607. *Pyridazines. Part II.*[1] *The Action of Grignard Reagents on 6-Aryl-2,3,4,5-tetrahydro- and -2,3-dihydropyridazin-3-ones*

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6-Aryl-2,3,4,5-tetrahydropyridazin-3-ones react with phenyl- and *p*-anisyl-magnesium bromide to give 3,6-diaryl-4,5-dihydropyridazines, which are spontaneously dehydrogenated to 3,6-diarylpyridazines. 6-Aryl-2,3-dihydropyridazin-3-ones, prepared by dehydrogenation of 6-aryl-2,3,4,5-tetrahydropyridazin-3-ones by bromine in acetic acid, react with phenylmagnesium bromide to give 6-aryl-2,3,4,5-tetrahydro-4-phenylpyridazin-3-ones. The structures assigned to the products are established by ultraviolet, infrared, and n.m.r. spectroscopy.

6-Aryl-2,3,4,5-tetrahydropyridazin-3-ones (Ia, b, c, and d) react with phenyl- and *p*-anisyl-magnesium bromide to give 3-aryl-6-phenyl- (IVa, b, c, and d) and 3-*p*-anisyl-6-arylpyridazines (IVc, e, f, and g), respectively. The product (IVc) obtained by the action of phenylmagnesium bromide on 6-*p*-anisyl-2,3,4,5-tetrahydropyridazin-3-one (Ic) is identical with that obtained by the action of *p*-anisylmagnesium bromide on 2,3,4,5-tetrahydro-6-phenylpyridazin-3-one (Ia).

The infrared spectra of the products lack the bands characteristic of OH, NH, and CO groups. This indicates that the reaction takes place by addition to the carbonyl group followed by elimination of water. Analytical data, however, indicate that these products have lost two hydrogen atoms, *i.e.*, they are pyridazines (IV) rather than 4,5-dihydropyridazines (III). The similarity of these compounds in their ultraviolet spectra (in ethanol) indicates that they all possess identical structures; their spectra are also very similar to that of terphenyl [2] (Table 1).

[1] Part I, T. Abdel-Nour, F. G. Baddar, and A. K. Fateen, *J.*, 1964, 5302.
[2] A. Gillam and E. S. Stern, "Electronic Absorption Spectra of Complex Molecules," Methuen, London, 1956, p. 210.

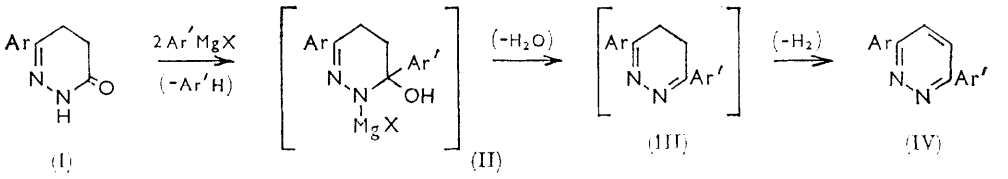
TABLE 1

Ultraviolet spectra of pyridazines

Compound	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$
(IVa)	279	27,800	231	6130
(IVb)	284	33,040	236	7040
(IVc)	298	37,600	241	6390
(IVd)	284	36,950	235	5200
(IVe)	299	38,060	244	5400
(IVf)	305	39,940	245	3590
(IVg)	302	38,580	242	6090
p-Terphenyl	276 *	35,000		
	280 †	25,000		

* In cyclohexane. † In chloroform.

Their structure, however, is rigidly established by the fact that the product of interaction of phenylmagnesium bromide with 2,3,4,5-tetrahydro-6-phenylpyridazin-3-one (Ia) is identical with 3,6-diphenylpyridazine (IVa), prepared by heating dibenzoylethylene with



Ar	Ar′	Ar	Ar′
a: Ph	Ph	c: *p*-C_6H_4·Me	*p*-C_6H_4·OMe
b: *p*-C_6H_4·Me	Ph	f: *p*-C_6H_4·OMe	*p*-C_6H_4·OMe
c: *p*-C_6H_4·OMe	Ph	g: *p*-C_6H_4Cl	*p*-C_6H_4·OMe
d: *p*-C_6H_4Cl	Ph		

hydrazine hydrate.[3] The ease of dehydrogenation of 3,6-diaryl-4,5-dihydropyridazines (III) to 3,6-diarylpyridazines (IV) has been described by Campbell and Khanna,[4] and established in the present investigation.

However, the compound of m. p. 266°, described by Campbell and Khanna [4] as 3,6-diphenylpyridazine, is different from that reported [3] and that now prepared (m. p. 219—220°). The experiment of Campbell and Khanna, involving heating of the hydrazone of *trans*-dibenzoylethylene in glacial acetic acid, was repeated, and the mixture was heated on a boiling-water-bath for 5 min. and for 30 min. In both cases three compounds, m. p. 219—220, 266, and 327—328°, were isolated in nearly equal amounts. However, when the mixture was only heated for 1 min. the compound of m. p. 219—220° was the main product mixed with traces of that melting at 327—328°. The compound of m. p. 219—220° is proved to be 3,6-diphenylpyridazine, but the other two compounds, although they gave the same analytical data as 3,6-diphenylpyridazine, have not yet had their structure established.

6-Aryl-2,3-dihydropyridazin-3-ones (V) are prepared by the dehydrogenation of the corresponding 6-aryl-2,3,4,5-tetrahydropyridazin-3-ones with bromine in glacial acetic acid.[5] Attempts to prepare 2,3-dihydro-6-*p*-tolylpyridazin-3-one (Vb) by heating β-*p*-toluoylacrylic acid with hydrazine hydrate gave a mixture of compound (Vb), and an unidentified high-melting product.

The infrared spectra of the 3-pyridazones (V) show a strong band between 1650 and 1680 $cm.^{-1}$ (Table 2) characteristic of the stretching frequency of the carbonyl group of cyclic amides.[6a] A shift of these bands to lower frequency (10—20 $cm.^{-1}$) as compared

[3] C. Paal and H. Schulze, *Ber.*, 1900, **33**, 3798.
[4] N. Campbell and N. M. Khanna, *J.*, 1949, 33S.
[5] E. A. Steck, R. P. Brundage, and L. T. Fletcher, *J. Amer. Chem. Soc.*, 1953, **75**, 1117.
[6] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1961, (*a*) p. 205; (*b*) p. 136; (*c*) p. 208; (*d*) p. 96; (*e*) p. 179.

TABLE 2

Infrared spectra of 3-pyridazones

Compound	NH and OH bands (cm.$^{-1}$) Solid (KBr)	Solution ($CHCl_3$)	CO of cyclic amide (KBr)
(Va)	3125—2860(br)	3448(sh); 3225—3030(br)	1650 *
(Vb)	3125—2880	3390(sh); 3125—3030	1650 *
(Vc)	3030—2860	3560(sh); 3333—3030	1650 *
(Vd)	3030—2940	3670, 3500(w); 3280—3125	1653 *
(Ve)	3125—2940	3485; 3225—3030	1656 *
(Vf)	3077—2899	3510; 3175—3030	1680
(Vg)	—	—	1666 (CCl_4)
(Vi)	—	—	1666 ,,
(Vj)	—	—	1660 ,,
(VIa)	3270, 3125(sh)	3450, 3270(sh)	1680
(VIb)	3333, 3205	3550, 3370	1686
(VIc)	3333, 3145	3500, 3310	1667
(VId)	3226, 3125	3448, 3226	1680
(VIe)	3250, 3125		1666

* A weak shoulder an 6 μ appeared at low concentrations.

with those of the corresponding 6-aryl-2,3,4,5-tetrahydropyridazin-3-ones [1] is attributed to the conjugation of the carbonyl group in the former compounds with a double bond.[6b]

The infrared spectra of the 6-aryl-2,3-dihydropyridazin-3-ones (V), however, differ from those of the 6-aryl-2,3,4,5-tetrahydropyridazin-3-ones (I) in the 3 μ region. Thus, whereas the latter compounds show two sharp bands in this region when run in the condensed phase (KBr),[1] the former show only one very broad band. When the spectra of (V), however, are run in chloroform, a weak sharp band and a strong broad band appear in the 3 μ region (Table 2).

The two sharp bands in the 3 μ region of the spectra of the 3-pyridazinones (I) [1] and (VI) (Table 2) indicate that these compounds are dimeric in the solid state,[6c] but monomeric in solution. The strong broad band in the spectra of 3-pyridazones (V) may indicate the partial existence of these compounds in the lactim form in polymeric association.[6d]

The ultraviolet spectra (in ethanol) of the 3-pyridazones (V) (Table 3) show that these compounds absorb at a shorter wavelength than the corresponding 3-pyridazinones (I).[1]

TABLE 3

Ultraviolet spectra of 3-pyridazones

Compound	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$
(Va)*	249	23,800	220	9100
(Vb)	256·5	26,770	223	8950
(Vc)	268	28,250	222	6900
(Vd)	257	27,700	220	8500
(VIa)	286	14,960	240	3290
(VIb)	289	16,670	242	4160
(VIc)	296	19,000	244	3170
(VId)	289	16,900	243	5240

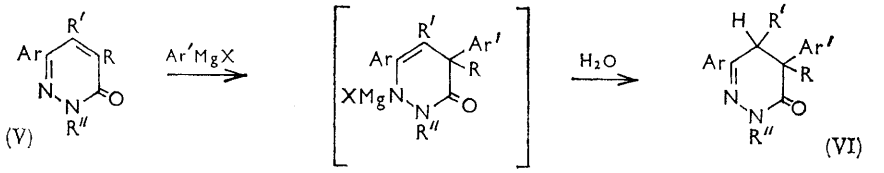
* S. Dixon, H. Gregory, and L. F. Wiggins, *J.*, 1949, 2139, gave $\lambda_{max.}$ 251·5 ($\varepsilon_{max.}$ 10,000).

This hypsochromic shift may be due to their existence in the lactim form, which confers on the molecule an aromatic character like benzene. Their spectra are very similar to that of biphenyl ($\lambda_{max.}$ 250 mμ, $\varepsilon_{max.}$ 18,000).[2]

The *N*-methyl derivatives (Vg, h, i, and j) are prepared by the action of dimethyl sulphate on an alkaline solution of the 3-pyridazones (Va, b, c, and d). The infrared spectra of compounds (Vg, i, and j) (in CCl_4) showed a strong sharp band between 1660 and 1667 cm.$^{-1}$, characteristic of the carbonyl of cyclic amides, whereas the NH band in the 3 μ region disappeared. This indicates that they are *N*-methyl and not *O*-methyl derivatives.

When 2,3-dihydro-6-*p*-tolylpyridazin-3-one was heated with phosphorus pentachloride at 100° it gave 3-chloro-6-*p*-tolylpyridazine. Its structure is supported by its infrared spectrum, from which the C=O and NH bands are absent.

Action of Phenylmagnesium Bromide on 3-Pyridazones (V).—When 3-pyridazones (Va, b, c, and d) reacted with phenylmagnesium bromide they gave compounds having a



	Ar	Ar'	R	R'	R''
(V and VI) a	Ph	Ph	H	H	H
b	*p*-C_6H_4·Me	Ph	H	H	H
c	*p*-C_6H_4·OMe	Ph	H	H	H
d	*p*-C_6H_4Cl	Ph	H	H	H
e	Ph	H	H	Ph	H
(V) f	Ph	—	Ph	H	H
g	Ph	—	H	H	Me
h	*p*-C_6H_4·Me	—	H	H	Me
i	*p*-C_6H_4·OMe	—	H	H	Me
j	*p*-C_6H_4Cl	—	H	H	Me

3-pyridazinone structure (VI). This was inferred from a study of their infrared, electronic, and nuclear magnetic resonance n.m.r. spectra. Their infrared spectra show two sharp bands in the 3 μ region and a sharp strong band in the 6 μ region (cf. VIa, b, c, and d in Table 2), very similar to the previously published data for 3-pyridazinones.[1] This is also supported by the n.m.r. spectrum of (VIc) which shows that the compound contains a $-CH_2-CH-$ group.*

The ultraviolet spectra of compounds (VIa, b, c, and d) (Table 3) are identical and are very similar to those of 2,3,4,5-tetrahydropyridazin-3-ones (Ia, b, c, and d).[1] This shows that the reaction takes place by 1,4-addition of the Grignard reagent either to the α,β-unsaturated C=O or C=N group to give rise to 6-aryl-2,3,4,5-tetrahydro-5- or -4-phenylpyridiazin-3-ones, respectively. The differentiation between these two structures is only possible by comparison with an authentic specimen. Thus 2,3,4,5-tetrahydro-4,6-diphenyl- (VIa) and -5,6-diphenyl-pyridazin-3-one (VIe) were prepared by heating β-benzoyl-α- and -β-phenylpropionic acid, respectively, with hydrazine hydrate. The product from 2,3-dihydro-6-phenylpyridazin-3-ones (Va) and phenylmagnesium bromide was identical with 2,3,4,5-tetrahydro-4,6-diphenylpyridazin-3-one (VIa) (mixed m. p. and infrared spectra). Also, heating of compound (VIa) with sodium hydroxide solution caused cleavage to β-benzoyl-α-phenylpropionic acid (a reaction characteristic of 3-pyridazinones).[7a] This indicates that the reaction takes place by 1,4-addition to the α,β-unsaturated cyano-group to give rise to 6-aryl-2,3,4,5-tetrahydro-4-phenylpyridazin-3-ones.

The failure of a Grignard reagent to add to the α,β-unsaturated carbonyl group may be due to the presence of the 3-pyridazones (IV) in solution in the lactim form.[7b]

Recently, Mostafa *et al.*[8] reported that 2,3-dihydro-6-phenyl-pyridazin-3-one with phenylmagnesium bromide gives 3,6-diphenylpyridazine (*i.e.*, 1,2-addition to the carbonyl group). This reaction was repeated under their conditions, and the product was a mixture of the starting material (major) and 2,3,4,5-tetrahydro-4,6-diphenylpyridazin-3-one (VIe) (minor).

* This was kindly run by Dr. A. Malera, research chemist, Varian A.G., Zurich.

[7] W. G. Overend, L. M. Turton, and L. F. Wiggins, *J.*, 1950, (*a*) p. 3505; (*b*) p. 3500.

[8] A. Mustafa, W. Asker, A. H. Harhash, K. M. Foda, H. H. Jahine, and N. A. Kassab, *Tetrahedron*, 1964, **20**, 531.

Attempted Synthesis of 1,2,3,6-*Tetrahydro*-6,6-*diphenylpyridazin*-3-*one*.—γγ-Diphenyl-γ-butyrolactone reacts with hydrazine hydrate to give 1,2,3,4,5,6-hexahydro-6,6-diphenylpyridazin-3-one. Its infrared spectrum shows two bands, at 3333 and 1667 cm.$^{-1}$, characteristic of the stretching frequency of the NH and CO of cyclic amides. Attempted dehydrogenation of this compound to 1,2,3,6-tetrahydro-6,6-diphenylpyridazin-3-one by bromine in acetic acid gave 4-hydroxy-4,4-diphenylbut-2-enoic acid lactone, owing to the cleavage of the former compound to γγ-diphenyl-γ-butyrolactone before dehydrogenation.

The structure of the unsaturated lactone was established by its infrared spectrum which showed a band at 1750 cm.$^{-1}$ characteristic of the CO of α,β-unsaturated γ-lactones,[6e] and by its identity with an authentic specimen prepared by the dehydrogenation of γγ-diphenyl-γ-butyrolactone with bromine in glacial acetic acid.

Experimental

Infrared and ultraviolet spectra were measured on Perkin-Elmer Infracord 137 and Spectracord 4000 A spectrophotometers, respectively.

Action of Hydrazine Hydrate on trans-*Dibenzoylethylene Monohydrazone*.—(i) A hot solution of *trans*-dibenzoylethylene (5 g.) in n-butanol (25 ml.) was treated portionwise with 85% hydrazine hydrate (5 ml.), and the mixture refluxed for 3 hr. The crystals which separated on cooling were recrystallised from ethanol to give 3,6-diphenylpyridazine (IVa), m. p. 219—220° (Found: C, 82·55; H, 5·3; N, 12·0. Calc. for $C_{16}H_{12}N_2$: C, 82·7; H, 5·2; N, 12·1%).

(ii) A solution of *trans*-dibenzoylethylene monohydrazone [4] (0·9 g.) in glacial acetic acid (2 ml.) was heated on a boiling-water-bath for 5 min. and for 30 min. The solid obtained on cooling was filtered off, m. p. 254—295°. It was crystallised from benzene to give compound (A) (0·3 g.), m. p. 327—328° (Found: C, 82·8; H, 5·1; N, 12·2%; *M*, 395. Calc. for $C_{32}H_{24}N_4$: C, 82·7; H, 5·2; N, 12·1%; *M*, 464·5).

The benzene mother-liquor was concentrated to give compound (B) (0·15 g.), m. p. 266—267° (Found: C, 82·8; H, 5·5; N, 11·7%; *M*, 383. Calc. for $C_{32}H_{24}N_4$: C, 82·7; H, 5·2; N, 12·1%; *M*, 464·5).

The remaining glacial acetic acid solution was diluted with water and left overnight. The precipitate (0·2 g.) was crystallised from ethanol to give 3,6-diphenylpyridazine, m. p. 219—220°, undepressed on admixture with the compound obtained by the previous method.

When the above reaction mixture was only heated for one minute, it gave mainly 3,6-diphenylpyridazine (0·5 g.) together with traces of compound *A* (0·02 g.).

Action of Hydrazine Hydrate on Dibenzoylethane.—A hot solution of dibenzoylethane (2 g.) in n-butanol (10 ml.) was treated with 85% hydrazine hydrate (2 ml.), and refluxed for 3 hr. in nitrogen. The product (0·9 g.), precipitated on cooling, had m. p. 140—180°, with gas evolution. On repeated crystallisation from ethanol, 3,6-diphenylpyridazine was obtained, m. p. and mixed m. p. 219—220°. When the crude product, m. p. 140—180°, was heated at 200—210° until gas evolution stopped, it remelted at 206—220°.

6-*Aryl*-2,3-*dihydropyridazin*-3-*ones* (Va—c, e, and f).—A solution of the 6-aryl-2,3,4,5-tetrahydropyridazin-3-ones (Ia—c) and (VIe and a) (0·11 mole) in glacial acetic acid (20 ml.) was mechanically stirred and treated portionwise with bromine (0·12 mole) at 60—70°. The solution was further stirred for 3 hr. then cooled in ice. The precipitated pale yellow product was filtered off, washed several times with cold ethyl acetate, and stirred with concentrated ammonium hydroxide for 15 min. The product was filtered off, dried, and crystallised from ethanol (Table 4).

Methylation of 6-*Aryl*-2,3-*dihydropyridazin*-3-*one*.—A solution of the 6-aryl-2,3-dihydropyridazin-3-one (Va—d) (0·013 mole) in 30% sodium hydroxide solution (2 ml.) was treated portionwise with dimethyl sulphate (0·02 mole), and the mixture was warmed at 70° for 2 hr.[7b] Water was distilled off under reduced pressure and the residue extracted with hot benzene. The benzene layer was washed with water, dried, and distilled off. The product was crystallised from light petroleum (b. p. 100—120°) to give the *N*-methyl derivatives (Vg—j), respectively (Table 4).

TABLE 4

3-Pyridazones (V)

Compd.	M. p.	Yield (%)	Found (%) C	H	N	Cl	Formula	Required (%) C	H	N	Cl
(Va)	199—200°	90	69·75	4·65	9·3		$C_{10}H_8N_2O$	69·75	4·7	9·3	
(Vb)	220—221 *	90	70·5	5·4	8·6		$C_{11}H_{10}N_2O$	70·95	5·3	9·0	
(Vc)	186—187	90	65·8	4·9	13·6		$C_{11}H_{10}N_2O_2$	65·3	5·0	13·9	
(Ve)	177—178	100	77·4	4·7	11·5		$C_{16}H_{12}N_2O$	77·40	4·9	11·3	
(Vf)	186—187	100	77·6	4·85	11·3		$C_{16}H_{12}N_2O$	77·40	4·9	11·3	
(Vg)	105—106	80	71·00	5·6	14·8		$C_{11}H_{10}N_2O$	70·95	5·4	15·05	
(Vh)	116—117	70	71·7	6·1	14·4		$C_{12}H_{12}N_2O$	72·0	6·0	14·0	
(Vi)	106—107	80	66·35	5·6	13·05		$C_{12}H_{12}N_2O_2$	66·65	5·6	13·0	
(Vj)	236—237	90	60·4	4·3	12·05	15·5	$C_{11}H_9N_2OCl$	59·9	4·1	12·7	16·1

* When β-*p*-toluoylacrylic acid (10 g.) was heated with 85% hydrazine hydrate (10 ml.) in isobutyl alcohol (50 ml.), a mixture of (Vb) (1·5 g.), m. p. 220—221°, and a compound (2·5 g.), m. p. 328—329° (pale yellow crystals from acetic acid) (Found: C, 71·3; H, 5·5; N, 15·6) was obtained but the structure of the latter is not yet established.

3-*Chloro*-6-p-*tolylpyridazine*.—A powdered mixture of 2,3-dihydro-6-*p*-tolylpyridazin-3-one (6·8 g.) and phosphorus pentachloride (34 g.) was heated at 100° for 1 hr. The cold mixture was made alkaline with sodium hydroxide solution, and extracted with chloroform. The product, m. p. 149—152°, was crystallised from light petroleum (b. p. 100—120°) to give 3-*chloro*-6-p-*tolylpyridazine* (60%), m. p. 153—154° (Found: C, 64·7; H, 4·6; Cl, 17·6; N, 13·1. $C_{11}H_9ClN_2$ requires C, 64·5; H, 4·4; Cl, 17·35; N, 13·7%).

Action of Grignard Reagents on 6-*Aryl*-2,3,4,5-*tetrahydropyridazin*-3-*ones*.—A solution of the arylmagnesium bromide [prepared from 0·07 mole bromobenzene or *p*-bromoanisole (0·07 mole- and magnesium (0·07 g.-atom)] in dry ether (50 ml.) was added to a hot solution of the 6-aryl)

TABLE 5

Pyridazines (IV) and 3-pyridazinones (VI)

Cmpd.	M. p.	Yield (%)	Solvent	Found (%) C	H	N	Cl	Formula	Required (%) C	H	N	Cl
(IVa)	219—220° *	70	Benzene	82·55	5·3	12·1		$C_6H_{12}N_2$	82·7	5·2	12·1	
(IVb)	185—186	70	Benzene	82·8	5·8	11·45		$C_{17}H_{14}N_2$	82·9	5·7	11·4	
(IVc)	195—196	70	Benzene	77·6	5·3	10·9		$C_{17}H_{14}N_2O$	77·8	5·4	10·9	
(IVd)	230—231	80	Xylene	72·2	4·15	11·0	13·5	$C_{16}H_{11}N_2Cl$	72·2	4·1	10·5	13·3
(IVe)	215—216	60	Benzene	77·6	6·1	10·1		$C_{18}H_{16}N_2O$	78·2	5·8	10·1	
(IVf)	234—235	40	Xylene	73·9	5·6	9·6		$C_{18}H_{16}N_2O_2$	73·95	5·5	9·6	
(IVg)	239—240	50	Xylene	68·3	4·2	9·4	11·9	$C_{17}H_{15}N_2OCl$	68·8	4·4	9·4	12·0
(VIa)	165—166 †	55	Ethanol	77·0	5·7	11·45		$C_{16}H_{14}N_2O$	76·8	5·6	11·2	
(VIb)	176—177	60	Ethanol	76·4	5·95	10·9		$C_{17}H_{16}N_2O$	77·25	5·8	10·6	
(VIc)	167—168	70	Ethanol	73·0	5·65	10·1		$C_{17}H_{16}N_2O_2$	72·8	5·75	10·0	
(VId)	163—164	60	Xylene	67·2	4·7	9·5	12·5	$C_{16}H_{12}N_2OCl$	67·5	4·6	9·8	12·5

* Campbell and Khanna [3] and Mostafa *et al.*[8] give the same m. p. † Identical with an authentic specimen, m. p. 167—168°, prepared by heating β-benzoyl-α-phenylpropionic acid (5 g.) with 85% hydrazine hydrate (5 ml.) in isobutyl alcohol (25 ml.) (Found: C, 77·2: H, 5·8; N, 11·2%).

2,3,4,5-tetrahydropyridazin-3-one (0·023 mole) in dry benzene (100 ml.). The mixture was refluxed for 6 hr. on a boiling-water-bath, left overnight at room temperature, then decomposed with a saturated solution of ammonium chloride. A solid was immediately deposited which was filtered off, or else the organic solvent layer was separated and the solvent removed. The products (IV) were crystallised from suitable solvents (Table 5).

Action of Phenylmagnesium Bromide on 6-*Aryl*-2,3-*dihydropyridazin*-3-*ones*.—A solution of phenylmagnesium bromide [prepared from bromobenzene (0·07 mole) and magnesium (0·07 g.-atom)] in dry ether (50 ml.) was added to a hot suspension of the 6-aryl-2,3-dihydropyridazin-3-one (0·023 mole) in dry benzene (100 ml.). The mixture was refluxed for 8 hr. on a boiling-water-bath, left overnight at room temperature, then decomposed with a saturated solution of ammonium chloride. The organic layer was separated, the solvent removed, and the product (VI) crystallised from a suitable solvent (Table 5).

Cleavage of 2,3,4,5-*Tetrahydro*-6-*phenyl- and* -4,6-*diphenyl-pyridazin*-3-*one*.—(i) *With hydrochloric acid*. A solution of 2,3,4,5-tetrahydro-6-phenylpyridazin-3-one (2·0 g.) in ethanol

(50 ml.) was heated with concentrated hydrochloric acid (30 ml.) on a boiling-water-bath, for 30 min.[9] The precipitated solid was crystallised from water–ethanol to give hydrazine hydrochloride (0·5 g.), m. p. 203°. The original filtrate was diluted with water, and the precipitated solid was extracted with sodium carbonate solution, filtered, and acidified. The precipitated acid was identified as β-benzoylpropionic acid (0·2 g.) by m. p. and mixed m. p. 115—116°.

(ii) *With sodium hydroxide.* The above pyridazinone (2 g.) was heated with 30% sodium hydroxide solution (10 ml.) on a boiling-water-bath for 3 hr.[7a] The product (1·5 g.), precipitated on acidification, was extracted with sodium carbonate solution, filtered, acidified, and crystallised from benzene to give β-benzoylpropionic acid, m. p. and mixed m. p. 115—116°.

2,3,4,5-Tetrahydro-4,6-diphenylpyridazin-3-one (1·0 g.) was similarly heated with 30% sodium hydroxide solution (10 ml.). The product (0·6 g.) was crystallised from benzene to give β-benzoyl-α-phenylpropionic acid, m. p. and mixed m. p. 154°.

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[9] W. G. Overend and L. F. Wiggins, *J.*, 1947, 239.