PHOTOISOMERIZATION OF 4-t-BUTYL-2-PYRIDONES AND CHEMICAL PROPERTIES OF THE RESULTING 2-AZABICYCLO[2.2.0]HEX-5-EN-3-ONE AND THE HEXAN-3-ONE SYSTEMS[1]

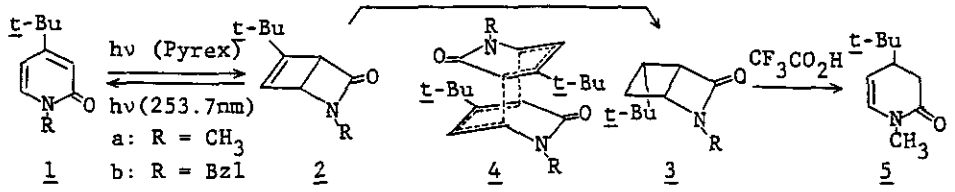
Eisuke Sato, Yoshiya Ikeda, and Yuichi Kanaoka*
Faculty of Pharmaceutical Sciences, Hokkaido University,
Sapporo 060, Japan
Haruo Okajima
School of Hygiene, Kyorin University, Hachioji 192, Japan

Abstract ——— Irradiation of 4-t-butyl-2-pyridones 1a,b gave their valence isomers 2a,b in good yields. Treatment of bicyclic photoproducts 2a and 3a with acid gave the products due to C-C bond cleavage of the 4-membered rings.

During our investigation on the photochemistry of conjugated nitrogen-carbonyl systems, we reexamined photoreactions of 2-pyridones as a standard heterocyclic system with the simplest conjugated cyclic amide structure. It is well known that irradiation of 2-pyridones gives [4+4]dimers and valence isomers in concentration-dependent reaction.[2] The "Dewar benzene" synthesis in 1962 represents an example of potentiality of synthesis of sterically hindered benzene which has a tendency to isomerize.[3] Therefore 2-pyridones, with a t-butyl group as a substituent at the 4-position, seemed to be good substrates for the study of photoisomerization. In this paper we wish to report some photoreactions of 4-t-butyl-2-pyridones and properties of the resulting 2-azabicyclo[2.2.0]hex-5-en-3-one and -hexan-3-one systems.

Irradiation of 2-pyridones 1a,b in acetonitrile (5 mM) through a Pyrex filter with a 500 W high-pressure mercury lamp gave bicyclic photoisomers 2a,b in good yields, and the dimers were not obtained. Even in higher concentrations (100 mM) of 1a, none of the [4+4]dimers of 1a were isolated as shown in Table I and Scheme 1. The cyclic "Dewar pyridone" structures of 2a and 2b were confirmed by spectral data. Thus ir spectra of 2a and 2b showed the presence of β-lactam (1735 cm^{-1}), and the mass spectra gave molecular ion peaks of 165 and 241, respectively, showing them

to be non-dimeric products, and t-butylcyclobutenium ion peak of 108.[2j] The ^{1}H-nmr spectra of 2a and 2b showed the presence of two aliphatic protons and one olefinic proton.



Scheme 1

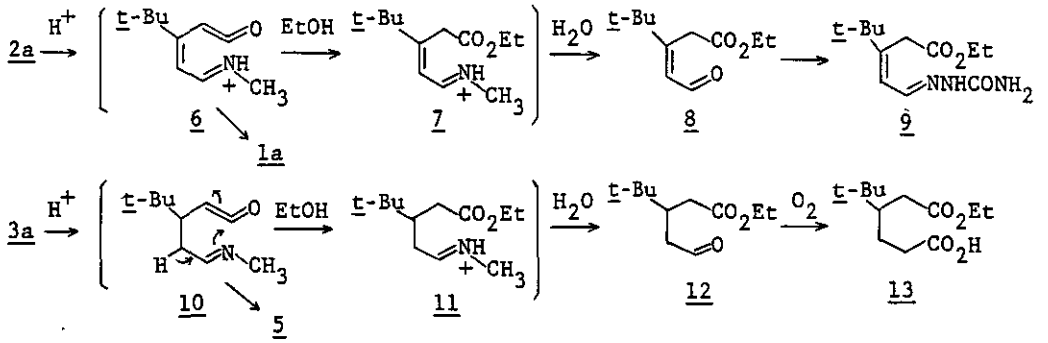
Table 1 Valence Isomerization of 2-Pyridones (1)

1	conc.(mM)	solvent	time(h)	yield(%) of 2	recovered st.mat.(%)
a	5	CH_3CN	2.5	92	-
a	100	CH_3CN	6	72	-
a	5	CH_3OH	3	92	-
a	5	acetone	6	46	43
b	5	CH_3CN	2.5	92	-
b	5	CH_3OH	3	88	-

Photoproducts (2) were hydrogenated over palladium under hydrogen atmosphere at room temperature to give saturated bicyclic cyclobutane derivatives 3a and 3b in 88 and 46 % yields, respectively, for further support of the assigned structure for 2. Obviously steric hindrance caused by interaction between a bulky t-butyl group and an N-substituent suppressed the competing dimer formation (4).

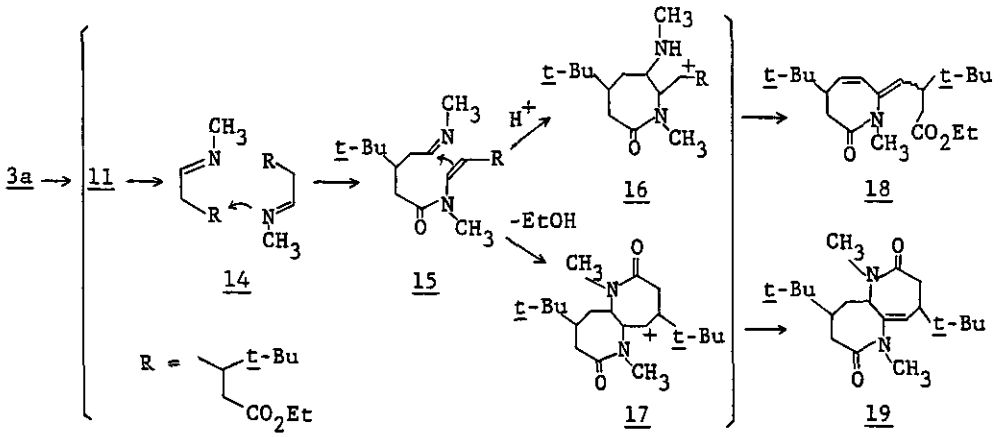
Thermal and photochemical reverse reactions of 2a to 2-pyridone 1a were then examined. Irradiation of 2a with 60 W low-pressure mercury lamp for 2 h gave 1a quantitatively, indicating that the photoisomerization between 1 and 2 is energy-dependent. The Dewar pyridone 2a was heated at 160 °C for 1 h to undergo partial reversion to 1a in 20 % yield with the starting material recovered in 76 %, the result being coincided well with that of Dewar pyridones.[2j] Chemical properties of the bicyclic products 2a and 3a are interesting especially with respect to β-lactam chemistry. For example, it is an interesting problem to see a possibility of selective opening of either the cyclobutane or β-lactam ring. First, acid treatment of 2a and 3a was examined. Photoproduct 2a was allowed to stand in CF_3CO_2H at room temperature for 3 days, and 2-pyridone 1a was regenerated in 95 % yield. This behavior is analogous to an acid-prompted isomerization of pentamethyl Dewar pyridone which was non-photochemically synthesized from alkyne and isocyanate.[4]

Compound 3a was heated in CF_3CO_2H under reflux for 10 h to give a monocyclic lactam 5 in 43 % yield (Scheme 1). Thus both cyclobutene and cyclobutane rings of 2a and 3a are cleaved by treatment with acid, but selective opening or survival of the β-lactam ring is unlikely to be achieved.



Scheme 2

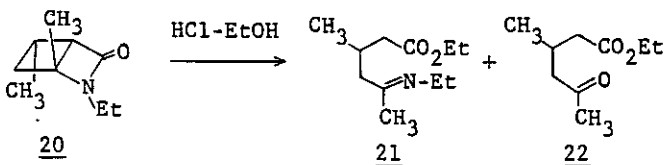
Solvolyses of 2a and 3a were also examined. Photoproduct 2a, allowed to stand overnight in 8.6 N HCl-EtOH at room temperature, gave 8, identified as the semicarbazone 9. A similar reaction of 3a gave 12 in a low yield (Scheme 2). Thus acid-catalyzed ethanolysis of 2a and 3a also results in simultaneous cleavage of the β-lactam bonds and cyclobutene or cyclobutane ring, plausible pathways being suggested. Compound 13 presumably arises by air oxidation of 12. When a similar reaction of 3a was carried out under reflux, unexpected seven-membered products 18 and 19 were isolated (Scheme 3). Ir spectrum of 18 showed the presence of an ester and an amide (1720, 1660 cm^{-1}), and the mass spectrum showed molecular ion peak of 349 indicative of a dimeric composition. The ^{1}H-nmr spectrum of 18 showed



Scheme 3

the presence of two t-butyl groups and one methyl group. The ^{13}C-nmr gave 17 different kinds of signals supporting the structure of 18. Ir spectrum of 19 showed the presence of amide and enamide carbonyl (1670, 1640 cm^{-1}), and the mass spectrum showed molecular ion peak of 334, ascertained its dimeric structure. The ^{1}H-nmr spectrum of 19 showed the presence of two t-butyl groups, two methyl groups and one olefinic proton. The ^{13}C-nmr of 19 showed 16 different kinds of signals suggesting the structure to be 19 (see experimental). Although stereochemistry of 19 is not clear from these spectral data, the conformation of both t-butyl groups of 19 may be quasi-equatorial to the respective lactam ring due to the steric hindrance with the N-methyl groups. The mechanism of the formation of 18 and 19 is tentatively assumed as shown in the pathways in Scheme 3. An imine intermediate 11, possibly generated via a ketene (10), may be bimolecularly condensed to the dimeric products followed by cyclization (Scheme 3).

Though Furrer had reported that compound 20 in 8.76 N HCl-EtOH under reflux for 2 h gave 21 and 22 (Scheme 4), none of such bimolecular condensed products as 18 and 19 were described.[2i] Probably a methyl group in the 5-position of 21 precludes the bimolecular condensation.



20 21 22

Scheme 4

Photoisomerization of 2-pyridones competes with dimerization, but 2-pyridones with a bulky substituent such as t-butyl, which suppresses bimolecular reaction, prefer valence isomerization to dimerization. These Dewar-pyridone compounds 2a and 3a undergo, by treatment with acid, ring opening of cyclobutene and cyclobutane simultaneously with a β-lactam-bond cleavage. Treatment of 3a with acidic ethanol solution gave new type of dimeric products by way of bimolecular reaction of complex intermediates.

EXPERIMENTAL

Melting points are uncorrected. Vacuum distillation was carried out by using a Büchi Kugelrohr apparatus and boiling points are uncorrected. Nmr spectra were taken on a JEOL JNM-FX 100 FT-nmr spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a Model JMS-D 300 mass spectro-

meter. Infrared spectra were recorded with JASCO IRA-1 infrared spectrometer. Preparative layer chromatography was carried out on silica gel (Kieselgel 60 PF_{254}, Merck, 20 x 20 cm). The light sources were a Type EHBW-1 (Eiko-sha) 500 W high-pressure or a Type PLI-60 (Eiko-sha) 60 W low-pressure mercury lamp.

4-t-Butyl-1-methyl-2-pyridone (1a)

After dropwise addition of Me_2SO_4 (22.6 g, 0.18 mol) to 4-t-butylpyridine (23 g, 0.17 mol), the mixture was heated in a boiling water-bath for 2 h. The separated salt was dissolved in 37 ml of water, and cooled to 0 °C in an ice-bath. Solutions of $K_3Fe(CN)_6$ (112 g, 0.34 mol) in 220 ml of water and of NaOH (27.9 g, 0.7 mol) in 50 ml of water were dropwise added from two separatory funnels to the well-stirred solution of the pyridinium salt at such a rate that the temperature was kept below 10 °C. The product was salted out by addition of anhyd. Na_2CO_3 (50 g) to the well-stirred solution. After filtration of precipitates, the filtrate was extracted with isoamyl alcohol, which was dried over anhyd. Na_2SO_4. Solvent was evaporated to leave an oil, which was distilled *in vacuo* to give 15.1 g (58 %) of colorless oil, bp 116-118 °C/3.0 mmHg. Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.64; H, 9.13; N, 8.45. IR (neat): 1655, 1580 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 1.24 (9H, s), 3.53 (3H, s), 6.26 (1H, dd, J=7.2, 2.0 Hz), 6.63 (1H, d, J=2.0 Hz), 7.23 (1H, d, J=7.2 Hz). MS (m/z): 165 (M^+, base), 150.

1-Benzyl-4-t-butyl-2-pyridone (1b)

A mixture of 4-t-butylpyridine (9.45 g, 70 mmol) and benzyl chloride (17.7 g, 140 mmol) in 30 ml of DMF was heated at 150 °C for 2 h. The mixture was diluted with 150 ml of water, and then extracted with benzene to remove an excess benzyl chloride. The ice-cooled aq. solution was worked up as described for 1a with 69 g (0.21 mol) of $K_3Fe(CN)_6$ in 300 ml of water and 40 g (0.7 mol) of NaOH in 80 ml of water. Aq.layer was extracted with $CHCl_3$, which was dried over anhyd. Na_2SO_4. After removal of solvent *in vacuo*, the residue was distilled *in vacuo* to give 6.4 g (43 %) of colorless solid, bp 200 °C (bath temp.)/0.4 mmHg, mp 65-70 °C. Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.49; H, 7.93; N, 5.86. IR (Nujol): 1660, 1600, 1590 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 1.23 (9H, s), 5.13 (2H, s), 6.18 (1H, dd, J=7.0, 2.0 Hz), 6.72 (1H, d, J=2.0 Hz), 7.16 (1H, d, J=7.0 Hz), 7.32 (5H, s). MS (m/z): 241 (M^+), 91 (base).

General Procedure of Photoreaction —— A solution of 1 (2.5 mmol) in 500 ml of CH_3CN was irradiated under N_2 atmosphere with 500 W high-pressure mercury lamp through a Pyrex filter. After irradiation, solvent was removed *in vacuo*. The residue was distilled *in vacuo* or recrystallized.

5-t-Butyl-2-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (2a)

From 413 mg (2.5 mmol) of 1a. Irradiated for 2.5 h. Distilled *in vacuo*, 380 mg (92 %) of colorless oil, bp 105 °C (bath temp.)/0.5 mmHg. Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.58; H, 9.20; N, 8.34. IR (neat): 1735, 1610 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 1.09 (9H, s), 2.78 (3H, s), 4.09 (2H, s), 6.15 (1H, s). MS (m/z): 165 (M^+), 150, 108, 93 (base).

2-Benzyl-5-t-butyl-2-azabicyclo[2.2.0]hex-5-en-3-one (2b)

From 603 mg (2.5 mmol) of 1b. Irradiated for 2.5 h. Distilled *in vacuo*, 553 mg (92 %) of colorless oil, bp 150 °C/0.5 mmHg. Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.93; N, 5.80. Found: C, 79.59; H, 8.10; N, 6.03. IR (neat): 1735, 1610 cm^{-1}. ^{1}H-

nmr ($CDCl_3$): δ 1.04 (9H, s), 4.00 (1H, d, J=2.2 Hz), 4.11 (1H, dd, J=2.2, 1.2 Hz), 4.32 (2H, s), 5.66 (1H, d, J=1.2 Hz), 7.1-7.5 (5H, m). MS (m/z): 241 (M^+), 199, 108, 93 (base).

5-t-Butyl-2-methyl-2-azabicyclo[2.2.0]hexan-3-one (3a)

A solution of 2a (970 mg, 5.9 mmol) in 30 ml EtOH was hydrogenated under H_2 atmosphere over 180 mg of 10 % Pd-carbon for 4 h. After filtration of Pd-carbon, solvent was removed in vacuo. The residue was distilled in vacuo to give 863 mg (88 %) of colorless oil, bp 105 °C (bath temp.)/0.5 mmHg. Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.63; H, 10.41; N, 8.56. IR (neat): 1730 cm^{-1}. ^1H-nmr ($CDCl_3$): δ 0.91 (9H, s), 1.82 (1H, ddd, J=13, 8.1, 1.7 Hz), 2.14 (1H, ddd, J=13, 10, 4.0 Hz), 2.57 (1H, ddd, J=10, 9.0, 8.1 Hz), 2.82 (3H, s), 3.52 (1H, dd, J=9.0, 2.9 Hz), 3.78 (1H, ddd, J=4.0, 2.9, 1.7 Hz). MS (m/z): 167 (M^+), 152, 110 (base).

5-t-Butyl-2-benzyl-2-azabicyclo[2.2.0]hexan-3-one (3b)

A solution of 2b (550 mg, 2.3 mmol) in 30 ml of MeOH was hydrogenated under H_2 atmosphere over 100 mg of 10 % Pd-carbon overnight. An oily residue was chromatographed on silica gel layer (20 x 20 cm) using CH_2Cl_2 as an eluent. Recrystallization from n-hexane gave 252 mg (46 %) of colorless needles, mp 78.5-79.5 °C. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.01; H, 8.73; N, 5.75. IR (Nujol): 1720 cm^{-1}. ^1H-nmr ($CDCl_3$): δ 0.91 (9H, s), 1.72 (1H, ddd, J=13, 8.0, 1.7 Hz), 2.06 (1H, ddd, J=13, 10, 4.0 Hz), 2.50 (1H, ddd, J=10, 9.0, 8.0 Hz), 3.49 (1H, dd, J=9.0, 3.0 Hz), 3.73 (1H, ddd, J=4.0, 3.0, 1.7 Hz), 4.18 (1H, d, J=14.9 Hz), 4.63 (1H, d, J=14.9 Hz), 7.2-7.4 (5H, m). MS (m/z): 243 (M^+), 186 91 (base).

Photochemical and Thermal Reverse Reaction of Dewar Pyridone (2a)

a) Photochemical reaction: A solution of 2a (165 mg, 1.0 mmol) in 200 ml of n-hexane was irradiated under N_2 atmosphere with 60 W low-pressure mercury lamp for 2 h. After the removal of solvent, the residue was distilled in vacuo. 153 mg (93 %) of 1a was obtained.

b) Thermal reaction: 165 mg (1.0 mmol) of 2a was heated in an oil bath at 160 °C for 1 h, and the residue was chromatographed on silica gel layer (20 x 20 cm) using AcOEt as an eluent to give 33 mg (20 %) of 1a with 125 mg (76 %) of recovered 2a.

Chemical Properties of 2a and 3a

a) Trifluoroacetic acid treatment; i) Reverse reaction of 2a to 1a: 223 mg (1.35 mmol) of 2a in 0.2 ml of CF_3CO_2H was stood for 3 d. After evaporation of TFA in vacuo, the residue was dissolved into acetone and neutralized with anhyd. Na_2CO_3. Precipitate was filtered off, the filtrate was condensed and distilled in vacuo to give 211 mg (95 %) of 1a. ii) Transformation of 3a to 1-methyl-4-t-butyl-1,2,3,4-tetrahydropyridin-2-one (5): 268 mg (1.62 mmol) of 3a in 0.3 ml of CF_3CO_2H was heated at 70 °C for 10 h. After evaporation in vacuo, the residue was chromatographed on silica gel layer (20 x 20 cm) using CH_2Cl_2-AcOEt (1:1) as an eluent to give 5, which was distilled in vacuo. 116 mg (43 %) of colorless oil, bp 80 °C (bath temp.)/0.3 mmHg. Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.60; H, 10.15; N, 8.38. IR (neat): 1660 cm^{-1}. ^1H-nmr ($CDCl_3$): δ 0.89 (9H, s), 2.1-2.6 (3H, m), 3.02 (3H, s), 5.08 (1H, dd, J=8.0, 3.7 Hz), 6.03 (1H, dd, J=8.0, 1.5 Hz). MS (m/z): 167 (M^+), 110 (base).

b) Acid-catalyzed solvolyses of 2a and 3a; i) 2a at room temperature to ethyl 3-t-butyl-5-oxo-3-pentenoate (8): A solution of 2a (292 mg, 1.77 mmol) in 0.3 ml of 8.6 N HCl-EtOH was kept at room temperature overnight. After removal of solvent, saturated aq. solution of Na_2CO_3 was added to the residue. The aq. layer was extracted with Et_2O, which was dried over anhyd. Na_2SO_4. After removal of solvent, the residue was chromatographed on silica gel layer (20 x 20 cm) using CH_2Cl_2 as an eluent to give 8. Distillation in vacuo gave 97 mg (28 %) of pale yellow oil, bp 90 °C (bath temp.)/0.7 mmHg. IR (neat): 1730, 1675 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 1.14 (9H, s), 1.26 (3H, t, J=6.0 Hz), 3.60 (2H, s), 4.18 (2H, q, J=6.0 Hz), 6.13 (1H, d, J=7.0 Hz), 9.91 (1H, d, J=7.0 Hz). Semicarbazone (9): colorless fine needles from CH_3CN, mp 154-155.5 °C. Anal. Calcd for $C_{12}H_{21}N_3O_3$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.58; H, 8.30; N, 16.65. IR (Nujol): 3420, 3310, 1730, 1690, 1670 cm^{-1}. ^{1}H-nmr (DMSO-d_6): δ 1.02 (9H, s), 1.16 (3H, t, J=6.0 Hz), 3.26 (2H, s), 4.05 (2H, q, J=6.0 Hz), 6.06 (1H, d, J=9.0 Hz), 6.1-6.3 (2H, broad), 6.67 (1H, d, J=9.0 Hz), 9.8-10.0 (1H, broad). MS (m/z): 255 (M^+), 196, 193, 192, 181, 166 (base). ii) 3a at room temperature to 3-t-butyl-glutaric acid monoethyl ester (13): A solution of 3a (1.3 g, 7.8 mmol) in 1.3 ml of 8.6 N HCl-EtOH was worked up as described for 2a to give 12 (IR: 1725, 1705 cm^{-1}), which was auto-oxidized to 13. Distillation in vacuo gave 221 mg (13 %) of colorless oil, bp 180 °C (bath temp.)/0.4 mmHg. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.29; H, 9.12. IR (neat): 3100, 1720, 1700 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 0.91 (9H, s), 1.25 (3H, t, J=6.0 Hz), 2.0-2.8 (7H, m), 4.12 (2H, q, J=6.0 Hz). iii) 3a at higher temperature: A solution of 3a (1.28 g, 7.67 mmol) in 1.3 ml of 8.6 N HCl-EtOH was heated to reflux for 3 h, then worked up as described for 2a to give 13 (136 mg, 9 %), 18 (253 mg, 19 %), and 19 (75 mg, 6 %). 1-Methyl-4-t-butyl-7-(2-t-butyl-3-ethoxycarbonyl)propyliden-1H,6H-2,3,4,7-tetrahydroazepin-2-one (18): colorless needles from n-hexane, mp 103-105.5 °C. Anal. Calcd for $C_{21}H_{35}NO_3$: C, 72.16; H, 10.09; N, 4.01. Found: C, 72.30; H, 10.05; N, 4.02. IR (Nujol): 1720, 1660 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 0.89 (9H, s), 0.90 (9H, s), 1.19 (3H, t, J=6.0 Hz), 2.1-2.8 (6H, m), 2.99 (3H, s), 4.06 (2H, q, J=6.0 Hz), 5.34 (1H, dd, J=16.3, 8.0 Hz), 5.99 (1H, d, J=16.3 Hz), 6.09 (1H, s). ^{13}C-nmr ($CDCl_3$): δ 14.42, 27.68, 28.26, 33.11, 33.40, 33.84, 34.92, 36.15, 41.05, 51.22, 60.09, 120.36, 127.37, 130.49, 131.66, 170.46, 173.21. MS (m/z): 349 (M^+), 292 (base). 5,11-Di-t-butyl-2,8-dimethyl-2,8-diazabicyclo[5.5.0]dodeca-6-en-3,9-dione (19): colorless needles from acetone-n-hexane, mp 202.5-203.5 °C. Anal. Calcd for $C_{20}H_{34}N_2O_2$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.78; H, 10.37; N, 8.24. IR (Nujol): 1670, 1640 cm^{-1}. ^{1}H-nmr ($CDCl_3$): δ 0.86 (9H, s), 0.96 (9H, s), 1.4-2.8 (8H, m), 2.99 (3H, s), 3.01 (3H, s), 4.16 (1H, s), 5.75 (1H, s). ^{13}C-nmr ($CDCl_3$): δ 26.78, 28.06, 28.26, 31.56, 33.32, 33.93, 34.02, 34.40, 35.30, 37.20, 43.16, 61.38, 119.13, 128.19, 169.88, 171.31. MS (m/z): 334 (M^+), 277 (base), 220.

REFERENCES AND NOTES

1) a) Photochemistry of conjugated nitrogen-carbonyl systems. 4. Part 3: E. Sato, Y. Ikeda and Y. Kanaoka, Chem. Pharm. Bull., 1987, 35, 507; b) Photoinduced

Reactions. 95. Part 94: K. Oda, M. Machida, K. Aoe, Y. Sato and Y. Kanaoka, Chem. Pharm. Bull., 1986, 34, 4414.

2) a) E. C. Taylor and W. W. Paudler, Tetrahedron Lett., 1960, 1; b) W. A. Ayer, R. Hayatsu, P. de Mayo, S. T. Reid and J. B. Sthorthers, ibid., 1961, 648; c) G. Slomp, F. A. MacKellar and L. A. Paquette, J. Am. Chem. Soc., 1961, 83, 4472; d) E. C. Taylor, R. O. Kan and W. W. Paudler, ibid., 1961, 83, 4484; e) L. A. Paquette and G. Slomp, ibid., 1963, 85, 765; f) E. C. Taylor and R. O. Kan, ibid. 1963, 85, 776; g) E. J. Corey and J. Streith, ibid., 1964, 86, 950; h) A. I. Meyers and P. Singh, J. Org. Chem., 1970, 35, 3022; i) H. Furrer, Chem. Ber., 1972, 105, 2780; j) R. C. De Selms and W. R. Schleith, Tetrahedron Lett., 1972, 3563; k) W. L. Dilling, N. B. Terfertiller and A. B. Mitchel, Mol. Photochem., 1973, 5, 371; l) E. Ager, G. E. Chivers and H. Suschitzky, J. Chem. Soc., Perkin Trans. 1., 1973, 1125; m) C. Kaneko, K. Shiba, H. Fujii and Y. Momose, J. Chem. Soc., Chem. Commun., 1980, 1177.

3) E. E. van Tamelen and S. P. Pappas, J. Am. Chem. Soc., 1962, 84, 3789.

4) H. Hogeveen and D. M. Kok, J. Org. Chem., 1982, 47, 997.

Received, 12th February, 1987