Acta Chemica Scandinavica B 39 (1985) 235–240

1,2,4-Triazin-3(2*H*)-ones in Covalent Adduct Formations

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The π-electron deficient 1,2,4-triazin-3(2*H*)-one system can be compared to carbonyl compounds in many of its reactions. In ethanol or acetone an ethoxy or acetonyl group was added at C(5) in 6-phenyl derivatives. The 5-phenyl isomers were less reactive but could be reduced by lithium tri-*tert*-butoxyaluminium hydride to the 4,5-dihydro derivatives. Dehydrogenation of the acetone adducts by DDQ introduced the new double bond in exocyclic position. The acetonylidene derivatives thus formed are assigned the (*Z*)-configuration from spectroscopy (NMR, IR, Raman).

A π-electron deficient heteromatic system possesses several chemical properties which are comparable to those of the carbonyl group. Thus typical carbonyl reactions such as hemiacetal formation, metal hydride reduction, carbon-carbon bond formation by organometallic reagents and by aldol reactions, have their equivalents in the π-electron deficient heteroaromatic systems. For the pyrimidine ring system, we have reported the equivalence in this context of hemiacetal formation,[1] the aldol reaction,[1,2] and dihydro formation by organometallic reagents.[2] In this report we describe studies of the 1,2,4-triazine system. The latter is more π-electron deficient than the corresponding pyrimidine system because of the additional nitrogen atom in the ring, which increases the polarization in the ring and decreases the aromatic stabilization. Hence the triazines are expected to be highly reactive towards nucleophiles.

1,2,4-Triazin-3(2*H*)-ones were used. The oxo function confers additional polarization on the ring system. In this case adduct forming reactions could also be regarded as 1,4-additions because of the oxo function in the heterocycle. Adduct formation appears to be a general property of π-electron deficient heterocycles, however, irrespective of the presence of an oxo function. Therefore these reactions are best compared with the 1,2-additions of the carbonyl group.

The parent compound, *viz.* 1,2,4-triazin-3(2*H*)-one, is fairly unstable and has been isolated as its covalent water adduct, the carbon-oxygen bond formation being at C(5).[4] Stabilization of the heterocycle is improved in the 5- and 6-phenyl substituted isomers *1* and *2*.

5-Phenyl-1,2,4-triazin-3(2*H*)-one (*1*) is available from 2-oxo-2-phenylethanal and thiosemicarbazide by a series of reaction steps.[5] The 6-phenyl isomer was to be prepared by hydrolytic replacement of the amino group in the 3-amino isomer; the latter was claimed to be formed selectively in the cyclocondensation between 2-oxo-2-phenylethanal and aminoguanidine under controlled pH conditions.[6] We obtained only mixtures of the 5- and 6-phenyl isomers. The 6-phenyl isomer *2*, however, was formed selectively in the reaction

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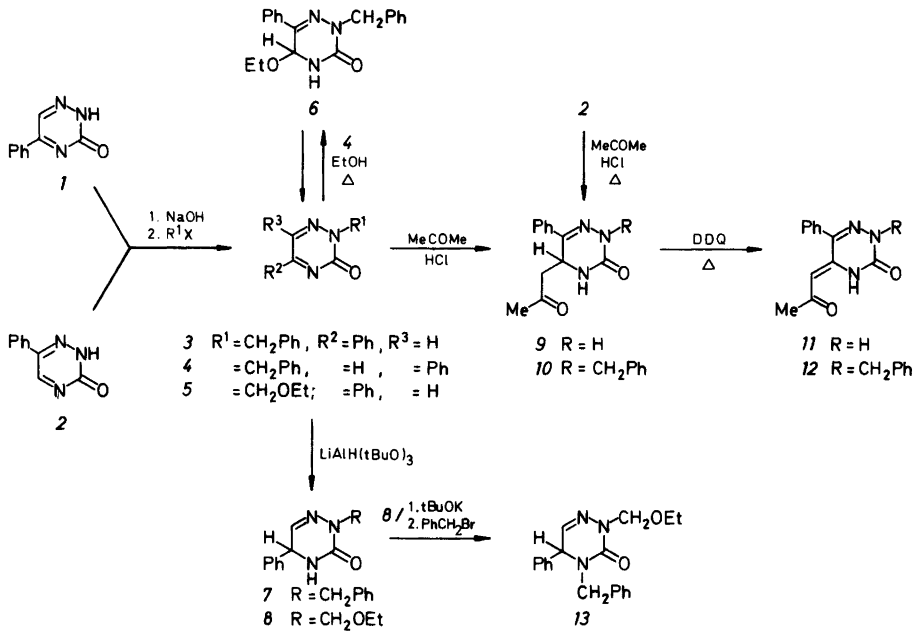

between 2-oxo-2-phenylethanal 1-oxime and semicarbazide.[7] Either isomer was *N*-alkylated by treatment of its sodium salt with benzyl bromide. *O*-Alkylation was not seen. The product is assigned the *N*(2)-alkylated structure (*3,4*) by analogy to related reactions of 1,2,4-triazin-3(2*H*)-ones.[8] Support for this assignment was also sought in a separate series of reactions. The sodium salt of the 5-phenyl isomer *1* was *N*-alkylated by chloromethyl ethyl ether and the product reduced, as discussed below, to a dihydro derivative which was *N*-benzylated to furnish a compound which could be assigned structure *13* in accordance with initial alkylation at *N*(2). The ^{1}H NMR spectrum of *13* showed two different *N*-substituted methylene groups; the protons of the ether methylene group resonate as a singlet whereas the methylene protons of the benzyl group are magnetically non-equivalent (*J* 15 Hz). The spectrum supports location of the benzyl group in close proximity of the chiral center as in structure *13*.

Aldehydes and ketones may form hemiacetals in ethanol. Similarly the π-electron deficient 6-phenyl heterocycle *2* forms a covalent adduct with ethanol. Previously, water and alcohol additions have also been observed in related molecules.[4,9] The adduct formation is reversible; heating the adduct under drying conditions leads to regeneration of the fully conjugated heterocycle. The ^{1}H NMR data are concistent with structure *6* which means that the addition was over the N(4)–C(5) double bond in agreement with C(5) being the most reactive position for nucleophilic substitution in this heterocyclic system.

The 5-phenyl isomer *3* did not form an adduct with ethanol (TLC, ^{1}H NMR) under the conditions which gave *6*, the equilibrium between the conjugated heterocycle and its ethanol adduct being in favour of the former. This finding correlates with relatively low reactivity for nucleophilic substitution at C(6). Under other conditions, however, adduct formation involving C(6) in 5-phenyl-1,2,4-triazines can be effected.[4]

In the metal hydride reduction of *3* and *5* using lithium tri-*tert*-butoxyaluminium hydride it is the N(4)–C(5) double bond which is reduced and hence the formation of the products

with structures *7* and *8* (^{1}H and ^{13}C NMR). This finding correlates well with previous observations in the studies of partial saturation of 1,2,4-triazines.[9,10] Despite the higher reactivity for nucleophilic reactions at C(5) than at C(6), it is notable that the former is reduced even when C(5) carries a phenyl group.

Enolizable carbonyl compounds may be involved in aldol reactions. Similarly enolizable carbonyl compounds are expected to add to π-electron deficient heterocycles. Thus the 6-phenyl derivative *4* forms a covalent adduct with acetone; the reaction is acid catalyzed. The 5-phenyl isomer did not react under the same reaction conditions. The acetonylation of the *N*-benzyl derivative is significantly faster than of the *NH*-parent compound *2* presumably because the *N*–*H* bond is more polarized than the *N*-benzyl bond towards the heterocyclic ring and hence have different effects on the π-electron distribution in the ring. The new carbon-carbon bond has been formed at C(5). In ^{1}H NMR this is manifested by an ABX system due to the CH_2CH-unit.

The subtituted, fully conjugated heterocycle was to be generated from the adducts *9* and *10* by the reaction with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The new double bond was formed exocyclic where it was conjugated with the oxo group. Thus the ^{1}H NMR spectrum shows no acetonyl methylene group but the presence of a vinyl proton at δ 5.47 for *11* and at δ 5.38 for *12*. The IR (KBr) absorption of the side-chain carbonyl group in *9* and *10* (1713 cm^{-1}) has been shifted to lower wave numbers (1643 and 1634 cm^{-1}) in the carbonyl conjugated structures *11* and *12* with double bond absorption at *ca.* 1570 cm^{-1}. The Raman spectrum of *9* shows bands at 1598 (m) and 1617 (m) cm^{-1} whereas in the dehydrogenated analogue *11* two strong bands are present at 1567 and 1585 cm^{-1} besides weaker bands at 1600 and 1630 cm^{-1}. In the IR spectrum weak absorption was observed at the wave numbers corresponding to the strong Raman bands. The Raman spectrum thus supports the presence of the exocyclic conjugated double bond as in *11*.

Only one double bond stereoisomer was formed and has been assigned the (*Z*)-configuration. The *NH*-proton for *12* in the NMR spectrum appeared at δ 12.5 and for *11* at δ 11.1 and 12.5. The low field NH absorptions are consistent with strong hydrogen bonding to the carbonyl oxygen atom whereby a pseudo six-membered ring is formed. The non-bonded interaction from the phenyl group is also expected to favour formation of the (*Z*)-isomer.

The above finding correlates well with the behaviour of 1,3-dicarbonyl compounds which may be extensively enolized into hydrogen bonded pseudo six-membered ring structures.

EXPERIMENTAL

The mass spectra are reported as MS[70 eV; (% rel.int.)] and by chemical ionization using isobutane as MS(CI). The ^{1}H NMR data were recorded at 60 MHz, and the ^{13}C NMR data at 15 MHz on a JMN–FZ 60 Fourier transform spectrometer. The high resolution IR (KBr) spectra of compounds *9*–*12* were recorded on a Perkin–Elmer model 225 spectrometer, and the Raman spectra on a DIOR RT-30 Raman spectrometer with monochromator; the excitation was by the 488 nm line from an argon-gas lazer (Coherent Radiation Model 52).

*5-Phenyl-1,2,4-triazin-3(2*H*)-one* 1 was prepared by hydrolysis of 3-methylthio-5-phenyl-1,2,4-triazine.[16] ^{13}C NMR (DMSO-d_6): δ 128.3–133.1 (Ph), 133.1 (C-6, d, J 162 Hz), 153.9 (C-5, s), 164.4 (C-3, s). MS: 173 (47, M), 117 (10), 116 (63), 103 (13), 102 (100), 90 (17), 89 (25).

*6-Phenyl-1,2,4-triazin-3(2*H*)-one* 2 was available by cyclocondensation.[7] ^{13}C NMR (DMSO-d_6): δ 128.0–129.9 (Ph), 133.3 (C-5), 153.1 (C-6), 163.7 (C-3).

*2-Benzyl-5-phenyl-1,2,4-triazin-3(2*H*)-one* 3. 5-Phenyl-1,2,4-triazin-3(2*H*)-one was dissolved in an equivalent of aqueous sodium hydroxide, the solution evaporated to dryness

and the residual sodium salt dried (70 °C, *in vacuo*). Part of this salt (2.0 g, 10 mmol) was suspended in dry DMF (150 ml) and benzyl bromide (2.2 g, 13 mmol) added dropwise with stirring at room temperature. The mixture was stirred for 3 h, the solvent distilled off at reduced pressure, the residue extracted with chloroform, the chloroform solution shaken with 0.2 M sodium hydroxide (3×5 ml) and washed with water and the dried ($MgSO_4$) solution evaporated.A chloroform solution of the residue was passed through a column of alumina (activity III, 20 g), the chloroform eluate evaporated and the residual yellow material recrystallized from acetonitrile; yield 1.7 g (64 %), m.p. 146 °C. Anal. $C_{16}H_{13}N_3O$: C,H. ^{1}H NMR ($CDCl_3$): δ 5.30 (CH_2Ph, s), 7.3–8.1 (2 Ph), 8.25 (H-6, s). ^{13}C NMR ($CDCl_3$): δ 56.3 (CH_2Ph, t), 128.6–133.0 (2 Ph), 133.6 (C-6, d, *J* 162), 153.8 (C-5, s), 164.1 (C-3, s). IR (KBr): 1667 cm^{-1}. MS: 263 (9, M), 172 (40), 117 (9), 116 (100), 91 (34), 89 (11). MS(CI): 264 (26, M+H), 106 (26), 91 (18).

2-Benzyl-6-phenyl-1,2,4-triazin-3(2H)-one 4 was prepared as above from 6-phenyl-1,2,4-triazin-3(2*H*)-one sodium salt. The crude product was purified by chromatography on silica gel using chloroform for eluation. The yellow compound, which is blue fluorescent under UV light, was recrystallized from ethyl acetate; yield 36 %, m.p. 146 °C. Anal. $C_{16}H_{13}N_3O$: C,H. ^{1}H NMR ($CDCl_3$): 5.30 (CH_2Ph, s), 7.4 (2 Ph), 8.95 (H-5, s). ^{13}C NMR ($CDCl_3$): δ 56.6 (CH_2Ph, t), 128.4–130.3 (2 Ph), 133.3 (C-5, d, *J* 162 Hz), 153.7 (C-6, s), 164.1 (C-3, s). IR (KBr): 1682 cm^{-1}. MS: 263 (6, M), 144 (37), 116 (100), 91 (78), 89 (13). MS(CI): 264 (94, M+H), 264 (19), 192 (12), 144 (26), 116 (100), 91 (93).

2-Ethoxymethyl-5-phenyl-1,2,4-triazin-3(2H)-one 5. A solution of chloromethyl ethyl ether (0.87 g, 9.2 mmol) in dry DMF (50 ml) was added dropwise during 3 h with stirring at 0 °C to a suspension of the sodium salt (prepared as for *3*) of 5-phenyl-1,2,4-triazin-3(2*H*)-one (1.50 g, 7.7 mmol) in dry DMF (150 ml). The mixture was stirred at 0 °C for 20 h before filtration, the filtrate evaporated to dryness at reduced pressure, the residue extracted with chloroform (150 ml), the chloroform solution shaken with 0.2 M sodium hydroxide (2×50 ml) and water, the dried ($MgSO_4$) solution evaporated and the residue crystallized from ethyl acetate; yield 0.98 g (56 %), m.p. 90 °C. Anal. $C_{12}H_{13}N_3O_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 1.20 and 3.71 (EtO), 5.40 (NCH_2O), 7.4–8.0 (Ph), 8.25 (H-6). ^{13}C NMR ($CDCl_3$) δ 15.1 and 66.2 (EtO), 81.5 (NCH_2O, t), 128.6–133.0 (Ph), 133.5 (C-6, d), 153.8 (C-5, s), 164.8 (C-3, s). IR (KBr): 1659 cm^{-1} (CO). MS(CI): 232 (64, M+H), 187 (42), 186 (77), 172 (100), 116 (82), 104 (11), 103 (29), 102 (11).

2-Benzyl-5-ethoxy-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2H)-one 6. A solution of 2-benzyl-6-phenyl-1,2,4-triazin-3(2*H*)-one (0.3 g, 1.1 mmol) in ethanol (150 ml) was heated under reflux for 3 h before the ethanol was removed at reduced pressure. The yield was 0.33 g (94 %), m.p. 148 °C. Anal. $C_{18}H_{19}N_3O_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 1.15 and 3.46 (OEt), 5.00 (CH_2Ph, s), 5.55 (C-5, d), 7.2–7.6 (2 Ph). IR (KBr): 2700–3300 (NH), 1680 cm^{-1} (CO). MS(CI): 310 (5, M+H), 265 (20), 264 (100), 116 (13), 91 (20).

2-Benzyl-5-phenyl-4,5-dihydro-1,2,4-triazin-3(2H)-one 7. A solution of 2-benzyl-5-phenyl-1,2,4-triazin-3(2*H*)-one (1.0 g, 3.8 mmol) in dry THF (50 ml) was added to lithium tri-*tert*-butoxyaluminium hydride (1.4 g, 5.7 mmol) in dry THF (100 ml) under nitrogen, and the mixture stirred at room temperature for 22 h. Water (300 ml) was then slowly added to the reaction mixture, the THF evaporated from the mixture, the residue extracted with ether (2×100 ml), the ether washed with 20 % aqueous ammonium chloride and water, and the dried ($MgSO_4$) solution evaporated. The residue was the white crystalline title compound; yield 0.82 g (81 %), m.p. 127 °C. Anal. $C_{16}H_{13}N_3O$: C, H. ^{1}H NMR ($CDCl_3$): δ 4.79 (CH_2Ph, s), 4.95 (H-5, t), 6.42 (NH, m), 6.67 (H-6, t), 7.2 (2 Ph). ^{13}C NMR ($CDCl_3$): δ 52.6 (CH_2Ph, t), 57.1 (C-5, d, *J* 144 Hz), 127.4–129.4 (2 Ph), 137.8 (C-6, d, *J* 193 Hz), 150.8 (C-3, s), IR (KBr): 1664 cm^{-1} (CO). MS(CI): 266 (100, M+H), 238 (11), 106 (38).

2-Ethoxymethyl-5-phenyl-4,5-dihydro-1,2,4-triazin-3(2H)-one 8 was prepared as above from 2-ethoxymethyl-5-phenyl-1,2,4-triazin-3(2*H*)-one (0.50 g, 2.2 mmol) and lithium tri-*tert*-butoxyaluminium hydride (1.15 g, 4.6 mmol); yield 0.42 g (84 %), m.p. 86 °C. Anal. $C_{12}H_{15}N_3O_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.15 and 3.52 (EtO), 5.00 (NCH_2O, s), 5.05 (C-5, d, *J* 3 Hz), 6.6 (NH, m), 6.71 (H-6, d, *J*, 3 Hz), 7.22 (Ph, s). ^{13}C NMR ($CDCl_3$): δ 15.2 and 64.5 (EtO), 56.8 (C-5, d, *J* 145 Hz), 78.1 (NCH_2O, t, *J* 158 Hz), 126.7–129.3 (Ph), 138.4 (C-6, d, *J* 191 Hz), 150.9 (C-3, s). IR (KBr): 3300–2800 (NH), 1652 (CO), 1597 cm^{-1}. MS(CI): 234 (2, M+H), 189 (23), 188 (100), 162 (16), 145 (22), 116 (11), 104 (2).

5-Acetonyl-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2H)-one 9. A mixture from concen-

trated hydrochloric acid (2 ml) and 6-phenyl-1,2,4-triazin-3(2*H*)-one (1.0 g, 5.8 mmol) in acetone (150 ml) was heated under reflux for 36 h (TLC monitoring). The acetone was then allowed to distill off, the residue dissolved in chloroform (150 ml), the chloroform solution shaken with 0.2 M sodium hydroxide and washed with water, the dried ($MgSO_4$) solution evaporated, the residue dissolved in chloroform and the solution chromatographed on silica gel. Biproducts were initially eluated with chloroform and finally the title compound was eluated with ethyl acetate; yield 0.63 g (47 %), m.p. 156 °C. Anal. $C_{12}H_{13}N_3O_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 2.13 (CH_3CO), 2.50 and 3.10 (CH_2CO, J 18, 10.3 Hz), 5.1 (H-5, m), 6.43 (NH, s), 7.4 (Ph), 8.87 (NH, s). C^{13}NMR ($CDCl_3$): δ 30.4 (*Me*CO), 45.3 (CH_2CO, t), 46.6 (C-5, d, J 141 Hz), 125.6–132.7 (Ph), 144.5 (C-6, s), 152.2 (C-3, s), 205.7 (Me*CO*, s). IR (KBr): 3370, 3225, 3093 (NH), 1713 (CH_3CO), 1693(CO). Raman: 1598 (m), 1617 (m) cm^{-1}. MS: 231 (4, M), 174 (22), 116 (10), 102 (16).

*5-Acetonyl-2-benzyl-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one* 10. Concentrated hydrochloric acid (1 ml) was added to a solution of 2-benzyl-6-phenyl-1,2,4-triazin-3(2*H*)-one (0.2 g, 0.8 mmol) in acetone (50 ml) and the solution kept at room temperature for 18 h. The solvent was then distilled off and the residue passed through a column of silica gel using chloroform for the eluation. Evaporation of the chloroform eluate left the crystalline, white adduct; yield 0.19 g (79 %), m.p. 184 °C. Anal. $C_{19}H_{19}N_3O_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 2.18 (MeCO), 2.50 and 3.00 (CH_2CO, J 18, 10, 3 Hz), 4.91 (CH_2Ph, s), 5.2 (H-5, m), 5.6 (NH, m), 7.3 (2 Ph). ^{13}C NMR ($CDCl_3$): δ 29.6 (*Me*CO), 45.3 (CH_2CO, t), 46.4 (C-5, d, J 14.7 Hz), 125.6–132.7 (2 Ph), 143.0 (C-6, s), 150.5 (C-3, s). IR (KBr): 2700–3500, 1713 (Me*CO*), 1682 cm^{-1} (CO). MS: 321 (4, M), 144 (22), 116 (65), 91 (100), 89 (11). MS (CI): 323 (21), 322 (M+H), 264 (20).

*5-Acetonylidene-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one* 11. A solution of 5-acetonyl-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one (0.10 g, 0.45 mmol) and DDQ (0.15 g, 0.65 mmol) in benzene (50 ml) was heated under reflux for 7 d (TLC monitoring). The cold reaction mixture was then filtered and the filtrate passed through a short column of alumina (activity III, 20 g). The column was washed with additional benzene (100 ml), the product eluated by chloroform, the chloroform eluate evaporated and the residual material chromatographed on silica gel, using dichloromethane, yield 0.11 g (74 %), m.p. 176 °C. Anal. $C_{12}H_{11}N_3O_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 2.17 (*Me*CO), 5.47 (=CHCO), 7.5 (Ph), 11.06 (NH), 12.48 (NH). ^{13}C NMR ($CDCl_3$): δ 30.9 (*Me*CO), 98.3 (CH_2CO, d, J 165 Hz), 129.9–132.7 (Ph), 141.7 (C-6, s), 144.6 (C-3, s), 146.7 (C-5, s), 200.5 (=CH*CO*, s). IR (KBr): 3220, 3115 (NH), 1696 (CO, 1643 (=CH*CO*), 1583 and 1567 (*C*=*C*HCO) cm^{-1}. Raman: 1567 (s; C=C), 1585 (s; C=C), 1600 (m), 1630 (w) cm^{-1}. MS: 229 (25, M), 215 (13), 214 (100), 212 (67), 199 (21), 186 (55), 143 (11).

*5-Acetonylidene-2-benzyl-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one* 12. A solution of 5-acetonyl-2-benzyl-6-phenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one (0.60 g, 2.6 mmol) and DDQ (0.90 g, 3.9 mmol) in benzene (250 ml) was heated under reflux for 2 days. The cold mixture was filtered, the filtrate passed through a short alumina column (activity III), the column washed with benzene, the product eluated with chloroform, the solvent evaporated, the residue dissolved in dichloromethane and chromatographed on an alumina column (activity II); yield 0.47 g (79 %), m.p. 132 °C. ^{1}H NMR ($CDCl_3$): δ 2.15 (*Me*CO), 5.10 (CH_2Ph), 5.38 (=*CH*CO, s), 7.4 (2 Ph), 12.53 (NH). ^{13}C NMR ($CDCl_3$): δ 30.9 (*Me*CO), 54.6 (CH_2Ph, t), 97.4 (=*CH*CO, d, J 165 Hz), 128.3–136.4 (2 Ph), 142 (C-6, s), 144.2 (C-3, s), 145.6 (C-5, s), 200.2 (=CH*CO*), s). IR (KBr): 3400–2800 (NH), 1697 (CO), 1634 (=CH*CO*), 1571 (C=CH*CO*) cm^{-1}. MS: 319 (22, M), 276 (10), 157 (16), 129 (28), 91 (58).

*4-Benzyl-2-ethoxymethyl-5-phenyl-3,4-dihydro-1,2,4-3(2*H*)-one* 13. A solution of benzyl bromide (0.82 g, 4.8 mmol) in dry DMF (10 ml) was added slowly with stirring to a mixture which had been prepared from 2-ethoxymethyl-5-phenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one (0.93 g, 4.0 mmol) and potassium *tert*-butoxide (0.54 g, 4.8 mmol) in dry DMF (100 ml). The mixture was stirred for 15 min before filtration, the filtrate evaporated to dryness at reduced pressure, the residue extracted with chloroform (150 ml), the washed and dried ($MgSO_4$) chloroform solution evaporated, and the residue chromatographed on a silica gel column using CH_2Cl_2–EtOAc 1:20. The title compound was obtained as a viscous oil which crystallized on standing; yield 0.42 g (33 %), m.p. 143 °C. ^{1}H NMR ($CDCl_3$): δ 1.25 and 3.67 (EtO), 3.52 and 5.33 (CH_2Ph, J 15 Hz), 4.72 (H-5, d, J 4 Hz), 5.15 (NCH_2O, s), 6.57 (H-6, J 4 Hz), 7.1 (2 Ph). ^{13}C NMR ($CDCl_3$): δ 15.3 and 64.7 (EtO), 47.3 (C-10, t), 59.6

(C-5, d, J 140 Hz), 79.2 (NCH_2O, t, J 158 Hz), 127.5–129.4 (2 Ph), 137.5 (C-6, d, J 184 Hz), 151.2 (C-3, s). IR (KBr): 1665 cm^{-1} (CO). MS: 323 (0, M), 263 (9), 172 (39), 116 (100). MS (CI): 324 (0, M+H), 265 (18), 264 (100), 172 (13), 116 (19), 91 (11).

REFERENCES

1. Gacek, M., Ongstad, L. and Undheim, K. *Acta Chem. Scand. B 33* (1979) 150.
2. Rise, F. and Undheim, K. *Acta Chem. Scand. 39* (1985) 195.
3. Rise, F., Ongstad, L., Gacek, M. and Undheim, K. *Acta Chem. Scand. B 37* (1983) 613.
4. Paudler, W.W. and Lee, J. *J. Org. Chem. 36* (1971) 3921.
5. Neunhoeffer, H., Hennig, H., Frühauf, H.W. and Mutterer, M. *Tetrahedron Lett. 37* (1969) 3147.
6. a. Ekeley, J.B., Carlson, R.E. and Ronzio, A.R. *Recl. Trav. Chim. Pays-Bas 59* (1940) 496; b. Elvidge, J.A., Newbold, G.T., Senciall, I.R. and Symes, T.G. *J. Chem. Soc.* (1964) 4157.
7. Lalezari, I., Sharghi, N., Shafiee, A. and Yalpani, M. *J. Heterocycl. Chem. 6* (1969) 403.
8. Daunis, J. and Pigière, C. *Bull. Soc. Chim. Fr.* (1973) 2818.
9. Vinot, N. and M'Packo, J.-P. *Bull. Soc. Chim. Fr.* (1972) 4637.
10. a. Mustafa, A., Asker, W., Mansour, A.K., Zaher, H.A.A. and Eloui, A.R. *J. Org. Chem. 28* (1963) 3519; b. Polonovski, M., Pesson, M. and Rajzman, P. *Bull. Soc. Chim. Fr.* (1955) 1166; c. Mansour, A.K., Awad, S.B. and Antoun, S. *Z. Naturforsch. Teil B 29* (1974) 792.

Received June 29, 1984.