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Studies on Ketene and Its Derivatives. LIII.[1] Reaction of Diketene with Diazoacetophenone and Ethyl Diazoacetate

Tetsuzo Kato and Nobuya Katagiri

Pharmaceutical Institute, Tohoku University[2]

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Diketene reacted with diazoacetophenone (Ia) to give two isomeric spiro compounds, 2-(*trans*-2-benzoyl-1-hydroxycyclopropane)-acetic acid β-lactone (IIa) and 2-(*cis*-2-benzoyl-1-hydroxycyclopropane)-acetic acid β-lactone (IIa′).

Similarly, *p*-methoxy-α-diazoacetophenone (Ib) was transformed to 2-[*trans*-2-(*p*-methoxybenzoyl)-1-hydroxycyclopropane]-acetic acid β-lactone (IIb) and 2-[*cis*-2-(*p*-methoxybenzoyl)-1-hydroxycyclopropane]-acetic acid β-lactone (IIb′).

Reaction of diketene with ethyl diazoacetate (Ic) gave furanone derivatives, 2,5-dihydro-2-ethoxycarbonyl-3-methylfuran-5-one (VII) and 2,5-dihydro-4-ethoxycarbonyl-methylfuran-2-one (VIII), together with 2-(*trans*-2-ethoxycarbonyl-1-hydroxycyclopropane)acetic acid β-lactone (IIc).

It is a well documented fact that pyrolysis or photolysis of diazo compound results in the elimination of nitrogen generating a carbene intermediate, which possesses sensitive activities and exhibits fascinating reactions.[3–5]

For example, ethyl diazoacetate reacts with dimethylketene to afford ethyl 3-methylcrotonate and 2,3-dihydro-3,3-dimethyl-5-ethoxyfuran-2-one.[6] This reaction can be explained as following: *i. e.*, ethoxycarbonylcarbene formed by the elimination of nitrogen from ethyl diazoacetate adds to the double bond of dimethylketene to give a cyclopropanone intermediate, which transforms to the products.

While investigating some potential uses of diketene, we studied its reactions with diazoacetophenone and ethyl diazoacetate, and have found that spiro compounds and furanone derivatives can be obtained by a novel reaction, which is the subject of this paper.

1) Reaction of Diketene with Diazoacetophenone (Ia)

When diazoacetophenone (Ia: R=C_6H_5) was heated with excess diketene in the presence of copper powder as a catalyst, two kinds of crystals of mp 74—75° (IIa) and mp 73—74° (IIa′) were separated by using silica gel column chromatography.

Both IIa and IIa′ had the same empirical formula of $C_{12}H_{10}O_3$. Though their melting points are approximately similar, the depression in admixture test indicates that they are isomerical with each other.

Both infrared (IR) spectra of IIa and IIa′ show the presence of the carbonyl at 1840 cm^{-1}, 1665 cm^{-1}, and 1840 cm^{-1}, 1675 cm^{-1}, respectively. These data suggest that both IIa and IIa′ have still a β-lactone moiety in their structures.

As shown in Fig. 1 and Fig. 2, in the nuclear magnetic resonance (NMR) spectra of IIa and IIa′ signals due to cyclopropane ring protons presented at such higher magnetic field as 1.87 ppm and 1.51 ppm, respectively.

1) Part LII: T. Kato and M. Sato, *Yakugaku Zasshi*, **92**, 1515 (1972).
2) Location: *Aobayama, Sendai, 980*, Japan.
3) J. Hine, "Divalent Carbon," Ronald Press, New York, 1964.
4) W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964.
5) V. Dave and E.W. Warnhoff, "Organic Reactions," Vol. 18, ed., by John Wiley and Sons, Inc., New York, N.Y., 1970, p. 217.
6) A.S. Kende, *Chem. & Ind.* (London), **75**, 1053 (1956).

These observations indicated that both IIa and IIa′ had the spiro moiety in their structures.

Consequently, IIa and IIa′ are steric isomers with each other, and both of which should be such spiro compound as three and four membered ring system, which was formed by the addition of carbene to the C=C double bond of diketene. The steric isomerization is due to *cis* or *trans* between benzoyl group and lactone ring methylene.

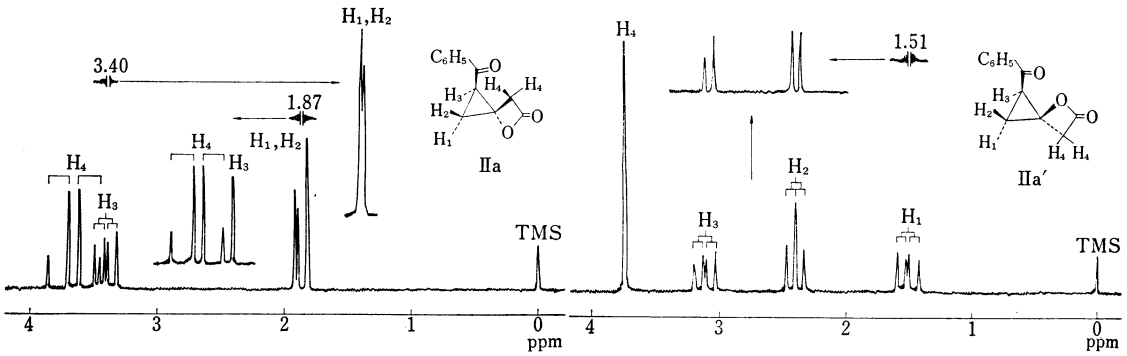

Fig. 1. NMR Spectrum of IIa in $CDCl_3$ (100 MHz)

Fig. 2. NMR Spectrum of II′a in $CDCl_3$ (100 MHz)

That is to say, the NMR spectrum of IIa (Fig. 1) shows signals at 1.87 ppm (triplet) and at 3.4 ppm (quartet). When double resonance technique is employed to the signal at 3.4 ppm, the triplet signal at 1.87 ppm changes to the doublet. Similarly, the quartet signal at 3.4 ppm changes to the singlet by irradiation to 1.87 ppm. Therefore, the signal at 1.87 ppm can be assigned to the methylene protons(H_1, H_2) of cyclopropane ring, and that of 3.4 ppm to the methine proton (H_3). Furthermore, the signal at 3.4—3.9 ppm (AB quartet, J=17 Hz, 2H) does not change by the above irradiation. This signal, therefore, is due to the methylene protons of lactone ring.

On the other hand, as shown in Fig. 2, the NMR spectrum of IIa′ shows signals at 1.51 ppm (1H, quartet, J=9.0 Hz, J=7.0 Hz), 2.40 ppm (1H, triplet, J=7.0 Hz, J=7.0 Hz), 3.12 ppm (1H, quartet, J=9.0 Hz, J=7.0 Hz) and 3.77 ppm (2H, singlet). Since both signals at 2.40 ppm and 3.12 ppm change to doublet by irradiation to 1.51 ppm, these three signals are owing to cyclopropane ring protons.

In general, in the vicinal proton of cyclopropane ring the coupling constant between *cis* proton is usually larger than that of *trans*.[7]

Consequently, as shown in Fig. 2, these signals were assigned to H_1, H_2 and H_3 protons in the oder of high magnetic field. On the other hand, the signal (2H, singlet) at 3.77 ppm due to the methylene protons of the lactone ring was not affected by using benzene as a solvent. In addition, the pattern of the lactone methylene protons of IIa showed AB quartet by the effect of benzoyl group, but that of IIa′ was observed as a singlet signal.

The above data demonstrated that the configuration between the benzoyl group and the methylene of lactone ring of IIa is *cis*, that of IIa′ being *trans*.

In the NMR spectrum of IIa H_1 and H_2 showed the approximately same chemical shift, because H_1 and H_2 were affected by lactone ring oxygen and benzoyl group to result in shifting to lower field, respectively. Therefore, H_2 of IIa′ is influenced from both lactone ring oxygen and benzoyl group to result in shifting to a lower field region (2.40 ppm).

Treatment of both IIa and IIa′ with 10% hydrochloric acid gave phenacylacetone (III). Ammonolysis of IIa and IIa′ gave 4-phenacylacetoacetamide (IV) and 2-carbamoyl-3-phenyl-

7) L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Ed., edited by D.H.R. Barton and W. Doering, Pergamon Press, New York, 1969, p. 272.

2-cyclopentenone (V). Hydrolysis of V with 10% hydrochloric acid afforded 3-phenyl-2-cyclopentenone (VI).

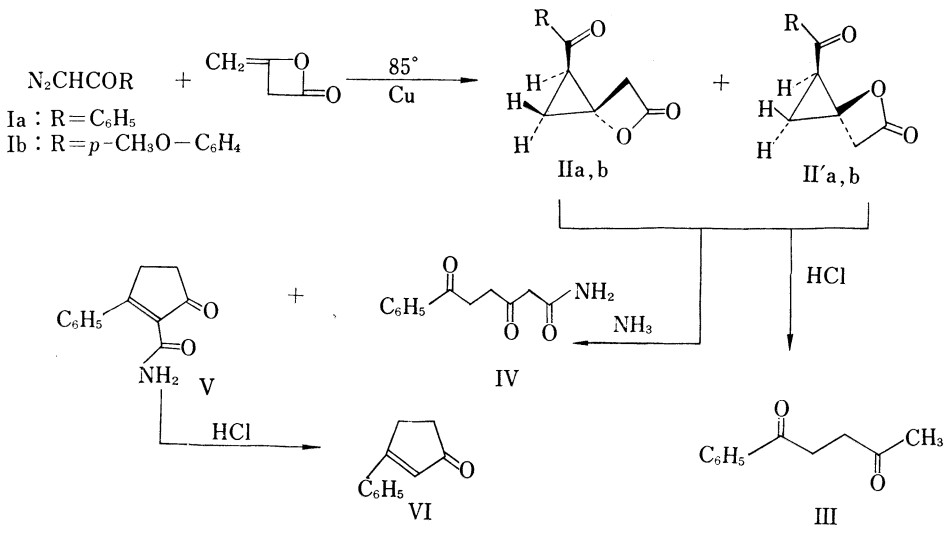

Chart 1

Based upon these spectral data and chemical behaviours the structure of 2-(*trans*-2-benzoyl-1-hydroxycyclopropane)acetic acid β-lactone (IIa) and 2-(*cis*-2-benzoyl-1-hydroxycyclopropane)acetic acid β-lactone (IIa') is unequivocally given for two steric isomers, respectively.

Employing the same procedure given for Ia, the reaction of *p*-methoxy-α-diazoacetophenone (Ib) with diketene gave 2-[*trans*-2-(*p*-methoxybenzoyl)-1-hydroxycyclopropane] acetic acid β-lactone (IIb) and 2-[*cis*-2-(*p*-methoxybenzoyl)-1-hydroxycyclopropane]acetic acid β-lactone (IIb').

2) Reaction of Diketene with Ethyl Diazoacetate (Ic)

When ethyl diazoacetate (Ic) was allowed to react with excess diketene in the presence of copper powder at 100°, three kinds of oily substances, bp 85—87° (2 mmHg) (IIc), bp 93° (2 mm Hg) (VII' and VII) and bp 130—134° (2 mm Hg) (VIII) were obtained by rectification. The NMR spectrum indicated that the fraction of bp 93° (2 mmHg) was a mixture of VII' and VII (bp 104—105° at 2 mmHg). VII' could not be isolated by any purification such as chromatography or distillation, and was transformed into VII as more stable isomer by gas–liquid chromatography (GLC) or heating.

When anhydrous copper sulphate was used as a catalyst in place of copper powder, VII and VIII were obtained.

All of these compounds (IIc, VII and VIII) have the same empirical formula of $C_8H_{10}O_4$.

The IR spectrum of IIc indicated the presence of the carbonyl group at 1850 cm^{-1} and 1725 cm^{-1} suggesting the β-lactone ring as a partial structure.

In the NMR spectrum of IIc (CCl_4) the signals due to cyclopropane ring protons at 1.47 ppm (H_2: 1H, triplet, J=6.8 Hz, J=6.8 Hz), 1.69 ppm (H_1: 1H, quartet, J=6.8 Hz, J=10.0 Hz) and 2.27 ppm (H_3: 1H, quartet, J=6.8 Hz, J=10.0 Hz) were observed besides the three-four pattern owing to ethyl protons. The signal of the methylene protons (H_4) at 3.64 ppm presented as singlet in $CDCl_3$, but changed to the AB quartet in benzene.

As shown in Chart 2, these signals were assigned to H_1, H_2 and H_3. Since the signal at 2.27 ppm is due to H_3, the signal at 1.69 ppm which shows the larger vicinal coupling con-

stants (J=10.0 Hz) can be assigned to H_1. Therefore, the signal at the highest field (1.47 ppm) can be assigned to H_2.

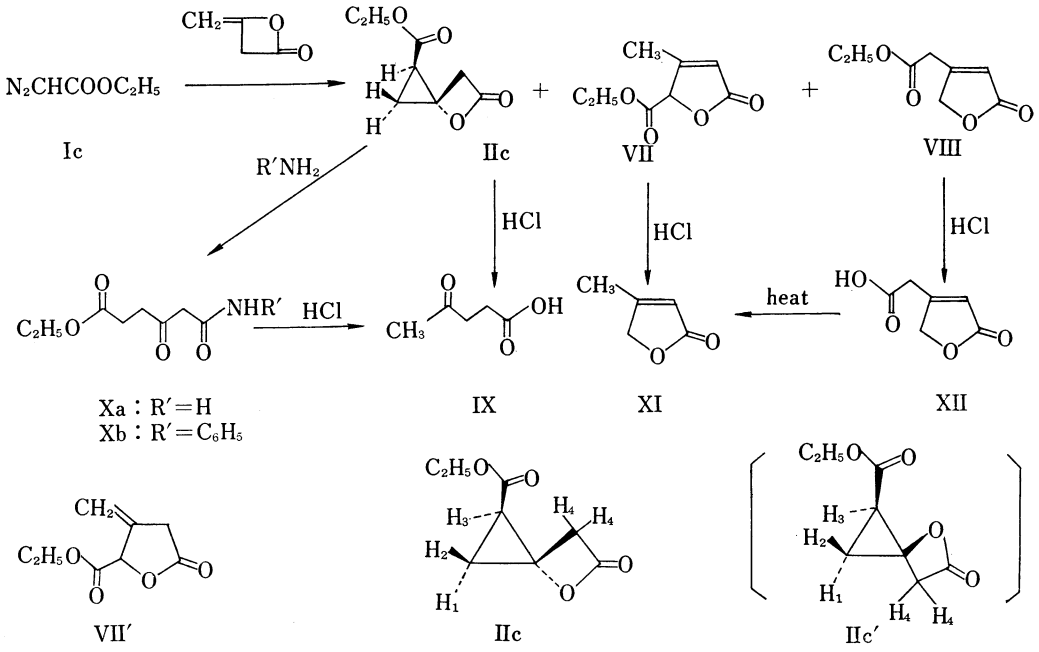

Chart 2

It is generally known that in the cyclopropane derivatives having an ethoxycarbonyl moiety *trans* proton towards ethoxycarbonyl was observed at the higher field than *cis* protons.[7] But in IIc *cis* proton (H_2) showed the higher field shift than *trans* proton (H_1) because of the affection of lactone ring oxygen as mentioned already in IIa and IIa'.

Though IIc' could be postulated as an isomer of IIc, the structure of IIc was given for this product by the following reason: that is, as discussed before, H_1 shifted to the lower field than H_2, and the methylene protons (H_4) of lactone ring was subject to the solvent effect in benzene.

IIc was hydrolyzed with 10% hydrochloric acid to give levulinic acid (IX) quantitatively together with evolution of carbon dioxide. IIc was treated with ammonia or aniline to be transformed into corresponding amide compounds (Xa, b). These data are consistent with the structure of the product as 2-(*trans*-2-ethoxycarbonyl-1-hydroxycyclopropane)acetic acid β-lactone (IIc).

On the other hand, as shown in Fig. 3, the IR spectrum of VII in chloroform showed the absorption at 1795 cm^{-1} (shoulder), 1770 cm^{-1} and 1740 cm^{-1} (shoulder), but in carbon tetrachloride these three absorptions splited completely. Moreover, with regard to the intensity, the absorption at 1795 cm^{-1} and 1740^{-1} was reversed.

It is reported that the IR spectrum of α,β-unsaturated γ-lactone having hydrogen at α-position exhibits two absorptions at about 1780 cm^{-1} and 1750 cm^{-1}, which are subject to the intensity variation by solvent or temperature.[8] Terefore, the absorption at 1770 cm^{-1} is due to the ester carbonyl, and VII is α,β-unsaturated γ-lactone derivatives. In the NMR spectrum of VII the signals at 2.17 ppm (3H, singlet), 5.26 ppm (1H, singlet) and 5.90 ppm (1H, singlet) were observed besides ethyl protons. VII was hydrolyzed with 10% hydrochloric acid to give a known compound, 4-methyl-2,5-dihydrofuran-2-one(XI).

8) R.N. Jones, C.L. Angell, T. Ito, and R.J.D. Smith, *Can. J. Chem.*, 37, 2007 (1959).

These spectral data and chemical behaviour indicated that the structure of VII was consistent with 2,5-dihydro-2-ethoxycarbonyl-3-methylfuran-5-one.

VII′ was isomerized to VII on heating and was transformed into XI by hydrolysis with 10% hydrochloric acid. In the NMR spectrum of VII′ the signals of methylene protons at 3.25 ppm and olefinic protons (2H) at 5.30 ppm were observed besides the signal owing to VII. Consequently, 2-ethoxycarbonyl-3-methylene-tetrahydrofuran-5-one was given for the structure of VII′.

The IR spectrum of VIII showed the absorption due to carbonyl group at 1785 cm^{-1} and 1740 cm^{-1}, and as shown in Fig. 3, the solvent effect was also observed as in the case of VII. Hydrolysis of VIII with 10% hydrochloric acid gave the carboxylic acid (XII), which was transformed into XI by heating. Based on these observations, 2,5-dihydro-4-ethoxycarbonylmethylfuran-2-one was given for the structure of VIII. In addition, the NMR spectrum of VIII was consistent this structure.

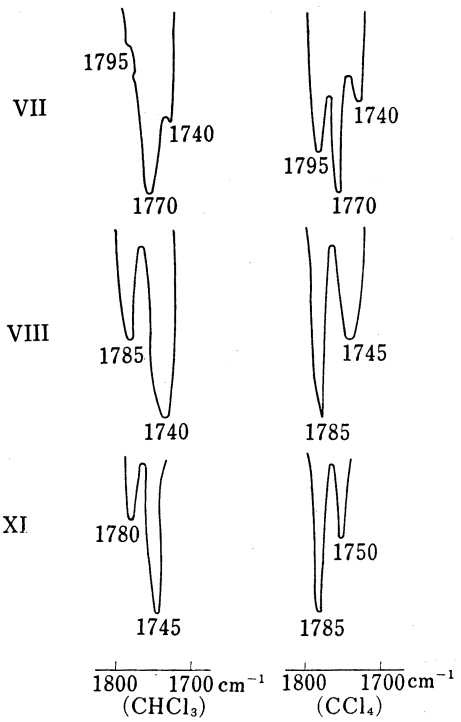

Fig. 3. Infrared Spectra of VII, VIII and XI

Experimental

Reaction of Diketene with Diazoacetophenone[9] (Ia)——A solution of Ia (2.9 g) in diketene (10 g) was added dropwise to a suspension of Cu powder (0.2 g) in diketene (11 g) with stirring over a period of 0.5 hr, during which time the temperature of the mixture was maintained at 85°. After cooling, Cu powder was filtered off, and excess diketene was removed from the filtrate under reduced pressure. The residue was purified by column chromatography on silica gel. The petroleum ether (bp 35—37°) eluted fraction was evaporated to give a crystalline substance. Recrystallization from cyclohexane gave 2-(*trans*-2-benzoyl-1-hydroxycyclopropane)acetic acid β-lactone (IIa) as colorless plates, mp 74—75°. Yield, 1.02 g (25%). *Anal.* Calcd. for $C_{12}H_{10}O_3$ (IIa): C, 71.28; H, 4.99. Found: C, 71.32; H, 5.07.

The benzene eluted fraction gave 2-(*cis*-2-benzoyl-1-hydroxycyclopropane)acetic acid β-lactone (IIa′) as colorless needles, mp 73—74° (ether–cyclohexane). Yield, 0.33 g (8%). *Anal.* Calcd. for $C_{12}H_{10}O_3$ (IIa′): C, 71.28; H, 4.99. Found: C, 70.87; H, 4.95.

Reaction of Diketene with *p*-Methoxy-α-diazoacetophenone[9] (Ib)——As above, Ib (3.5 g) was treated with diketene (21 g) in the presence of Cu powder (0.2 g) to give a crystalline solid, which was purified by chromatography on silica gel using ether as eluent to afford 2-[*trans*-2-(*p*-methoxybenzoyl)-1-hydroxycyclopropane]acetic acid β-lactone (IIb) and 2-[*cis*-2-(*p*-methoxybenzoyl)-1-hydroxycyclopropane]acetic acid β-lactone (IIb′). The former, on recrystallization from ether, gave colorless plates of mp 109—111° (IIb). Yield: 1.2 g (26%). *Anal.* Calcd. for $C_{13}H_{12}O_4$ (IIb): C, 67.27; H, 5.21. Found: C, 66.88; H, 5.21. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1840, 1660. NMR ($CDCl_3$, ppm): 1.8—1.9 (2H, double doublet, J=8.0 Hz, J=9.0 Hz), 3.34 (1H, quartet, J=8.0 Hz, J=9.0 Hz), 3.4—3.9 (2H, quartet AB type, J=17 Hz), 3.88 (3H, singlet), 6.95 (2H, ring protons), 7.98 (2H, ring protons).

The second product was recrystallized from ether to give colorless prisms of mp 90—91° (IIb′). Yield: 0.1 g (2%). *Anal.* Calcd. for $C_{13}H_{12}O_4$ (IIb′): C, 67.27; H, 5.21. Found: C, 66.95; H, 5.27. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1840, 1670. NMR ($CDCl_3$, ppm): 1.47 (1H, quartet, J=7.0 Hz, J=9.5 Hz), 2.39 (1H, triplet, J=7.0 Hz, J=7.0 Hz), 3.09 (1H, quartet, J=7.0 Hz, J=9.5 Hz), 3.76 (2H, singlet), 3.86 (3H, singlet), 6.95 (2H, ring protons), 7.98 (2H, ring protons).

9) M.S. Newman and P. Beal, *J. Am. Chem. Soc.*, **71**, 1506 (1949).

Phenacylacetone (III)——1) A solution of IIa (0.5 g) in EtOH (8 ml) and 20% HCl (5 ml) was refluxed for 2 hr, during which time CO_2 was detected by passing the gas evolved into a $Ba(OH)_2$ solution. The reaction mixture was condensed *in vacuo*, and the residue was extracted with ether. The ether fraction was evaporated to give an oily substance (III), to which a solution of semicarbazide hydrochloride (0.3 g) and sodium acetate (0.3 g) in water (5 ml) was added. After warming in a water bath for 1 hr, crystals separated were collected by filtration, and washed with ether. Recrystallization from EtOH gave 0.3 g of phenacylacetone semicarbazone[10] as pale yellow prisms, mp 188—189°. 2) Similar treatment of IIa′ (0.5 g) gave 0.35 g of phenacylacetone semicarbazone.

Reaction of IIa with Ammonia——To MeOH (10 ml) saturated with ammonia was added IIa (0.5 g) with ice-cooling. After being allowed to stand under ice-cooling for 20 min, the reaction mixture was neutralized with CO_2 gas. Crystals separated was filtered off, and filtrate was condensed to dryness *in vacuo* to give a crystalline solid, which was washed with ether. Recrystallization from benzene gave 4-phenacylacetoacetamide (IV) as colorless leaves, mp 114—116°. Yield: 0.3 g (55%). The mother liquor was condensed to give 2-carbamoyl-3-phenyl-2-cyclopentenone (V) as pale yellow needles, mp 127—129°. Yield, 90 mg(17%). *Anal.* Calcd. for $C_{12}H_{13}O_3N$ (IV): C, 65.74; H, 5.98; N, 6.39. Found: C, 65.89; H, 6.09; N, 6.27. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360, 3180, 1710, 1680, 1650. NMR ($CDCl_3$, ppm): 2.8—3.5 (4H, multiplet), 3.57 (2H, singlet), 6.00 (1H, broad), 7.00 (1H, broad), 7.2—8.1 (5H, ring protons). *Anal.* Calcd. for $C_{12}H_{11}O_2N$ (V): C, 71.62; H, 5.51; N, 6.96. Found: C, 71.42; H, 5.77; N, 6.97. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1675 (shoulder). NMR ($CDCl_3$, ppm): 2.5—3.2 (4H, multiplet), 5.85 (1H, broad), 7.2—7.9 (6H, ring protons, NH proton).

Hydrolysis of V with 10% HCl——A suspension of V (0.5 g) in 10% HCl (15 ml) was heated under reflux for 5 hr. The reaction mixture was condensed *in vacuo*, and the residue was extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhydrous Na_2SO_4, and was condensed to give a crystalline solid, which was submitted to column chromatography on silica gel using ether–petroleum ether (1: 3) as eluent. Recrystallization of eluate from cyclohexane gave 3-phenyl-2-cyclopentenone[10] (VI) as pale yellow needles, mp 82—83°.

Reaction of Diketene with Ethyl Diazoacetate[11] (Ic)——1) In the Presence of Cu Powder: A solution of Ic (11.4 g) in diketene (25 g) was added dropwise to a suspension of Cu powder (1 g) in diketene (42 g) with stirring over a period of 0.5 hr, during which time the temperature of the mixture was maintained at 100°. After cooling, Cu powder was filtered off, and excess diketene was removed from the filtrate under reduced pressure. The residue was extracted with ether. The ether extract was evaporated to give a brown oily substance, which was distilled under reduced pressure in a claisen flask equipped with an efficient fractionating column giving 5.5 g (32.4%) of 2-(*trans*-2-ethoxycarbonyl-1-hydroxycyclopropane)acetic acid β-lactone (IIc) as a colorless oil, bp 85—87° (2 mmHg), 2.4 g[12] of bp 93° (2 mmHg) as a colorless oil, and 2.5 g (14.7%) of 2,5-dihydro-4-ethoxycarbonylmethylfuran-2-one (VIII) as a pale yellow oil, bp 130—134° (2 mmHg). *Anal.* Calcd. for $C_8H_{10}O_4$ (IIc): C, 56.46; H, 5.92. Found: C, 56.87; H, 6.16. *Anal.* Calcd. for $C_8H_{10}O_4$ (VIII): C, 56.46; H, 5.92. Found: C, 56.41; H, 5.97. NMR (CCl_4, ppm): 1.23 (3H, triplet, $J=8$ Hz), 3.51 (2H, singlet), 4.13 (2H, quartet, $J=8$ Hz), 4.82 (2H, singlet), 5.93 (1H, singlet).

2) In the Presence of Anhydrous $CuSO_4$: As above, Ic (11.4 g) was treated with diketene (67 g) in the presence of anhydrous $CuSO_4$ (1 g) to give 1.3 g (7.7%) of 2,5-dihydro-2-ethoxycarbonyl-3-methylfuran-5-one (VII) as a colorless oil, bp 103—107° (2 mmHg), and 3.2 g (18.8%) of VIII. *Anal.* Calcd. for $C_8H_{10}O_4$ (VII): C, 56.46; H, 5.92. Found: C, 56.18; H, 6.09.

Hydrolysis of IIc with 10% HCl——A suspension of IIc (1.5 g) in 10% HCl (10 ml) was heated under reflux for 0.5 hr, during which time the evolution of CO_2 was detected (as $BaCO_3$).

Following the procedure given for III, IIc (1.5 g) was hydrolyzed with 10% HCl (10 ml) to give levulinic acid[13] (IX) as a colorless oil, bp 107—109° (4 mmHg). Yield: 0.8 g (76%).

Reaction of IIc with Ammonia——IIc (2 g) was added to MeOH (20 ml) saturated with ammonia with ice-cooling. The reaction mixture was allowed to stand at room temperature for 0.5 hr, and was condensed. The residue was recrystallized from ether to afford 4-ethoxycarbonylmethylacetoacetamide (Xa) as colorless leaves, mp 48—49°. Yield: 0.8 g (36.4%). *Anal.* Calcd. for $C_8H_{13}O_4N$ (Xa): C, 51.33; H, 7.00; N, 7.48. Found: C, 51.33; H, 7.10; N, 7.61. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 3340, 2980, 1720, 1680. NMR ($CDCl_3$, ppm): 1.24 (3H, triplet, $J=7$ Hz), 2.72 (4H, multiplet), 3.44 (2H, singlet), 4.07 (2H, quartet, $J=7$ Hz), 6.15 (1H, broad), 6.85 (1H, broad).

Reaction of IIc with Aniline——A solution of IIc (0.85 g) and aniline (0.46 g) in abs. ether (10 ml) was warmed in a water bath for 5 hr. The reaction mixture was condensed, and the residue was purified by

10) W. Borshe and A. Fels, *Ber.*, **39**, 1926 (1906).
11) E.B. Womack and A.B. Nelson, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horning, John Wiley & Sons, Inc., New York, N.Y., 1955, p. 392.
12) The NMR spectrum showed a mixture of 2-ethoxycarbonyl-3-methylene-tetrahydrofuran-5-one (VII′) and VII in the ratio of 5: 1.
13) B.F. Mckenzie, "Organic Syntheses," Coll. Vol. I, ed. by A.H. Blatt, John Wiley and Sons, Inc., New York, N.Y., 1932, p. 335.

chromatography on silica gel using ether as eluent. Recrystallization of eluate from ether gave 4-ethoxycarbonylmethylacetoacetanilide (Xb) as colorless needles, mp 70—71°. Yield: 0.6 g (30.8%). *Anal.* Calcd. for $C_{14}H_{17}O_4N$ (Xb): C, 63.86; H, 6.51; N, 5.32. Found: C, 63.74; H, 6.58; N, 5.30. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 2980, 1715, 1680. NMR ($CDCl_3$, ppm): 1.23 (3H, triplet, $J=7$ Hz), 2.73 (4H, multiplet), 3.58 (2H, singlet), 4.10 (2H, quartet, $J=7$ Hz), 7.1—7.6 (5H, ring protons), 8.95 (1H, broad).

Hydrolysis of Xa with 10% HCl——Following the procedure given for III, Xa (1 g) was hydrolyzed with 10% HCl (10 ml) to give IX. Yield: 0.4 g (67%).

2,5-Dihydro-4-methylfuran-2-one[14] (XI)——1) A suspension of VII (1.7 g) in 10% HCl (30 ml) was heated under reflux for 1 hr, during which time CO_2 was indentified. The reaction mixture was condensed *in vacuo*, and the residue was extracted with ether. The ether layer was dried over, and was evaporated to give an oily substance, which was distilled under reduced pressure to afford XI as a colorless oil, bp 78° (3 mmHg). Yield: 0.4 g (41%). 2) As above, VII′ (2 g) was treated with 10% HCl (30 ml) to give XI. Yield: 0.9 g (78%). 3) XII (0.5 g) was heated at 210° in a silicon bath for 20 min tc give 0.42 g (100%) of XI with the evolution of CO_2.

Isomerization of VII′ to VII——1) GLC Condition: Column; 5% DC-11 on chromosorb W (60—80 mesh, 1 m). temperature; column 170°, injection chamber 224°, detector 258°. carrier gas; He, flow rate 60 ml/min. retention time; 1 min.

The IR spectrum of sample collected was identical in every respects with that of VII.

2) Thermolysis: A suspension of VII′ (2 g) and Cu powder (0.1 g) was heated at 180° in an oil bath with stirring for 1 hr. After cooling, ether was added to the reaction mixture, and Cu powder was filtered off. The fitrate was evaporated, and the residue was distilled under reduced pressure to give 0.8 g (40%) of VII, bp 104—105° (2 mmHg).

Hydrolysis of VIII with 10% HCl——A suspension of VIII (2 g) in 10% HCl (15 ml) was warmed in a water bath for 2 hr. The reaction mixture was condensed *in vacuo*, and the residue was extracted with ether. The ether layer was dried over anhydrous Na_2SO_4. Evaporation of ether gave an oily substance, which was purified by chromatography on silica gel using ether as eluent. Recrystallization of eluate from ether gave 4-carboxymethyl-2,5-dihydrofuran-2-one (XII) as colorless plates, mp 50—53°. Yield: 0.86 g (51.5%). *Anal.* Calcd. for $C_6H_6O_4$ (XII): C, 50.71; H, 4.26. Found: C, 5.98; H, 4.29. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 2920, 1780, 1745, 1720, 1635. NMR ($CDCl_3$, ppm): 3.62 (2H, singlet), 4.96 (2H, singlet), 6.15 (1H, singlet), 10.40 (1H, broad).

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