Access to the 2,3-Dihydropyridazin-3-one and as-Triazino[3,4-a]phthalazine Ring Systems from 4-Aryl-2-oxo-butanoic Acids [1]

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A novel series of 2,3-dihydropyridazin-3-ones **15** were synthesized *via* condensation between hydrazines and 4-(p-chlorophenyl)-2-hydroxy-2-(2-oxo-2-substituted ethyl)butanoic acids **8** which in turn were prepared by the reaction of substituted benzylpyruvic acids **6** with methyl alkyl(aryl) ketones **7**. Dehydration of **8b-d** by a mixture of glacial acetic acid and hydrochloric acid afforded 4-(p-chorophenyl)-2-(substituted phenacyl)-2-butenoic acids **10**. Condensation reaction of **10** with hydrazines gave type **15** compounds in good yields. Also, a new series of as-triazino[3,4-a]phthalazines **20** was obtained from the reaction of substituted benzylpyruvic acids **6** with hydralazine to give the hydralazones **19** which underwent dehydrative cyclization reaction with PPA to afford **20**. Structure assignments are based on ¹H, ¹³C nmr and ir spectra.

The pyridazinone ring is an integral feature in the structure of a large number of highly biologically active compounds. A group of pyridazinones are well known as highly active herbicides [2] and their metabolism in plants was investigated. There are some recent reports [3] indicating that some pyridazinones display an antiinflammatory activity. The development of general methods for the construction of this ring system is therefore an important synthetic target. Towards this goal, we have recently developed an approach for the formation of pyridazinone system **1** *via* the reaction of the α-formylhydrazones **2** with the Wittig reagent **3** (Scheme I) [4].

Scheme I
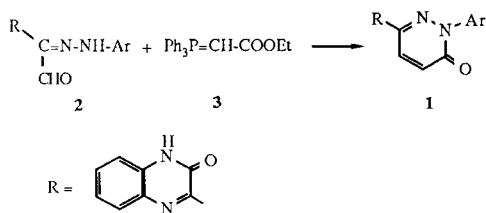
In the present report the elaboration of the carbon framework (Scheme III) for the pyridazinone was acheived *via* functionalized pyruvic acid derivatives. In addition, the reactivity of 1-hydrazinophthalazine (hydralazine, a potent antihypertensive agent) toward these pyruvic acid analogs as well as the annelation reaction of the hydralazones to give as-triazino[3,4-a]phthalazine system was also investigated.

I. Construction of β-Hydroxycarbonyl Entities.

The functionalized pyruvic acids required for this study were prepared by Cordier methodology [5] by treatment of

arylidenepyruvic acids **4** with potassium borohydride to yield lactic acid analogs **5**. Subsequent isomerization of **5** by heating with 5% sodium hydroxide solution directly furnished the starting materials **6** (Scheme II). When type **6** compounds were treated with methyl alkyl(aryl) ketones **7** in aqueous ethanolic alkaline medium at 0°, colorless solids were obtained. On the basis of elemental analysis and spectroscopic data, these products were confirmed to be of type **8** rather than **9**. Compounds **8a-d** are existing practically exclusively in the open form in both solid state and in solutions of chloroform or dimethyl sulfoxide. Their ¹H nmr spectra (Table I) exhibited a characteristic YCH₂CH₂Z; *e.g.* A₂X₂ patterns [6] which appeared as a triplet and multiplet. Characteristic also were a doublet of doublet in the region of δ 2.92-3.56, of two protons intensity, due to nonequivalent methylene protons adjacent to carbonyl group. Absorptions in the regions 1680-1700, 1708-1733 and 3495-3550 cm⁻¹ in their infrared spectra indicated the presence of carbonyl, carboxyl and hydroxyl groups respectively. A conclusive evidence for structure as **8** was provided by ¹³C nmr. Thus, ¹³C nmr spectrum of **8a** in dimethyl sulfoxide-d₆ illustrate the chemical shifts typical for the 2-acetonyl-4-(p-chlorophenyl)-2-hydroxybutanoic acid system. Signals at 28.550, 40.984, 51.254 and 73.943 ppm, on the the basis of chemical shifts and off-resonance decoupled spectrum, were assigned to C-3, C-4, C-1′ and C-2 respectively. The resonances at 176.040 and 206.042 ppm were determined to correspond to C-1 and C-2′ respectively.

### II. Dehydration of the β-Hydroxycarbonyl Compounds 8.

When a solution of **8b-d** in acetic acid was treated with 36% hydrochloric acid and heated on a water-bath for three hours, a colorless product was obtained in each case.

Table I

Physical Properties of 4-(*p*-Chlorophenyl)-2-hydroxy-2-(2-oxo-2-substituted-ethyl)butanoic Acids **8**

Compound		Yield	MP	Molecular	Analyses Calcd./Found		IR (cm⁻¹) [c]			¹H-NMR (δ) [d]
No.	R	%	(°C) [a]	Formula [b]	C	H	νCO	νCOO	νOH	(Deuteriochloroform)
8a	CH₃	89	134 (B)	C₁₃H₁₅ClO₄	57.8 / 57.7	5.5 / 5.7	1680	1708	3550	1.88 (t, 2H, CH₂), 2.15 (s, 3H, CH₃), 2.49, 2.73 (2m, 2H, CH₂-Ar), 2.92 (dd, J = 16 Hz, 2H, CH₂CO), 7.26 (dd, 4H, Ar)
8b	C₆H₅	75	130 (B)	C₁₈H₁₇ClO₄	65.0 / 65.0	5.1 / 5.1	1690	1730	3500	2.10 (t, 2H, CH₂), 2.77 (m, 2H, CH₂-Ar), 3.56 (dd, J = 16 Hz, 2H, CH₂CO), 7.23, 7.57, 7.82 (2m, dd, 9H, Ar)
8c	*p*-CH₃C₆H₄	76	145 (C)	C₁₉H₁₉ClO₄	65.8 / 65.9	5.5 / 5.5	1700	1733	3500	2.09 (t, 2H, CH₂), 2.43 (s, 3H, CH₃), 2.75 (m, 2H, CH₂Ar), 3.52 (dd, J = 16 Hz, 2H, CH₂CO), 7.20, 7.82 (m, d, 8H, Ar)
8d	*p*-CH₃OC₆H₄	40	149 (B)	C₁₉H₁₉ClO₅	62.9 / 63.1	5.2 / 5.5	1690	1720	3495	2.07 (t, 2H, CH₂), 2.70 (m, 2H, CH₂Ar), 3.44 (dd, J = 16 Hz, 2H, CH₂CO), 3.87 (s, 3H, OCH₃), 7.1, 7.83 (m, d, 8H, Ar)

[a] Recrystallization solvent: B = benzene, C = chloroform. [b] Mass spectral data are in a good agreement with the proposed structure. [c] In potassium bromide. [d] The ¹H-nmr spectrum of **8a** was obtained in dimethyl sulfoxide-d₆.

Scheme II

a) Ar = p-ClC₆H₄

b) Ar = p-CH₃C₆H₄

Scheme III
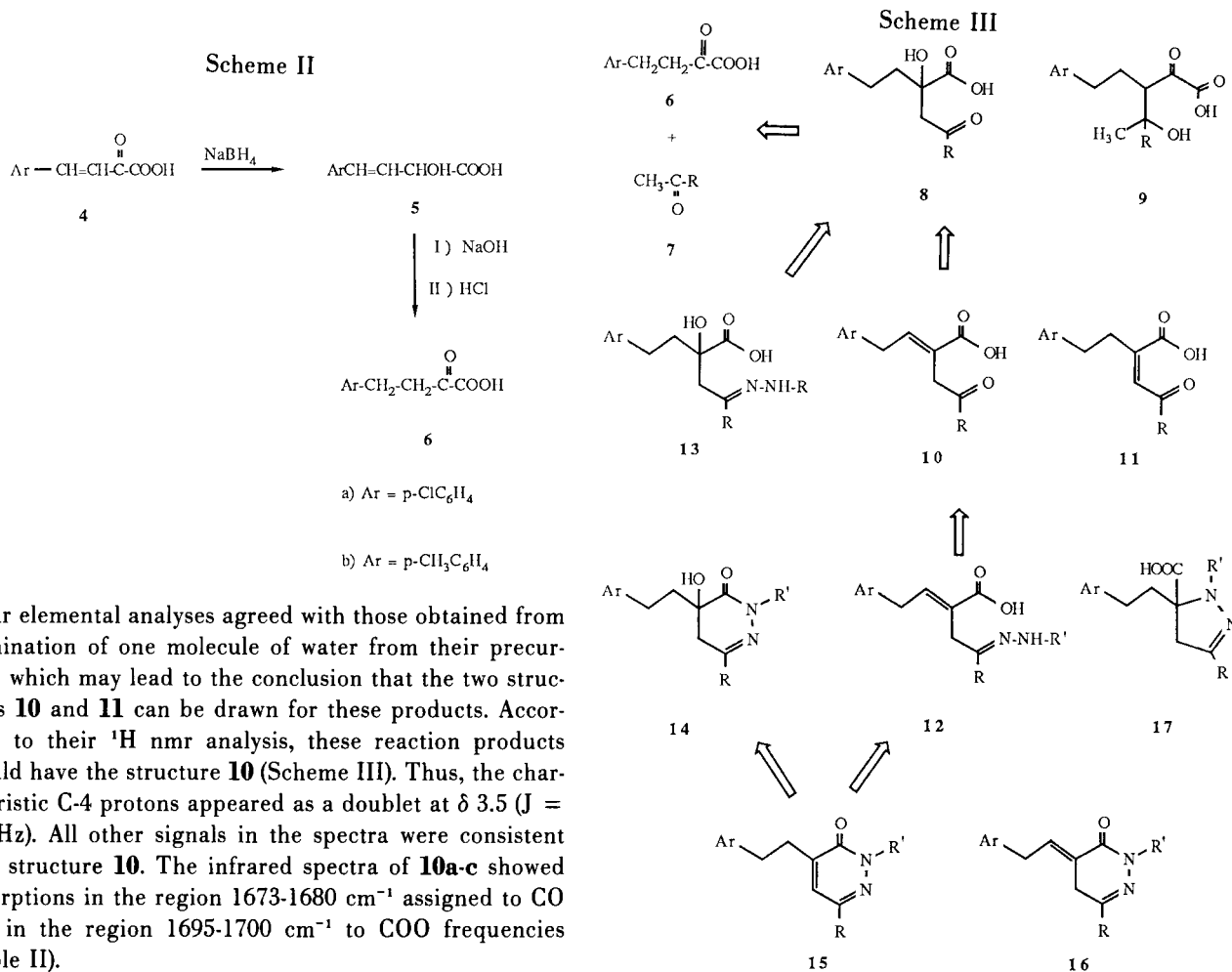
Their elemental analyses agreed with those obtained from elemination of one molecule of water from their precursors, which may lead to the conclusion that the two structures **10** and **11** can be drawn for these products. According to their ¹H nmr analysis, these reaction products should have the structure **10** (Scheme III). Thus, the characteristic C-4 protons appeared as a doublet at δ 3.5 (J = 7.5 Hz). All other signals in the spectra were consistent with structure **10**. The infrared spectra of **10a-c** showed absorptions in the region 1673-1680 cm⁻¹ assigned to CO and in the region 1695-1700 cm⁻¹ to COO frequencies (Table II).

Table II

Physical Properties of 4-(*p*-Chlorophenyl)-2-(substituted-phenacyl)-2-butenoic Acids **10**

Compound		Yield	Mp	Molecular	Analyses Calcd./Found		IR(cm⁻¹) [b]		¹H-NMR (δ)
No.	R	%	(°C) [a]	Formula	C	H	νCO	νCOO	(Deuteriochloroform)
10a	C$_6$H$_5$	27	158	C$_{18}$H$_{15}$ClO$_3$	68.7 68.5	4.8 4.9	1680	1695	3.47 (d, J = 7.5 Hz, 2H, CH$_2$-Ar), 4.07 (s, 2H, CH$_2$CO), 7.30, 8.00 (m, d, 10H, Ar, =CH)
10b	*p*-CH$_3$C$_6$H$_4$	95	179	C$_{19}$H$_{17}$ClO$_3$	69.4 69.5	5.2 5.2	1678	1698	2.36 (s, 3H, CH$_3$), 3.45 (d, J = 7.5 Hz, 2H, CH$_2$-Ar), 4.03 (s, 2H, CH$_2$CO), 7.20, 7.83 (m, d, 9H, Ar, =CH)
10c	*p*-CH$_3$OC$_6$H$_4$	95	169	C$_{19}$H$_{17}$ClO$_4$	66.2 66.0	4.9 5.0	1673	1700	3.49 (d, J = 7.5 Hz, 2H, CH$_2$-Ar), 3.87 (s, 3H, OCH$_3$), 4.03 (s, 2H, CH$_2$CO), 6.97, 7.20, 8.00 (d, m, d, 9H, Ar, =CH)

[a] Recrystallization solvent: benzene. [b] In potassium bromide.

Table III

Physical Properties of 4-[2-(*p*-Chlorophenyl)ethyl]-6-substituted-2,3-dihydropyridazin-3-ones **15**

Compound No.	R	Ṙ	Yield % [a]	Mp (°C) [b]	Molecular Formula	Analyses Calcd./Found			IR(cm⁻¹) [c]		¹H-NMR (δ) [d]
						C	H	N	νOCN	νNH	(Deuteriochloroform)
15a	CH$_3$	H	65 (A)	189	C$_{13}$H$_{13}$ClN$_2$O	62.8 63.1	5.2 5.2	11.3 11.1	1660	3140	2.20 (s, 3H, CH$_3$), 2.81 (s, 4H, CH$_2$-CH$_2$), 6.75 (s, 1H, =CH), 7.13 (m, 4H, Ar), 11.78 (s, 1H, NH is deuterium oxide exchangeable)
15b	C$_6$H$_5$	H	75 (A) 76 (B)	192	C$_{18}$H$_{15}$ClN$_2$O	69.6 69.5	4.8 5.2	9.0 9.0	1663	3145	2.95 (s, 4H, CH$_2$-CH$_2$), 7.40 (m, 10H, Ar, =CH), 12.10 (s, 1H, NH is deuterium oxide exchangeable)
15c	*p*-CH$_3$C$_6$H$_4$	H	54 (A) 76 (B)	175	C$_{19}$H$_{17}$ClN$_2$O	70.3 69.9	5.2 5.6	8.6 8.6	1668	3155	2.40 (s, 3H, CH$_3$), 3.00 (s, 4H, CH$_2$-CH$_2$), 7.20, 7.58 (m, d, 9H, Ar, =CH), 12.60 (s, 1H, NH is deuterium oxide exchangeable)
15d	*p*-CH$_3$OC$_6$H$_4$	H	53 (A) 76 (B)	234	C$_{19}$H$_{17}$ClN$_2$O$_2$	67.0 66.7	5.0 5.3	8.2 8.2	1670	3140	2.84 (s, 4H, CH$_2$-CH$_2$), 3.77 (s, 3H, OCH$_3$), 6.95, 7.26 (dd, m, 8H, Ar), 7.70 (s, 1H, =CH), 12.93 (s, 1H, NH is deuterium oxide exchangeable)
15e	CH$_3$	*p*-BrC$_6$H$_4$	55 (A)	154	C$_{19}$H$_{16}$BrClN$_2$O	56.5 56.1	4.0 4.2	6.9 7.2	1665		2.34 (s, 3H, CH$_3$), 2.82 (s, 4H, CH$_2$-CH$_2$), 6.85-7.63 (m, 9H, Ar, =CH)
15f	C$_6$H$_5$	*p*-BrC$_6$H$_4$	40 (B) 67 (C) 58 (D)	149	C$_{24}$H$_{18}$BrClN$_2$O	61.9 61.6	3.9 4.1	6.0 5.8	1650		3.00 (s, 4H, CH$_2$-CH$_2$), 7.23, 7.42, 7.70 (3m, 14H, Ar, =CH)
15g	*p*-CH$_3$C$_6$H$_4$	*p*-BrC$_6$H$_4$	54 (B) 52 (C) 62 (D)	99	C$_{25}$H$_{20}$BrClN$_2$O	62.6 62.4	4.2 4.0	5.8 5.9	1653		2.36 (s, 3H, CH$_3$), 2.94 (s, 4H, CH$_2$-CH$_2$), 7.23, 7.62 (2m, 13H, Ar, =CH)
15h	*p*CH$_3$OC$_6$H$_4$	*p*-BrC$_6$H$_4$	47 (B) 88 (C) 69 (D)	123	C$_{25}$H$_{20}$BrClN$_2$O$_2$	60.5 60.9	4.0 4.4	5.7 5.4	1653		2.97 (s, 4H, CH$_2$-CH$_2$), 3.83 (s, 3H, OCH$_3$), 7.12, 7.66 (2m, 13H, Ar, =CH)

[a] Yield of the method used. [b] Recrystallization solvent: ethanol. [c] In potassium bromide. [d] The ¹H-nmr spectrum of **15d** was obtained in dimethyl sulfoxide-d$_6$.

III. Synthesis of 2,3-Dihydropyridazin-3-ones 15.

Inspection of type 8 compounds shows that it is a potentially valuable system for the preparation of pyridazinones as one can envisage different electrophilicity over three carbon centers, C-1, C-2 and C-2'.

The reaction of compounds 8 with hydrazine was first studied. Thus, when compounds 8a-d were refluxed with hydrazine hydrate in ethanol for three hours, they did not give the anticipated hydrazone derivatives 13 or type 17 compounds but colorless products were obtained whose elemental analysis indicated the loss of three molecules of water during the condensation process. Such a result could agree with structures 15 and 16. A characteristic singlet of four protons intensity in ^{1}H nmr spectra of these products in the region of δ 2.81-3.00 was attributed to the presence of YCH$_2$CH$_2$Z system which agreed with their structure as 15a-d and not the alternative structure 16. Further confirmation of structure 15 is derived from analysis of the ^{13}C nmr spectrum of 15b. The expected signals for the YCH$_2$CH$_2$Z carbons system were observed at δ 30.839 and 32.006 which were assigned on the basis of their positions and from its off-resonance decoupled spectrum. Resonance at δ 160.736 was attributed to the amide carbon atom.

The reactivity of 8 was further explored towards the reaction with p-bromophenylhydrazine instead of hydrazine hydrate. It was found that this reaction proceeded differ-

ently depending on the nature of R. Thus, the reaction of 8a (R = CH$_3$) with p-bromophenylhydrazine afforded in one step 15e (Scheme III) which was confirmed by its elemental analysis and spectroscopic data (Table III). Treatment of 8b-d with p-bromophenylhydrazine afforded colorless solids. However, neither the elemental analysis nor the spectroscopic data of these products are compatible with a structural assignment as type 15. On the basis of their elemental analysis, the condensation proceeds with the loss of two molecules of water. Examination of their ^{1}H nmr spectra (Table IV) showed in addition to the presence of YCH$_2$CH$_2$Z patterns, a doublet of doublet of two protons intensity which were assigned to the nonequivalent methylene protons at C-5. A characteristic up field signal in the region of δ 3.73-3.96 which was deuterium oxide exchangeable was assigned to the hydroxyl proton, which confirmed their structure as 14a-c. The expected hydroxyl absorption in the region of 3400-3420 cm^{-1} and the amide absorption at 1670 cm^{-1} in their infrared spectra were observed. Dehydration of 14 was effected by heating in a mixture of hydrochloric acid and acetic acid or in polyphosphoric acid to afford 15 in high yield.

Particularly interesting in this report is the study of the reactivity of type 10 compounds toward nucleophiles (e.g. hydrazines). Thus, the reaction of 10 with the hydrazine hydrate or p-bromophenylhydrazine afforded the corresponding pyridazinones 15. Presumably preliminary forma-

Table IV

Physical Properties of 2-(p-Bromophenyl)-4-[2-(p-chlorophenyl)ethyl]-4-hydroxy-6-(substituted-phenyl)-2,3,4,5-tetrahydropyridazin-3-ones 14

| Compound | | Yield | MP | Molecular | Analyses Calcd./Found | | | IR (cm^{-1}) [b] | | ^{1}H-NMR (δ) |
No.	R	%	(°C) [a]	Formula	C	H	N	νOCN	νOH	(Deuteriochloroform)
14a	C$_6$H$_5$	46	175	C$_{24}$H$_{20}$BrClN$_2$O$_2$	59.6 59.6	4.1 4.4	5.8 5.8	1670	3420	1.93 (t, 2H, CH$_2$), 2.70 (m, 2H, CH$_2$-Ar), 3.20 (dd, J = 16 Hz, 2H, CH$_2$-C=N), 3.73 (bs, 1H, OH is deuterium oxide exchangeable), 7.03, 7.40, 7.70 (3m, 13H, Ar)
14b	p-CH$_3$C$_6$H$_4$	45	169	C$_{25}$H$_{22}$BrClN$_2$O$_2$	60.3 60.8	4.4 4.3	5.6 5.8	1670	3400	1.93 (t, 2H, CH$_2$), 2.36 (s, 3H, CH$_3$), 2.70 (m, 2H, CH$_2$-Ar), 3.18 (dd, J = 16 Hz, 2H, CH$_2$-C=N), 3.86 (s, 1H, OH is deuterium oxide exchangeable), 7.13, 7.56 (2m, 12H, Ar)
14c	p-CH$_3$OC$_6$H$_4$	37	194	C$_{25}$H$_{22}$BrClN$_2$O$_3$	58.4 58.1	4.3 4.4	5.5 5.5	1670	3410	1.93 (t, 2H, CH$_2$), 2.71 (m, 2H, CH$_2$Ar), 3.16 (dd, J = 16 Hz, 2H, CH$_2$-C=N), 3.83 (s, 3H, OCH$_3$), 3.93 (s, 1H, OH is deuterium oxide exchangeable), 7.00, 7.53 (2m, 12H, Ar)

[a] Recrystallization solvent: ethanol. [b] In potassium bromide.

tion of hydrazones **12** at C-2′ followed by dehydrative cyclization to give **16** which suffer 1,3-sigmatropic shift to give the more stable pyridazinone isomers **15**.

IV. Synthesis of *as*-Triazino[3,4-*a*]phthalazines **20**.

Traditionally, preparation of hydralazones involves the condensation of hydralazine **18** with carbonyl compounds. Interest in the pharmacology of these compounds has resulted in numerous compounds having various substituents [7]. Certain hydralazones are well known to undergo annelation reaction to form five as well as six-membered ring to phthalazine. To exploit the availabilty of the versatile compound **18** to provide interesting compounds for biological testing, we hereby investigate such reaction on type **6** compounds. Thus, treating an aqueous solution of the hydrochloride of **18** with equimolar amount of the sodium salt of aralkylpyruvic acids **6a-b**, whereby the hydrochloride of **18** was neutralized *in situ* to **18**, afforded yellow products whose spectral data and elemental analyses are compatible with the anticipated hydralazone structure **19a-b** (Scheme IV). Several attempts to cyclize compounds **19a-b** by the known methods such as boiling in water [8,9], acetic acid [10], or dimethyl sulfoxide [8,9] for several hours were unsuccessful. However, when **19a-b** were heated in polyphosphoric acid for one hour on a steam-bath they afforded colorless products whose elemental analyses indicated the loss of one molecule of water which agreed with structure **20a-b** (Scheme IV).

Scheme IV
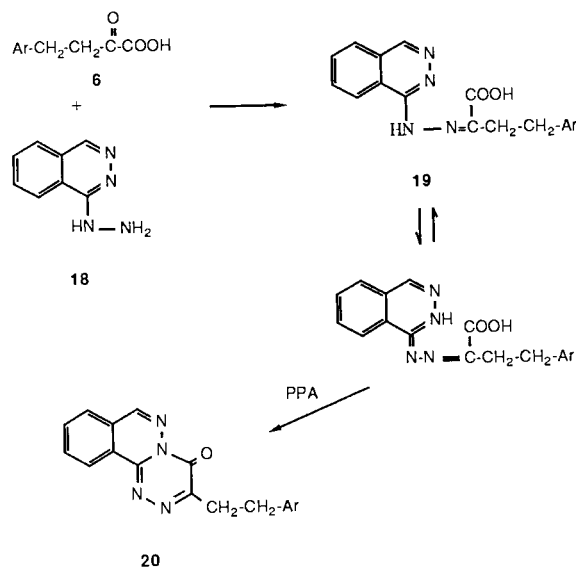
a) Ar = p-ClC$_6$H$_4$

b) Ar = p-CH$_3$C$_6$H$_4$

EXPERIMENTAL

Melting points were determined with Meltemp apparatus with a

76-mm immersion thermometer, and are uncorrected. Infrared spectra were recorded with a Pye Unicam SP1025 spectrometer. The ^{1}H nmr were taken on a Varian EM-390 spectrometer. The ^{13}C nmr were recorded with a Nicolet NT300 narrow bore spectrometer with 1180E data system. Chemical shifts are expressed in δ scale relative to tetramethylsilane as an internal standard. Elemental analyses were performed at Faculty of Science, Cairo University, Cairo, Egypt.

2-Acetonyl-4-(*p*-chlorophenyl)-2-hydroxybutanoic Acid (8a).

A solution of **6a** (1.6 g, 7.5 mmoles) in acetone (1.7 ml) was treated with a solution of potassium hydroxide (0.73 g) in water (17 ml) and the reaction mixture was left overnight at room temperature. The solution was then acidified with concentrated hydrochloric acid to give a sticky product which solidified upon cooling. The precipitated solid was removed by filtration and crystallized from benzene (Table I).

4-(*p*-Chlorophenyl)-2-hydroxy-2-(substituted-phenacyl)butanoic Acids 8b-d. General Procedure.

To a solution of **6a** (10 mmoles) and **7** (10 mmoles) in ethanol (5 ml) was added to a solution of potassium hydroxide (1.12 g) in water (6 ml) and the reaction mixture was kept at O° for two days. The mixture was then acidified with concentrated hydrochloric acid and the product which was solidified after two days was collected. Yields and the physical properties are summarized in Table I.

4-(*p*-Chlorophenyl)-2-(substituted-phenacyl)-2-butenoic Acids 10a-c. General Procedure.

To a solution of **8** (2 g) in glacial acetic acid (12 ml) was added 36% hydrochloric acid (12 ml), and the mixture was refluxed on a water-bath for three hours. The reaction mixture was cooled to give a sticky product which was solidified within 24 hours. It was filtered off and dried. Yields and physical properties are summarized in Table II.

4-[2-(*p*-Chlorophenyl)ethyl]-6-substituted-2,3-dihydropyridazin-3-ones 15. General Procedures.

A) A solution of appropriate **8** (0.5 g) in ethanol (10 ml) was refluxed with hydrazine hydrate 99% (1 ml) (for the preparation of **15e**, a solution of *p*-bromophenylhydrazine (0.35 g) in ethanol (7 ml) was used, instead) on a water-bath for three hours. The product which separated out on concentration was filtered off and dried. This method was successful in the preparation of **15a-e**.

B) To a solution of appropriate **10** (0.4 g) in ethanol (10 ml) was added hydrazine hydrate 99% (1 ml) (for the preparation of **15f-h**, a solution of an equivalent amount of *p*-bromophenylhydrazine in ethanol (10 ml) was used, instead) and the mixture was heated under reflux for three hours. The product that separated out on cooling was collected.

C) To a solution of **14** (0.8 g) in glacial acetic acid (15 ml) was added 36% hydrochloric acid (10 ml) and the mixture was refluxed on a water-bath for one hour. The reaction mixture was then poured onto crushed ice to give a sticky product which was solidified after two days.

D) A suspension of **14** (0.2 g) in polyphosphoric acid (2 g) was heated on a water-bath for thirty minutes. The reaction mixture was neutralized with sodium bicarbonate solution and the product which separated out was filtered off, washed with water and dried.

For the methods of preparation, yields and physical data see Table III.

2-(*p*-Bromophenyl)-4-[2-(*p*-chlorophenyl)ethyl]-4-hydroxy-6-(substituted-phenyl)-2,3,4,5-tetrahydropyridazin-3-ones 14.

They were obtained by the above method (A) using **8a-d** and *p*-bromophenylhydrazine (instead of hydrazine hydrate). Yields and physical properties are summarized in Table IV.

Substituted Benzylpyruvic Acid Hydralazones 19. General Procedure.

A solution of the appropriate sodium salt of substituted benzyl pyruvic acid (4.6 mmoles) in water (20 ml) was treated with a solution of hydralazine hydrochloride (4.6 mmoles) in water (10 ml) with stirring. The yellow precipitate which separated out immediatly, was filtered off, washed with water and dried.

p-Chlorobenzylpyruvic Acid Hydralazone (**19a**).

Compound **19a** was obtained in a yield of 75%, mp 176°; ir (potassium bromide): 1700, 3080 cm⁻¹.

Anal. Calcd. for $C_{18}H_{15}ClN_4O_2$: C, 60.9; H, 4.2; N, 15.8. Found: C, 60.5; H, 4.3; N, 16.0.

p-Methylbenzylpyruvic Acid Hydralazone (**19b**).

Compound **19b** was obtained in a yield of 78%, mp 165°; ir (potassium bromide): 1680, 1800-3300 cm⁻¹.

Anal. Calcd. for $C_{19}H_{18}N_4O_2$: C, 68.3; H, 5.4; N, 16.8. Found: C, 68.5; H, 5.6; N, 16.9.

as-Triazino[3,4-*a*]phthalazines **20**. General Procedure.

A suspension of the hydralazone **19** (1.25 g) in polyphosphoric acid (20 g) was heated on a water-bath for one hour. The reaction mixture was neutralized with sodium bicarbonate solution and the pricipitated product was collected.

3-[2-(*p*-Chlorophenyl)ethyl]-4*H*-*as*-triazino[3,4-*a*]phthalazin-4-one (**20a**).

Compound **20a** was obtained in a yield of 97%, mp 266°; ir (potassium bromide): 1680 cm⁻¹; ¹H nmr (deuteriochloroform): δ 3.30 (m, 4H, CH₂CH₂), 7.20, 7.88, 8.90 (3m, 9H, ArH).

Anal. Calcd. for $C_{18}H_{13}ClN_4O$: C, 64.2; H, 3.9; N, 16.6. Found: C, 64.6; H, 4.3; N, 16.8.

3-[2-(*p*-Methylphenyl)ethyl]-4*H*-*as*-triazino[3,4-*a*]phthalazin-4-one (**20b**).

Compound **20b** was obtained in a yield of 81%, mp 221°: ir (potassium bromide): 1680 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.30 (s, 3H, CH₃), 3.23 (m, 4H, CH₂CH₂), 7.13, 7.90, 8.87 (3m, 9H, ArH).

Anal. Calcd. for $C_{19}H_{16}N_4O$: C, 72.2; H, 5.1; N, 17.7. Found: C, 72.2; H, 5.5; N, 17.6.

REFERENCES AND NOTES

[1] This is Part I of the series "Keto Acids and Lactones", A Part of the series "Scope of the Reactions of Hydrazines and Hydrazones".

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