HETEROCYCLES, Vol. 4, No. 5, 1976

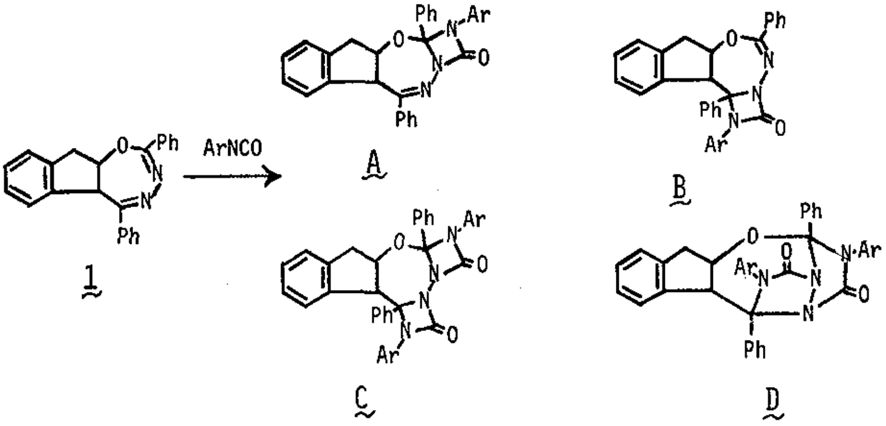
REACTIONS OF DIHYDROINDENO-1,3,4-OXADIAZEPINE DERIVATIVE WITH ARYL ISOCYANATES AND DIMETHYL ACETYLENEDICARBOXYLATE

Koji Oe and Otohiko Tsuge*
Research Institute of Industrial Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812, Japan

The reaction of dihydroindeno[3,2-f]-1,3,4-oxadiazepine derivative **1** with excess of phenyl (**2a**) and p-tolyl isocyanate (**2b**) afforded novel 1:1 adducts, tetrahydroindeno[2,3-e]-3H-1,3,4-triazepin-2-ones **3a** and **3b**, in good yields respectively. Similarly, **1** reacted with dimethyl acetylenedicarboxylate to yield dihydroindeno[3,2-d]-2,3-diazepine compound **6**. The reaction pathways for the formation of **3** and **6** are also proposed.

It is known that isocyanates react with anils to afford 1,3-diazetidinones (1:1 cycloadducts)[1] or 1,3,5-triazinediones (2:1 cycloadducts).[1,2] On the other hand, azines having the conjugated system C=N-N=C exhibits a curious behavior toward cycloaddition reactions. Benzaldazines react with cyanic acid,[3] thiocyanic acid,[3,4] phenyl[4] and benzoyl isocyanates,[5] methyl acrylate,[6] and maleic anhydride[7,8] to yield the corresponding criss-cross adducts (1:2 cycloadducts), while the reaction of benzaldazines with thiobenzoyl isocyanate give the mono- or bis-Diels-Alder type adducts of the isocyanate as a diene to the C=N bonds of azines.[5]

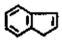
Recently, we have found that the photochemical reaction of 2,5-diphenyl-1,3,4-oxadiazole with indene in ethyl ether afforded a novel seven-membered cyclic compound, cis-2,5-diphenyl-5a,10a-dihydroindeno[3,2-f]-1,3,4-oxadiazepine (**1**), in moderate yield.[9] The compound **1** contains the conjugated C=N-N=C bond (azine structure) in its ring system. Accordingly, in the reaction of aryl isocyanate with **1**, we might expect the formation of mono [2+2] cycloadducts **A**, **B**, or bis [2+2] cycloadduct **C**, besides a criss-cross adduct **D**.



This paper deals with the reaction of oxadiazepine **1** with aryl isocyanate which led to the formation of a triazepine compound. In this context, the reaction of **1** with dimethyl acetylenedicarboxylate is also described.

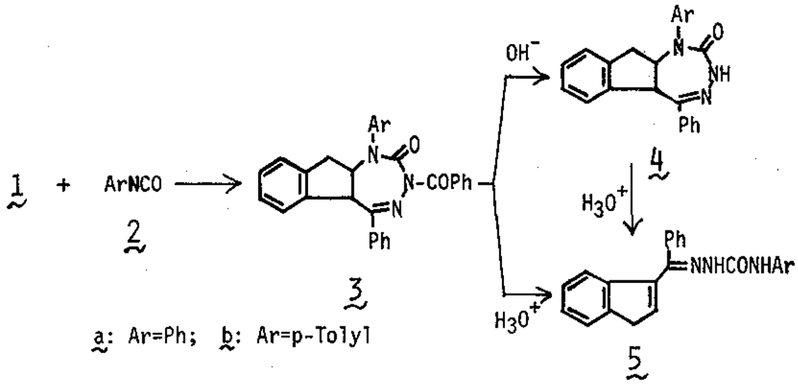
When oxadiazepine **1** was heated with excess of phenyl isocyanate (**2a**) and p-tolyl isocyanate (**2b**) without solvent at 80-90° for 10 min, the corresponding 1:1 adducts **3a** and **3b** were obtained in 98 and 90% yields respectively.[10] The ir spectra of **3a** and **3b** showed no bands ascribable to ν_{NH}; this indicates that both **3a** and **3b** are cycloadducts.

3a: colorless prisms; mp 208-209°; ir (KBr) 1745, 1680 cm^{-1} (CO); nmr ($CDCl_3$) δ 3.3-4.0 (2H, m, $C\underline{H}_2$), 4.65-4.85 (2H, m, 2 x $>C\underline{H}$), 6.8-7.8 (19H, m, aromatic protons); mass m/e 457 (M^+), 342 (M^+ - ), 341, 237 (342^+ - PhCO), 222 (341^+ - PhNCO), 180 ($PhC\equiv\overset{+}{N}Ph$), 119 ($PhNCO^+$), 116 ($^+$), 115, 105, 77.

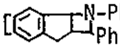
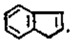
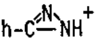
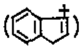
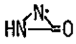
3b: colorless prisms; mp 217-218°; ir (KBr) 1750, 1675 cm^{-1} (CO); nmr ($CDCl_3$) δ 2.33 (3H, s, $C\underline{H}_3$), 3.0-4.0 (2H, m, $C\underline{H}_2$), 4.6-4.8 (2H, m, 2 x $>C\underline{H}$), 6.5-7.8 (18H, m, aromatic protons); mass m/e 471 (M^+), 366 (M^+ - PhCO), 356 (M^+ - ), 355, 251 (356^+ - PhCO), 223 (356^+ - tolyl-NCO), 194 ($PhC\equiv\overset{+}{N}$-tolyl), 133 (tolyl-NCO^+), 116, 115, 105, 91, 77.

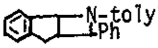
The corresponding [2+2] cycloadducts A or B (Ar=Ph or p-tolyl) seemed to be excluded from the potential structures for 3a and 3b, because it would not be reasonable to assign the absorption bands at 1680 and 1675 cm^{-1} in 3a and 3b to the C=N bonds in A and B. On the basis of chemical conversions, 3a and 3b were assigned 3-benzoyl-1,5-diphenyl- and 3-benzoyl-5-phenyl-1-p-tolyl-1,2,5a,10a-tetrahydroindeno[2,3-e]-3H-1,3,4-triazepin-2-one respectively.

When 3a was treated with methanolic potassium hydroxide under reflux for 5 min, and then at room temperature for 2 hr, 4a and benzoic acid were obtained



a: Ar=Ph; b: Ar=p-Tolyl

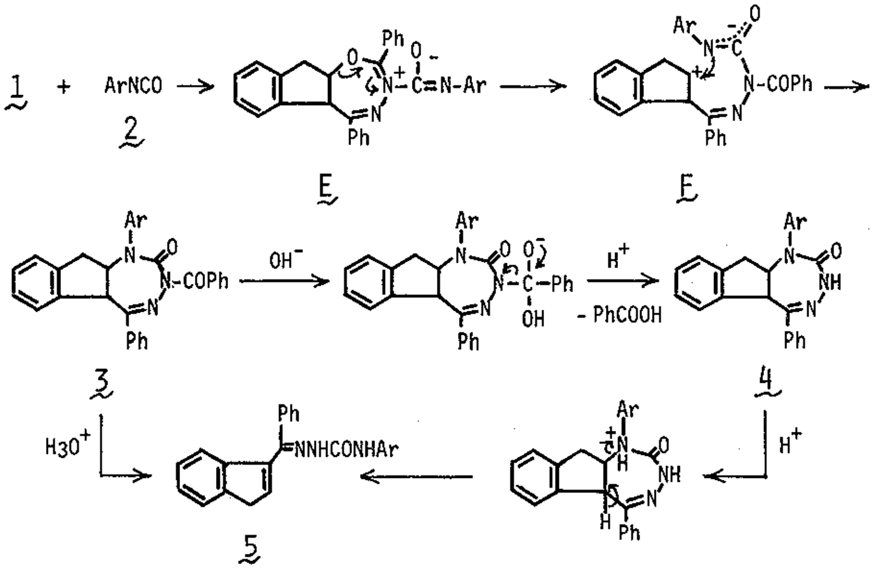
in 97 and 56% yields respectively. The molecular formula of 4a [mp 190-192^{0} dec] agreed with that of a compound formed by hydrolytic cleavage of benzoyl group from 3a. 4a: ir (KBr) 3200 (NH), 1700 cm^{-1} (CO); nmr (pyridine-d_5) δ 3.1-3.7 (2H, m, C$\underline{H_2}$), 4.7-5.0 (2H, m, 2 x ≥C$\underline{H}$), 7.0-7.8 (14H, m, aromatic protons), 10.05 (1H, br, N$\underline{H}$); mass m/e 353 (M^{+}), 295 ([]$^{+}$), 237 (M^{+} - ), 218 (295^{+} - Ph), 202 (295^{+} - PhNH$_2$), 180 (PhC≡$\overset{+}{N}$Ph), 118 (Ph-), 116 (), 115, 105 (PhCH=NH^{+}), 94, 77. Treatment of 4a with methanolic hydrochloric acid under reflux for several minutes afforded 3-benzoylindene 4-phenylsemicarbazone (5a), mp 192-193^{0}, as colorless prisms in 80% yield. 5a: ir (KBr) 3280, 3220 (NH), 1650 cm^{-1} (CO); nmr (CDCl$_3$) δ 2.82, 3.55 (each 1H, dd, C$\underline{H_2}$), 4.62 (1H, dd, =C$\underline{H}$, J=3 and 9 Hz), 6.65, 7.6 (each 1H, br, N$\underline{H}$), 6.1-7.4 (14H, m, aromatic protons); mass m/e 353 (M^{+}), 309 (M^{+} - CONH$_2$), 296 (M^{+} - ), 295, 234 (M^{+} - PhNCO), 233, 219 (234^{+} - NH), 218, 204 (M^{+} - PhNHCONNH), 180, 119 (PhNCO^{+}), 115, 104, 93, 77. On the basis of the spectral data of 4a and of the formation of 5a, it is apparent that 4a is 1,5-diphenyl-1,2,5a,10a-tetrahydroindeno[2,3-e]-3H-1,3,4-triazepin-2-one.[11]

Similarly, treatment of 3b with methanolic potassium hydroxide afforded an 80% yield of 1-p-tolyl-5-phenyl-1,2,5a,10a-tetrahydroindeno[2,3-e]-3H-1,3,4-triazepin-2-one (4b) as colorless plates, which on further treatment with hydrochloric acid was converted into 3-benzoylindene 4-p-tolylsemicarbazone (5b) in 85% yield. 4b: mp 193-194^{0}; ir (KBr) 3220 (NH), 1700 cm^{-1} (CO); nmr (pyridine-d_5) δ 2.25 (3H, s, C$\underline{H_3}$), 3.0-3.6 (2H, m, C$\underline{H_2}$), 4.5-5.0 (2H, m, 2 x ≥C$\underline{H}$), 6.7-7.7 (13H, m, aromatic protons), 9.86 (1H, br, N$\underline{H}$); mass m/e 367 (M^{+}), 309 ([]$^{+}$), 251 (M^{+} - ), 218 (309^{+} - Tolyl), 194 (PhC $\overset{+}{N}$-tolyl), 133, 132, 118, 116, 115, 105, 104, 91, 77. 5b: mp 192-193^{0}; ir (KBr) 3270, 3200 (NH), 1640 cm^{-1} (CO); nmr (CDCl$_3$) δ 2.18 (3H, s, C$\underline{H_3}$), 2.79, 3.54 (each 1H, dd, C$\underline{H_2}$), 4.60 (1H, dd, =C$\underline{H}$, J=3.8 and 8.3 Hz), 6.0-7.7 (15H, m, 2 x N$\underline{H}$ (δ 7.6

and 6.6 which were assigned by exchange with D_2O) and aromatic protons).

Semicarbazones 5a and 5b were directly obtained from the hydrolysis of 3a and 3b with hydrochloric acid in methanol in 71 and 64% yields respectively.

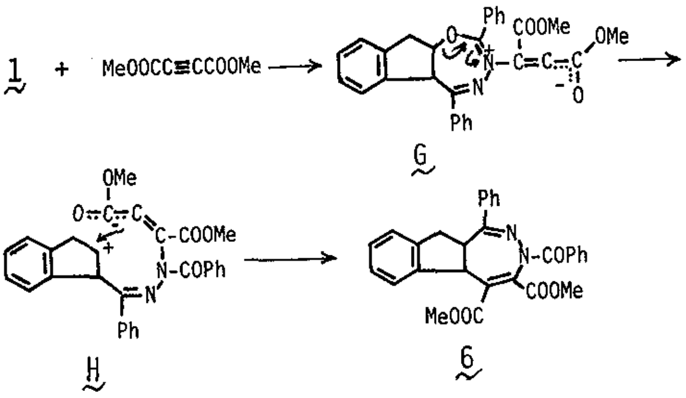
The pathway for the formation of 3 from 1 and 2 is interpreted as depicted in Scheme 1. Isocyanate 2 would react with the N3 atom of 1 to form an dipolar intermediate E. Subsequent recyclization via an intermediate F produced by ring opening of E would give the triazepinone compound 3. The formation of 4 and 5 from 3 can be reasonably understood as depicted in Scheme 1.



Scheme 1

If the reaction of oxadiazepine 1 with isocyanate 2 would proceed through the formation of betaines E and F, we might expect the formation of a diazepine compound from the reaction of 1 with acetylenedicarboxylic acid ester.

When **1** was heated with excess of dimethyl acetylenedicarboxylate at 70-90° for 30 min, the expected 3-benzoyl-4,5-bis(ethoxycarbonyl)-1-phenyl-5a,10b-dihydroindeno[3,2-d]-2,3-diazepine (**6**) was obtained in 63% yield. **6**: colorless prisms; mp 156-157°; ir (KBr) 1755, 1715, 1650 cm^{-1}; nmr (CDCl$_3$) δ 2.4-2.9 (2H, m, C$\underline{H}_2$), 3.83, 3.93 (each 3H, s, C$\underline{H}_3$), 4.5-4.9 (2H, m, 2 x $\geq$C$\underline{H}$), 6.8-8.0 (14H, m, aromatic protons); mass m/e 480 (M$^+$), 449 (M$^+$ - OMe), 421 (449$^+$ - CO), 365 (M$^+$ - ), 255, 229, 116, 115, 105, 89, 77.



The formation of diazepine compound **6** might be interpreted by the pathway *via* betaines **G** and **H** as depicted in the above scheme.

REFERENCES

1 R. Richter, Chem. Ber., 1969, **102**, 938.

2 R. Richter, ibid., 1968, **101**, 3002.

3 J. R. Bailey and N. H. Moore, J. Amer. Chem. Soc., 1917, **39**, 1322.

4 J. R. Bailey and A. T. McPherson, ibid., 1917, **39**, 1322.

5 O. Tsuge and S. Kanemasa, Bull. Chem. Soc. Japan, 1972, **45**, 3591.

6 M. Haring and T. Wagner-Jauregg, Helv. Chim. Acta, 1957, **40**, 852.

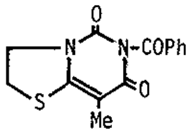
7 T. Wagner-Jauregg, Chem. Ber., 1930, **63**, 3213.

8 J. van Alphen, Rec. Trav. Chim., 1942, **61**, 892.

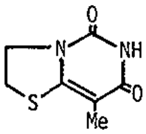
9 K. Oe and O. Tsuge, J. Org. Chem. in submission.

10 All new compounds gave elementary analyses in good accord with the assigned structures.

11 The absorption band ascribable to ν_{CO} in the triazepinone ring of **3a** appeared at 1745 cm^{-1}, while that of **4a** was observed at 1700 cm^{-1}. A similar shift of ν_{CO} was observed in the following pyrimidinedione compounds.[12]



ν_{CO} 1740, 1695, 1645 cm^{-1}



ν_{CO} 1690, 1655 cm^{-1}

12 O. Tsuge and S. Kanemasa, Tetrahedron, 1972, **28**, 4734.

Received, 23rd February, 1976