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

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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 (I), in moderate yield. The compound I contains the conjugated C=N-N=C bond (azine structure) in its ring system. Accordingly, in the reaction of aryl isocyanate with I, 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 I with aryl isocyanate which led to the formation of a triazepine compound. In this context, the reaction of I with dimethyl acetylenedicarboxylate is also described.

When oxadiazepine I 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. The ir spectra of 3a and 3b showed no bands ascribable to ν\textsubscript{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\(_3\)) \(\delta\) 3.3-4.0 (2H, m, CH\(_2\)), 4.65-4.85 (2H, m, 2 x \(\beta\)-CH), 6.8-7.8 (19H, m, aromatic protons); mass m/e 457 (M\(^+\)), 342 (M\(^+\) - \(\text{Ar}^\text{CO}\)), 341, 237 (342\(^+\) - PhCO), 222 (341\(^+\) - PhNCO), 180 (PhC\(=\text{NH}\)), 119 (PhNCO\(^+\)), 116 (Ar\(^\text{Ph}\)), 115, 105, 77.

3b: colorless prisms; mp 217-218°; ir (KBr) 1750, 1675 cm\(^{-1}\) (CO); nmr (CDCl\(_3\)) \(\delta\) 2.33 (3H, s, CH\(_3\)), 3.0-4.0 (2H, m, CH\(_2\)), 4.6-4.8 (2H, m, 2 x \(\beta\)-CH), 6.5-7.8 (18H, m, aromatic protons); mass m/e 471 (M\(^+\)), 366 (M\(^+\) - PhCO), 356 (M\(^+\) - \(\text{Ar}^\text{Ph}\)), 355, 251 (356\(^+\) - PhCO), 223 (356\(^+\) - tolyl-NCO), 194 (PhO\(=\text{N}-\text{tolyl}\)), 133 (tolyl-NCO\(^+\)), 116, 115, 105, 91, 77.

The corresponding [2+2] cycloaducts \(A\) 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.

\[ \begin{align*}
1 + \text{ArNCO} & \rightarrow 2 \\
2 & \rightarrow 3 \\
3: \text{Ar}=\text{Ph}; \ 4: \text{Ar}=\text{p-Tolyl} \\
\end{align*} \]
in 97 and 56% yields respectively. The molecular formula of $\text{A}_4$ [mp 190-192° dec] agreed with that of a compound formed by hydrolytic cleavage of benzoyl group from $\text{A}_3$. $\text{A}_4$: ir (KBr) 3200 (NH), 1700 cm$^{-1}$ (CO); nmr (pyridine-d$_5$) δ 3.1-3.7 (2H, m, CH$_2$), 4.7-5.0 (2H, m, 2 x =CH), 7.0-7.8 (14H, m, aromatic protons), 10.05 (1H, br, NH); mass m/e 353 (M$^+$), 295 ([M+H$^+$]+), 218 (295$^+$ - Ph). 202 (295$^+$ - PhNH$_2$), 180 (PhC=NHPh), 118 (Ph-$^N$-NH$^+$), 116 (CH$_2$), 115, 105 (PhCH=NH$^+$), 94, 77. Treatment of $\text{A}_4$ with methanolic hydrochloric acid under reflux for several minutes afforded 3-benzoylindene 4-phenylsemicarbazone ($\text{A}_{5a}$), mp 192-193°, as colorless prisms in 80% yield. $\text{A}_{5a}$: ir (KBr) 3280, 3220 (NH), 1650 cm$^{-1}$ (CO); nmr (CDC$_3$) δ 2.82, 3.55 (each 1H, dd, CH$_2$), 4.62 (1H, dd, =CH, J=3 and 9 Hz), 6.65, 7.6 (each 1H, br, NH), 6.1-7.4 (14H, m, aromatic protons); mass m/e 353 (M$^+$), 309 (M$^+$ - CONH$_2$), 296 (M$^+$ - HN$^N$-0), 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 $\text{A}_4$ and of the formation of $\text{A}_{5a}$, it is apparent that $\text{A}_4$ is 1,5-diphenyl-1,2,5a,10a-tetrahydroindeno[2,3-e]-3H-1,3,4-triazepin-2-one.$^{11}$

Similarly, treatment of $\text{A}_3$ 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 ($\text{A}_5$) as colorless plates, which on further treatment with hydrochloric acid was converted into 3-benzoylindene 4-p-tolylsemicarbazone ($\text{A}_{5b}$) in 85% yield. $\text{A}_5$: mp 193-194°; ir (KBr) 3220 (NH), 1700 cm$^{-1}$ (CO); nmr (pyridine-d$_5$) δ 2.25 (3H, s, CH$_3$), 3.0-3.6 (2H, m, CH$_2$), 4.5-5.0 (2H, m, 2 x =CH), 6.7-7.7 (13H, m, aromatic protons), 9.86 (1H, br, NH); mass m/e 367 (M$^+$), 309 ([CH$_2$-N$_3$-Ph$^+$]+), 251 (M$^+$ - CH$_2$), 218 (309$^+$ - Tolyl), 194 (PhC=NH-tolyl), 133, 132, 118, 116, 115, 105, 104, 91, 77. $\text{A}_{5b}$: mp 192-193°; ir (KBr) 3270, 3200 (NH), 1640 cm$^{-1}$ (CO); nmr (CDC$_3$) δ 2.18 (3H, s, CH$_3$), 2.79, 3.54 (each 1H, dd, CH$_2$), 4.60 (1H, dd, =CH, J=3.8 and 8.3 Hz), 6.0-7.7 (15H, m, 2 x NH (δ 7.6

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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 a dipolar intermediate E. Subsequent recyclication via an intermediate E 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 E, 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 (CDCl₃) δ 2.4-2.9 (2H, m, CH₂), 3.83, 3.93 (each 3H, s, CH₃), 4.5-4.9 (2H, m, 2 x CH), 6.8-8.0 (14H, m, aromatic protons); mass m/e 480 (M⁺), 449 (M⁺ - OMe), 421 (449⁺ - CO), 365 (M⁺ - Ph), 255, 229, 116, 115, 105, 89, 77.

The formation of diazepine compound 6 might be interpreted by the pathway via betaines 5 and H as depicted in the above scheme.
REFERENCES

10 All new compounds gave elementary analyses in good accord with the assigned structures.
11 The absorption band ascribable to νCO 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 νCO was observed in the following pyrimidinedione compounds. 12

![Chemical Structures]

νCO 1740, 1695, 1645 cm⁻¹  νCO 1690, 1655 cm⁻¹


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