For the purpose of revealing the origin of the doublet splitting, 3-hydroxytetronic acid, which have two hydrogens at the C-4 position, was investigated in place of L-ascorbic acid. As a result, an analogous spectrum was observed with that of Fig. 2, suggesting that the radical species have the same basic structure as that given by the reaction of L-ascorbic acid with hydrazine. The ESR spectrum, shown in Fig. 3, consisted of nine triplets (relative intensities 1:2:1) due to the splitting of the nitrogen hyperfine components by two equivalent hydrogen nuclei. The latter could be ascribed to either the C_4–H_2 of 3-hydroxytetronic acid or the hydrazine N–H_2.

When D_2O is used as the solvent, the hydrazine N–H_2 will be substituted by deuterium. The spectrum recorded in D_2O was, however, exactly the same as that given in Fig. 3, proving that the triplet splitting arises from the C_4–H_2 of 3-hydroxytetronic acid. Since the structure (A) has no hydrogen at the C_4 position, it should be excluded. Moreover, during the reaction between triose-reductone and hydrazine, ESR spectra similar to that of Fig. 1 were observed. In this kind of reaction, no pyrrole-ring structure like (A) can be produced.

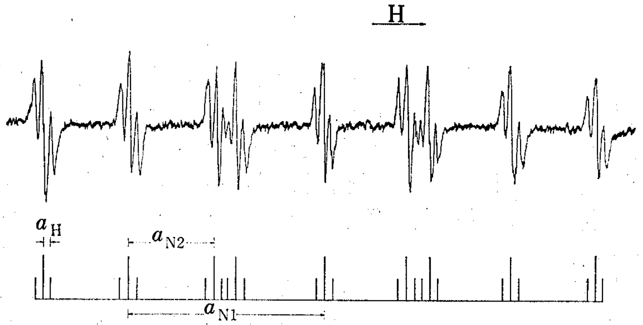

Fig. 3. The ESR Spectrum of 3-Hydroxytetronic Acid–Hydrazine Free Radical in H_2O,D_2O (a_{N1}=4.85G, a_{N2}=2.17G, a_H=0.20G)

Further investigations are still continuing as to the possible structure of the radical species produced during the reaction of L-ascorbic acid with hydrazine.

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Addition Reactions of Heterocumulenes. I. Cycloaddition Reaction of Dimethylketene with α-Diimines

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The reaction of ketenes with isolated C=N groups to give β-lactam is well known[2] but their reaction with conjugated C=N groups has received little attention. Pfleger and Jäger[3] proposed the structure of the addition reaction product of diphenylketene to N,N′-(dimethylethanediylidene)dianiline (Ia) as the Diels–Alder type, but our examination of the same reaction product found that it is the [2+2] cycloadduct, β-lactam (II).[4]

Recently, Burpitt, *et al.*[5] reported the reaction of dimethylketene with Ia to give 3,4-dihydro-3,3,5,6-tetramethyl-1,4-diphenyl-2(1H)-pyrazinone (IIIa). The structural assignment of IIIa was made on the basis of Pfleger and Jäger's report.[3]

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[1] Location: *35-23, Nozawa 1-chome, Setagaya-ku, Tokyo.*

[2] D.A. Nelson, *Tetrahedron Letters*, **1971**, 2543; A.K. Bose, G. Spiegelman, and M.S. Manhas, *ibid.*, **1971**, 3167.

[3] R. Pfleger and A. Jäger, *Chem. Ber.*, **90**, 2460 (1957).

[4] M. Sakamoto and Y. Tomimatsu, *Yakugaku Zasshi*, **90**, 1386 (1970).

[5] R.D. Burpitt, K.C. Brannock, R.G. Nations, and J.C. Martin, *J. Org. Chem.*, **36**, 2222 (1971).

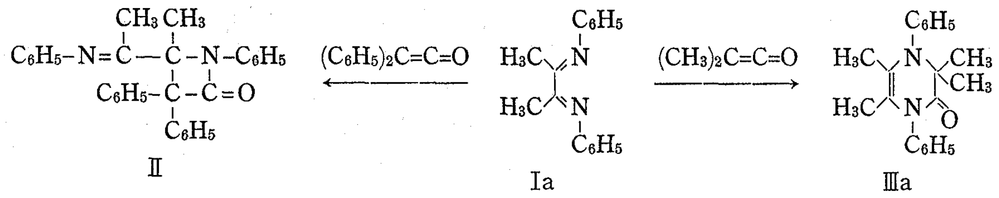

Chart 1

When this reaction was re-examined in our laboratory in an effort to obtain a sample of IIIa to study the photochemistry of pyrazine compounds, the results obtained were different from those report by Burpitt, *et al.*[5] The adduct, mp 160—161°, obtained from reaction of dimethylketene with Ia is not IIIa, but 4-(1-anilideneethyl)-3,3,4-trimethyl-1-phenyl-2-azetidinone (IVa). The evidence for this structural assignment is the subject of the present paper.

Reaction of dimethylketene with Ia in dry benzene gave the 1:1 molar adduct (IVa) and its structure was determined from the following spectral data and elemental analysis. The infrared (IR) spectrum of IVa showed the presence of a carbonyl in four-membered ring lactam (1736 cm^{-1})[6] and imine (1657 cm^{-1})[7] group, and its nuclear magnetic resonance (NMR) spectrum (ppm in $CDCl_3$) indicated three singlet signals at 1.40 (CH_3), 1.45 (CH_3), and 1.89 ($CH_3 \times 2$). The above data are in agreement with those described by Burpitt, *et al.*[5]

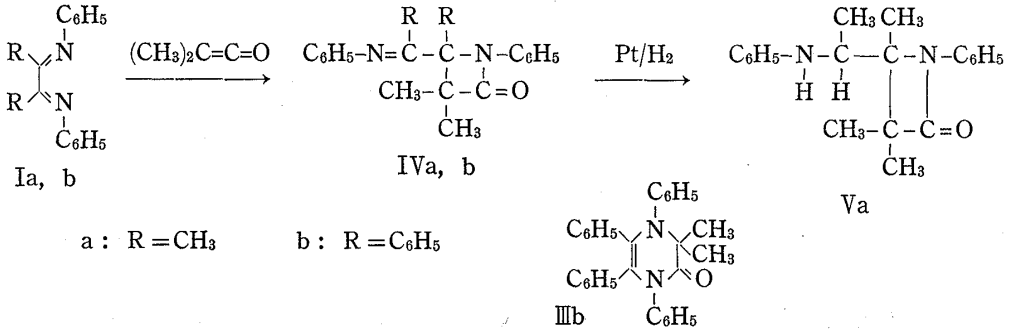

Chart 2

Further proof for the structure IVa was obtained by the fact that the catalytic hydrogenation of IVa with platinum oxide in acetic acid afforded 4-(1-anilinoethyl)-3,3,4-trimethyl-1-phenyl-2-azetidinone (Va). In the IR spectrum of Va, the absorption (1657 cm^{-1}) due to imine ($-\overset{|}{\mathrm{C}}=\mathrm{N}-$) stretching band in IVa disappeared and sharp absorptions at 3348 and 1722 cm^{-1} appeared due to a secondary amino and a lactam carbonyl groups, respectively. In addition, the NMR spectrum (ppm in $CDCl_3$) of Va showed the following signals, 1.21 (doublet, $J=7.0$ Hz, $\mathrm{C\underline{H}_3{-}\underset{|}{\overset{|}{C}}{-}H}$), 1.39, 1.48, 1.77 (each singlet, $CH_3 \times 3$), 3.44 (broad, NH), and 4.07 (quartet, $J=7.0$ Hz, $\mathrm{CH_3{-}\underset{|}{\overset{|}{C}}{-}\underline{H}}$). These results indicate that this adduct has the structure of 2-azetidinone (IVa) rather than the six-membered heterocyclic structure (IIIa) proposed by Burpitt, *et al.*[5]

Furthermore, the adduct obtained from the reaction of dimethylketene with N,N'-(diphenylethanediylidene)dianiline (Ib) was also not a pyrazine derivative (IIIb), as proposed by Burpitt, *et al.*,[5] but 4-anilidenebenzyl-3,3-dimethyl-1,4-diphenyl-2-azetidinone (IVb). The structure of IVb was supported by the following data. The mass spectrum of IVb exhibits the molecular ion (*m/e*, 430), two strong bands at 1760 and 1641 cm^{-1} in its IR spectrum indicates the presence of a carbonyl in four-membered ring lactam[6] and an imine ($-\overset{|}{\mathrm{C}}=\mathrm{N}-$)[7]

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[6] H. Bestian, H. Biener, K. Clauss, and H. Heyn, *Ann. Chem.*, **718**, 94 (1968); C.W. Bird, *J. Chem. Soc.*, **1965**, *3016*; R, Huisgen, B.A.Davis, and M. Morikawa, *Angew. Chem. Intern. Ed. Engl.*, **7**, 826 (1968).

[7] L.J. Bellamy, "Advances in Infrared Group Frequencies," Methuen & CO. Ltd., 1968, pp. 49—52.

group, respectively. The adduct (IVb) did not undergo catalytic hydrogenation by steric hindrance of phenyl groups under similar conditions to those employed for IVa.

Further work on the reactions of ketene with conjugated C=N compounds is in progress.

Experimental[8]

4-(1-Anilideneethyl)-3,3,4-trimethyl-1-phenyl-2-azetidinone (IVa)——To a solution of isobutyryl chloride (25 g) in dry benzene (150 ml), dry Et_3N (25 g) in dry benzene (100 ml) was added dropwise with stirring in N_2 atmosphere. The mixture was heated in a water bath (bath temperature 60—65°) for 6 hr and then filtered to remove $Et_3N \cdot HCl$. The reaction mixture was distilled to give dimethylketene–benzene solution (150 ml). To this solution, N,N′-(dimethylethanediylidene)dianiline (3 g) in dry benzene (40 ml) was added and the mixture was stirred at room temperature for 10 hr. After allowing the mixture to stand overnight at room temperature, benzene was evaporated *in vacuo*, and residual crystals were recrystallized from cyclohexane to give 3.32 g (86%) of IVa as colorless crystals, mp 160—161° (lit.[5] mp 160—161°). *Anal.* Calcd. for $C_{20}H_{22}ON_2$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.49; H, 7.35; N, 9.19. Mass Spectrum *m/e*: 306 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1736, 1657. NMR (in $CDCl_3$) δ: 1.40 (3H, s), 1.45 (3H, s), 1.89 (6H, s), 6.60—7.47 (10H, m).

4-Anilidenebenzyl-3,3-dimethyl-1,4-diphenyl-2-azetidinone (IVb)——In the same way as above, a mixture of dimethylketene–benzene solution (173 ml) obtained from isobutyryl chloride (25 g) and N,N′-(diphenylethanediylidene)dianiline (2 g) in dry benzene (40 ml) was stirred at room temperature for 10 hr. After allowing the mixture to stand overnight at room temperature, benzene was evaporated *in vacuo.* The residue was taken up in hot cyclohexane (*ca.* 150 ml), insoluble material was filtered off, and the filtrate was evaporated to dryness *in vacuo.* The residue was recrystallized from acetonitrile to give IVb (2.07 g, 87%) as colorless crystals, mp 198—199° (lit.[5] mp 198—199°). *Anal.* Calcd. for $C_{30}H_{26}ON_2$: C, 83.69; H, 6.09; N, 6.51. Found: C, 83.78; H, 6.20; N, 6.60. Mass Spectrum *m/e*: 430 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1760, 1641. NMR (in $CDCl_3$) δ: 0.96 (3H, s), 1.80 (3H, s), 6.48—7.46 (20H, m).

4-(1-Anilinoethyl)-3,3,4-trimethyl-1-phenyl-2-azetidinone (Va)——To a solution of 1 g of IVa dissolved in 42 ml of glacial AcOH was added. 1 g of PtO_2 and the mixture was catalytically hydrogenated under ordinary hydrogen pressure at room temperature (15°). After uptake of one equiv. of hydrogen (*ca.* 1.5 hr), the catalyst was removed by filtration and the filtrate was evaporated *in vacuo.* The residue was dissolved in ethyl acetate, washed with 10% Na_2CO_3 and then with water, and dried over Na_2SO_4. The solvent was evaporated and the resulting solid was recrystallized from EtOH to give Va (0.55 g, 55%) as colorless needles of mp 168—169°. *Anal.* Calcd. for $C_{20}H_{24}ON_2$: C, 77.88; H, 7.84; N, 9.08. Found: C, 77.83; H, 7.89; N, 9.00. Mass Spectrum *m/e*: 308 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3348, 1722. NMR (in $CDCl_3$) δ: 1.21 (3H, d, $J=7.0$ Hz), 1.39 (3H, s), 1.48 (3H, s), 1.77 (3H, s), 3.44 (1H, broad), 4.07 (1H, q, $J=7.0$ Hz), 6.53—7.42 (10H, m). The signal of δ 3.44 is disappeared upon addition of D_2O.

Acknowledgement The authors are indebted to the staff of the Central Analysis room of this College for the NMR and mass spectral measurements and for elemental analysis.

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[8] All melting points were measured in a Yanagimoto mp apparatus and are uncorrected. NMR spectra were measured with a Japan Electron Optics Co., Model PS-100 (100 Mc) spectrometer with tetramethylsilane as internal reference. Mass spectra were taken on a Japan Electron Optics Co., JMS-OISG-2 spectrometer. IR spectra were measured on a Nihon Bunko Jasco DS-701G spectrometer.