The thienyl chromones were sparingly soluble in cold amyl alcohol and hence, the process was modified as described. M.p.s, yields and solvents of crystallisation are given below :

IIIa, 202-03°, 60%, ethanol ;
IIIb, 192-93°, 65%, ethanol ;
IIIc, 194-95°, 50%, ethanol ;
IIId, 180-81°, 50%, ethanol ;
IIIe, 197-98°, 75%, ethanol ;
IIIf, 222-23°, 55%, acetic acid.

Preparation of 3-Hydroxychromones :

To a well cooled solution of a chalcones (0.001 mole) in methanol containing NaOH solution (2%, 3 ml), was added with stirring, H_2O_2 (30%, 2.5 ml) in drops and left overnight in a refrigerator. The solid was worked up as usual and recrystallised from acetic acid. The m.p., and yields are as under :

IVa, 262-63°, 60% ; IVb, 265-66°, 75% ;
IVc, 269-70°, 78% ; IVd, 245-46°, 55% ;
IVe, 256-57°, 72% ; IVf, 254-55°, 50%.

Ir Values :

γ_{max}^{KBr} IVa, 3260, 1610 ; IVb, 3260, 1640 ; IVc, 3260, 1635 ; IVd, 3250, 1610 ; IVe, 3260, 1600 ; IVf, 3180, 1605.

Acetylation of 3-Hydroxychromones :

Mere heating of the 3-hydroxychromones with acetic anhydride and cooling gave quantitative yields of the corresponding acetyl derivatives.

Va, 215-16° ; Vb, 184-85° ; Vc, 214-15° ;
Vd, 204-05° ; Ve, 182-83° ; Vf, 224-25°.

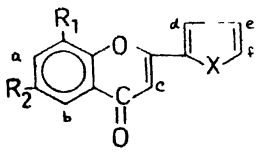
Preparation of Chromones from-β-Diketones :

The chromones were obtained by the usual procedure[1]. The yields were :

IIIa, 80% ; IIIb, 75% ; IIIc, 70% ;
IIId, 85% ; IIIe, 92% ; IIIf, 90%.

Usual ir peaks were observed in all the cases.

PMR Data (in δ) ; solvent $CDCl_3$:



III(a-c) ; X=O
III(d-f) ; X=S

CH_3 protons	a	b	c	d	e	f
IIIa 2.47	7.69	7.90	6.70	7.21	6.60	7.60
IIIb 2.51	7.58	8.10	6.69	7.08	6.60	7.58
IIIc	7.82	8.09	6.70	7.21	6.60	7.61
IIId	7.81	8.07	6.67	7.75	7.16	7.58
IIIe 2.44	7.70	7.87	6.68	7.70	7.16	7.54
IIIf 2.55	7.5-7.7	8.10	6.66	7.5-7.7	7.16	7.5-7.7

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Synthesis and Reactions of *p*-(Diphenylphosphino)benzoic Acid

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A number of workers[1,2] have prepared *p*-(diphenylphosphino) benzoic acid (1). In this investigation we wish to report a convenient method for the preparation of (1) and some of its reactions.

$(C_6H_5)_2P\text{-}C_6H_4COOH\text{-}p$ (1) $(C_6H_4)_2P\text{-}C_6H_4CH_3\text{-}p$ (2)

We prepared the acid (1) by a one-step oxidation of *p*-tolyldiphenylphosphine, (2) using potassium permanganate, instead of the reported two-step oxidation[3]. Also, the phosphine (2) was prepared from *p*-tolyldichlorophosphine, $p\text{-}CH_3C_6H_4PCl_2$, and phenylmagnesium bromide. The ir spectra

TABLE 1—*p*-(DIPHENYLPHOSPHINO)BENZANILIDES 3a-e AND BENZOYLHYDRAZONES 5a-e

Compd.	Ar	m.p.°C	Yield%	Solvent of Cryst.	Molecular Formula
3a	C_6H_5	185	65	E	$C_{25}H_{20}NO_2P$
b	*m*-ClC_6H_4	108	70	B	$C_{25}H_{19}ClNO_2P$
c	*p*-$CH_3C_6H_4$	196	74	B	$C_{26}H_{22}NO_2P$
d	*m*-$CH_3OC_6H_4$	225	45	E	$C_{26}H_{22}NO_3P$
e	*p*-$CH_3OC_6H_4$	208	80	E/H_2O	$C_{26}H_{22}NO_3P$
5a	*o*-ClC_6H_4	over 250	75	B	$C_{26}H_{20}ClN_2O_2P$
b	*m*-ClC_6H_4	234	68	E	$C_{26}H_{20}ClN_2O_2P$
c	*p*-ClC_6H_4	242	88	A	$C_{26}H_{20}ClN_2O_2P$
d	*p*-$O_2NC_6H_4$	over 250	80	A	$C_{26}H_{20}N_3O_4P$
e	3,4-$O_2CH_2C_6H_3$	over 250	70	A	$C_{27}H_{21}N_2O_4P$

A=Acetic Acid ; B=Benzene ; E=Ethanol.
: All the compounds gave satisfactory C, H and N analysis.

of the acid (1) showed absorption bands at 1240 cm^{-1} (P=O)[4a], 1430 cm^{-1} (P-C_6H_5)[4b] and 1700 cm^{-1} (C=O).

The structure of the phosphinobenzoic acid (1) is further confirmed by converting its acid chloride to anilides (3a-e) and the methyl ester to the hydrazide (4). Reaction of the hydrazide with aromatic aldehydes afforded the hydrazones (5a-e). The ir spectra of the anilides and the hydrazide showed an amide I band at 1650-1680 cm^{-1} and amide II band at 1540-1560 cm^{-1}. The hydrazones showed the C=N band at 1560 cm^{-1}. All the compounds showed the characteristic P=O stretching at 1180-1190 cm^{-1} and the νP-C_6H_5 at 1460 cm^{-1}.

A-CONHAr (3)
3a, Ar=C_6H_5
b, =*m*-ClC_6H_4
c, =*p*-$CH_3C_6H_4$
d, =*m*-$CH_3OC_6H_4$
e, =*p*-$CH_3OC_6H_4$

A-CONHNH$_2$ (4)

A-CONHN=CHAr' (5)
5a-c, Ar'=*o,m,p*-ClC_6H_4
5d, Ar'=*p*-$NO_2C_6H_4$
5e, Ar'=$CH_3O_2C_6H_3$

A-=$(C_6H_5)_2$P(O)-C_6H_4

Experimental

Melting points are uncorrected. Ir spectra were recorded on a Beckman IR-SA unit as KBr pellets. *p*-Tolyldichlorophosphine was prepared by the method previously described[5]. *p*-Tolyldiphenylphosphine (2) was prepared by adding *p*-tolyldichlorophosphine (one mole) to phenylmagnesiumbromide (2.2 mole) in dry THF. The reaction mixture was worked up as reported by Monagle[2]. The phosphine (2) was then oxidized to the acid (1) by cautiously adding it to an ice-cooled solution of potassium permanganate and the mixture was then heated on a steam bath for 7 hr. The reaction mixture was then treated as reported by Morgan[5]. Yield 87%. m.p. 273-274°.

p-(Diphenylphosphino)benzanilides (3a-e) :

The acid chloride of (1) was prepared by refluxing 2 g of the acid with thionyl chloride (10 ml) until solution was complete (5 hr). The excess thionyl chloride was distilled off and the residue pumped off. To the acid chloride, the equivalent two moles of the aromatic amine was added in dry benzene. The mixture was then refluxed for 4 hrs, cooled and filtered. The solid product was dried, washed with water, dil. HCl, and finally with water. The product was crystallised from the proper solvent. The physical data are in Table 1.

p-(*Diphenylphosphino*) *benzoic hydoazide (4) :*

Methyl *p*-(diphenylphosphino)benzoate was prepared according to known procedure[6]. The hydrazide was then prepared by dissolving the methyl ester (0.1 mole) in 100 ml ethanol. Hydrazine hydrate (6.5 ml) was added and the mixture was heated on a steam bath for 6 hr. The colorless crystals which were separated on concentration and cooling was collected and crystallised from water. Yield 60%, m.p. 98°.

Analysis for $C_{19}H_{17}N_2O_2P$, Calcd : C, 67.86; H, 5.06; N, 8.33, Found : C, 67.65; H, 5.12; N, 8.24.

p-(Diphenylphosphino)benzoylhydrazones (5a-e) :

The hydrazide (4) was refluxed with an equivalent amount of the appropriate aromatic aldehyde in ethanol for 6 hr. The hydrazones were generally separated from the cold solution and were filtered and crystallised from proper solvent. The physical data are listed in Table 1.

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Synthesis of Hydrazones of *o*-Ethylmalonanilic Acid Hydrazide as Antitubercular Compounds

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ISONICOTINIC acid hydrazide[1] and its N'-isopropyl derivative are effective drugs in the treatment of human tuberculosis. Although tuberculostatic activity has been shown by some other pyridine and non-pyridine hydrazides none is found superior to isonicotinic acid hydrazide. With a view to reduce toxicity due to free amino group, the condensation products of a number of hydrazides with various aldehydes and ketones were also examined[2]. Hydrazones have been found to possess antibacterial activity[3,4]. In addition they have also been reported to possess antifungal[5,6,7] as well as insecticidal activity[8,9,10,11]. A number of hydrazones have been synthesised through the condensation of *o*-ethylmalonanilic acid hydrazide with a number of aldehydes and ketones. The hydrazide was obtained by the action of hydrazine hydrate on *o*-ethylmalonanilate. The latter was obtained by condensing *o*-ethylaniline[12] with ethyl malonate. Hydrazones were obtained in the usual way.

Experimental

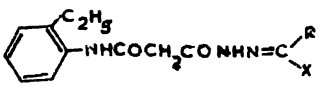
Melting points are uncorrected.

o-Ethylmalonanilate : *o*-Ethylaniline (3.6 g) and ethyl malonate (7.2 g) were taken in a round bottomed flask and the mixture heated to very gentle ebullition with an air condenser. After one hour the mixture was cooled and 10 ml of ethanol was added. The crystals of the dianilide which separated were recrystallised from petroleum ether, m.p. 68°, yield 2.83 g (40%). (Found : C, 65.78 ; H, 7.02 ; N, 5.52 $C_{18}H_{17}NO_3$ requires : C, 66.38 ; H, 7.23 ; N, 5.95%).

o-Ethylmalonanilic acid hydrazide : To *o*-ethylmalonanilate (2 g) dissolved in absolute alcohol (10 ml), 99% hydrazine hydrate (2 ml) was added dropwise with constant stirring. This mixture was set aside for one hour and the solid separated was recrystallised from ethanol, m.p. 156°, yield 97%. (Found : C, 60.30 ; H, 6.24 ; N, 18.77 $C_{11}H_{15}N_3O_2$ requires : C, 59.72 : H, 6.78 ; N, 19.00%).

Preparation of Hydrazones : An alcoholic solution of equimolecular quantities of aldehyde or ketone and *o*-ethylmalonanilic acid hydrazide were refluxed on a water bath for 2 hrs. The reaction mixture was cooled and the solid was filtered, washed with alcohol and crystallised from alcohol-acetic acid (Table 1).

TABLE 1



R	X	Yield (%)	m.p. (°C)	Formula	Analysis(%) Found	Calcd.
Phenyl	H	99	235	$C_{18}H_{19}N_3O_3$	C 69.72	69.90
					H 5.86	6.14
					N 13.24	13.59
2-nitrophenyl	H	51	222	$C_{18}H_{18}N_4O_4$	C 60.58	61.01
					H 4.80	5.09
					N 15.26	15.65
3-nitrophenyl	H	49	220	$C_{18}H_{18}N_4O_4$	C 60.52	61.01
					H 5.13	5.09
					N 15.42	15.65
4-nitrophenyl	H	60	265	$C_{18}H_{18}N_4O_4$	C 60.72	61.01
					H 4.93	5.09
					N 15.62	15.65
2-hydroxyphenyl	H	99	220	$C_{18}H_{19}N_3O_3$	C 66.18	66.46
					H 5.72	5.84
4-hydroxy-3-methoxyphenyl	H	67	195	$C_{19}H_{21}N_3O_4$	C 63.89	64.22
					H 5.22	5.91
					N 11.29	11.83
Phenylvinyl	H	98	206	$C_{20}H_{21}N_3O_2$	C 71.06	71.64
					H 5.73	6.26
					N 11.96	12.53
Furfuryl	H	93	227	$C_{16}H_{17}N_3O_3$	C 63.89	64.21
					H 5.30	5.69
					N 13.67	14.05
Thiophenyl	H	70	207	$C_{16}H_{17}N_3O_2S$	C 60.72	60.90
					H 5.10	5.09
					N 12.89	13.01
Trichloromethyl	H	47	152	$C_{12}H_{14}O_3O_2Cl_3$	C 44.86	44.50
					H 3.60	3.99
4-methylphenyl	CH_3	88	188	$C_{20}H_{23}N_3O_2$	C 70.62	71.21
					H 6.33	6.82

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