* (4; Me ester).—To a solution of the acid (4) (40 mg) in ethanol (2 ml), was added a solution of diazomethane in ether. After 10 min the solvent was distilled off and the residue was crystallized from cyclohexane to give needles of (4; Me ester) (32 mg, 76%), m.p. 130—131.5 °C (Found: C, 61.0; N, 7.95. $C_{13}H_{20}O_5$ requires C, 60.9; H, 7.85%), $\nu_{max.}$ (KBr) 3 540, 1 738, 1 702, and 1 679 $cm^{-1}$; $\nu_{max.}$ ($CHCl_3$) 3 660, 3 540, 1 740, and 1 712 $cm^{-1}$.

*Methyl* 4,4-*Dimethyl*-2,6-*dioxocyclo-octan*-1-*ylacetate* (5; Me ester).—A mixture of the acid (3) (112 mg) and 10% Pd–C (60 mg) in methanol (10 ml) was shaken in hydrogen at room temperature for 3 h during which time 10 ml of hydrogen was absorbed. The catalyst was filtered off, and the filtrate was contracted. The residue was crystallized from ethyl acetate to give needles of (5) (80 mg, 71%), m.p. 160—162 °C, $\nu_{max.}$ (KBr) 3 200—2 300, 1 720, and 1 700 $cm^{-1}$.

To a solution of the crystals (68 mg) obtained above in THF (5 ml), was added an ether solution of diazomethane. After 5 min, the solvent was distilled off and the residue was crystallized from n-hexane to give needles of (5; Me ester) (60 mg, 83%), m.p. 81—82° (Found: C, 64.5; H, 8.25. $C_{13}H_{20}O_4$ requires C, 65.0; H, 8.4%), $\nu_{max.}$ (Nujol) 1 750 and 1 695 $cm^{-1}$; δ($CDCl_3$) 1.07 (3 H, s, $CH_3$), 1.11 (3 H, s, $CH_3$), 1.80—3.15 (11 H, m), and 3.62 (3 H, s, $OCH_3$).

*Reaction of Isophorone* (6) *with Diketen to give* 8-*Hydroxy*-4,4,6-*trimethyl*-2-*oxo*-cis-*bicyclo*[4.2.0]*octan*-8-*ylacetic Acid* β-*Lactone* (7a, b).—A solution of isophorone (6) (1.4 g, 0.01 mol) and diketen (9 g, 0.1 mol) in acetonitrile (12 ml) was photolysed with ice-cooling for 3 h, during which time nitrogen was bubbled through the solution. After evaporation of the solvent and excess of diketen at < 40 °C, the resulting residue was chromatographed on a silica gel (30 g) column using benzene as eluent. The benzene eluate was concentrated under reduced pressure at <40 °C to give *ca.* 1 g of a crystalline solid [mixture of (7a) and (7b)]. Elution was continued with the same solvent to give an oily substance [crude (8a) and (8b)], $\nu_{max.}$ ($CHCl_3$) 1 835 and 1 700 $cm^{-1}$. The crystalline substance obtained above was rechromatographed on a silica gel (20 g) column using n-hexane–diethyl ether (20 : 1) as eluent. The eluate was evaporated at <40 °C to give the lactone (7a) as needles (0.1 g, 5%), m.p. 96—97 °C (from n-hexane) (Found: C, 70.35; H, 7.9. $C_{13}H_{18}O_3$ requires C, 70.25; H, 8.15%), $\nu_{max.}$ ($CHCl_3$) 1 835 and 1 695 $cm^{-1}$; δ($CDCl_3$), 0.99 (3 H, s, $CH_3$), 1.01 (3 H, s, $CH_3$), 1.45 (3 H, s, $CH_3$), 1.60 (2 H, s, $CH_2$), 1.76—2.47 (2 H, ABq, *J* 23 Hz, $CH_2$), 2.45 (2 H, s, $CH_2$), 2.96—3.94 (2 H, ABq, *J* 16 Hz, $CH_2$), and 3.03 (1 H, s, CH). Subsequent elution gave the lactone (7b) as needles (0.3 g, 14%), m.p. 86.5—87.5 °C (from n-hexane) (Found: C, 70.4; H, 7.9. $C_{13}H_{18}O_3$ requires C, 70.25; H, 8.15%), $\nu_{max.}$ ($CHCl_3$) 1 830 and 1 687 $cm^{-1}$; δ($CDCl_3$) 0.90 (3 H, s, $CH_3$), 1.05 (3 H, s, $CH_3$), 1.31 (3 H, s, $CH_3$), 1.52—2.12 (2 H, ABq, *J* 14 Hz, $CH_2$), 1.95—2.55 (2 H, ABq, *J* 16 Hz, $CH_2$), 2.17—2.68 (2 H, ABq, *J* 15 Hz, $CH_2$), 2.97 (1 H, s, CH), and 3.13—3.72 (2 H, ABq, *J* 17 Hz, $CH_2$).

3-*Anilino*-1-*hydroxy*-5,7,7-*trimethylbicyclo*[3.3.1]*non*-2-*ene*-2-*carboxanilide* (9).—(1) A mixture of the lactone (7a) (10 mg) and aniline (0.05 ml) was set aside at room temperature for 3 h. The mixture was evaporated under reduced pressure and the resulting crystalline residue was recrystallized from ether–cyclohexane to give needles of (9) (8 mg, 45%), m.p. 185—192 °C (decomp.) (Found: C, 77.25; H, 7.7; N, 7.1. $C_{25}H_{30}N_2O_2$ requires C, 76.9; H, 7.75; N, 7.15%), $\nu_{max.}$ ($CHCl_3$) 3 360, 3 200—3 060, 1 625, 1 600, and 1 555 $cm^{-1}$; δ($CDCl_3$) 0.94 (3 H, s, $CH_3$), 1.02 (6 H, s, 2 × $CH_3$), 0.90—1.60 (4 H, m), 2.00—2.50 (4 H, m), 3.48 (1 H, s, OH), 6.88—7.50 (11 H, m), and 11.70 (1 H, s, NH).

(2) Following a procedure similar to that described above, reaction of the lactone (7b) (10 mg) with aniline afforded the amide (9) (8 mg, 45%).

7-*Hydroxy*-4,4,6-*trimethyl*-2-*oxo*-cis-*bicyclo*[4.2.0]*octan*-7-*ylacetanilide* (11a, b).—(1) To the oily substance [200 mg, crude (8a, b)] obtained in the photoreaction of isophorone (6) with diketen mentioned above, aniline (0.5 ml) was added. After 3 h at room temperature, the reaction mixture was concentrated and absorbed onto a silica gel (10 g) column. Elution with chloroform gave the anilide (11a) (20 mg), m.p. 244 °C (decomp.) (Found: C, 72.2; H, 8.15; N, 4.4. $C_{19}H_{25}NO_3$ requires C, 72.35; H, 8.0; N, 4.45%), $\nu_{max.}$ (KBr) 3 420, 3 200, 1 725, 1 685, 1 600, and 1 520 $cm^{-1}$; δ(pyridine) 1.00 (6 H, s, 2 × $CH_3$), 1.57 (3 H, s, $CH_3$), 1.48—2.26 (2 H, ABq, *J* 14 Hz, $CH_2$), 2.35 (2 H, broad s, $CH_2$), 2.52—3.08 (3 H, m), and 2.77—3.57 (2 H, ABq, *J* 16 Hz, $CH_2$); *m/e:* 315 ($M^+$), 177, and 176. Subsequent elution with ether gave the anilide (11b) as needles (30 mg), m.p. 159—160 °C (Found: C, 72.5; H, 8.05; N, 4.3. $C_{19}H_{25}NO_3$ requires C, 72.35; H, 8.0; N, 4.45%), $\nu_{max.}$ (KBr) 3 380, 1 685, 1 670, 1 600, and 1 550 $cm^{-1}$; δ(pyridine) 0.88 (3 H, s, $CH_3$), 0.99 (3 H, s, $CH_3$), 1.20 (3 H, s, $CH_3$), 1.26 (1 H, dd, *J* 15 Hz, *J* 2.5 Hz), 2.10 (1 H, dd, *J* 15 Hz, *J* 2.5 Hz), 2.65 (1 H, d, *J* 15 Hz), 2.76 (1 H, d, *J* 15 Hz),

2.32—2.72 (3 H, m), and 2.88 (2 H, s, $CH_2$); *m/e* 315 ($M^+$), 297 ($M^+ - H_2O$), and 177.

(2) A solution of isophorone (6) (1.4 g) and diketen (9 g) in acetonitrile (12 ml) was photolysed under the same conditions as those described above. The reaction mixture was evaporated under reduced pressure to give an oily residue to which aniline (4 ml) was added. After 3 h, the mixture was concentrated under reduced pressure and the residue was absorbed on a silica gel (60 g) column. Elution with benzene gave aniline and the anilide (9) (0.6 g, 15%). Subsequent elution with chloroform furnished the anilide (11a) (0.2 g, 6%). Elution was continued with ether to give the anilide (11b) (0.3 g, 9%).

1,3-*Dihydroxy*-5,7,7-*trimethylbicyclo*[3.3.1]*non*-1-*ene*-2-*carboxanilide* (10).—A solution of the anilide (9) (50 mg) in a mixture of 10% hydrochloric acid (5 ml) and methanol (5 ml) was heated under reflux for 30 min. The mixture was condensed, and extracted with chloroform. The chloroform extract gave a crystalline substance, recrystallization of which from cyclohexane gave compound (10) as needles (17 mg, 43%), m.p. 143—144 °C (Found: C, 72.3; H, 8.15; N, 4.25. $C_{19}H_{25}NO_3$ requires C, 72.35; H, 8.0; N, 4.45%), $\nu_{max.}$ ($CHCl_3$) 3 280, 1 615, 1 600, and 1 545 $cm^{-1}$; $\delta$($CDCl_3$) 0.85 (3 H, s, $CH_3$), 0.88 (3 H, s, $CH_3$), 0.94 (3 H, s, $CH_3$), 0.97—2.10 (6 H, m), 2.04 (2 H, s, $CH_2$), 2.77 (1 H, s, OH), 7.15—7.73 (5 H, m), 9.95 (1 H, broad s, NH), and 15.76 (1 H, s, OH).

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