uct was obtained when attempts were made to nitrate I in glacial acetic acid.

EXPERIMENTAL[6]

9,12-Diphensuccinadione (II). A modification of Roser's[7] procedure was employed which involved the rapid addition of 20 g. of *meso*-α,β-diphenylsuccinic acid[8] to 50 ml. of concentrated sulfuric acid at 150°. When solution was complete, the reaction mixture was poured onto a stirred mixture of ice and water. The solid product was washed with water, treated with 100 ml. of 10% aqueous sodium carbonate, washed with water, and then air dried. After recrystallization from 95% ethanol, 8.55 g. (50.8%) of II was obtained, m.p. 211–213°.

The Bisformyl derivative of 9,12-diaminodiphensuccindane (III). A solution containing 10 g. (0.043 mole) of II in 15 ml. of 90% formic acid and 100 ml. of formamide was heated at the reflux temperature for 24 hr. Dilution with water gave a crude orange product. Recrystallization from 95% ethanol yielded 8.64 g. (69.1%) of III, m.p. 265–267°.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52. Found: C, 73.54; H, 5.86.

9,12-Diaminodiphensuccindane (IV). A mixture of 5.0 g. (0.017 mole) of II and 50 ml. of 5% hydrochloric acid was heated under reflux for 24 hr. After filtration and basification with 40 ml. 10% aqueous sodium hydroxide, the product was extracted with chloroform. On evaporation of the solvent, 3.74 g. (95%) of IV was obtained which melted at 48–57° after one recrystallization from chloroform-ether. A sample of IV was converted to a yellow-orange picrate by treatment of an ethanolic solution of the base with picric acid. After recrystallization from absolute alcohol, it melted at 242–243°.

Anal. Calcd. for $C_{25}H_{22}O_{14}N_8$: C, 48.51; H, 3.19; N, 16.15. Found: C, 48.07; H, 3.23; N, 15.86.

9,12-Bisdimethylaminodiphensuccindane (V). *Method A.* A solution of 2.90 g. (0.0125 mole) of IV in a mixture of 40 ml. of 88% formic acid and 16.5 g. of 40% formalin was heated at the reflux temperature for 12 hr. After the excess formic acid and formaldehyde had been removed by distillation at reduced pressure, the residue was neutralized with 5% aqueous sodium hydroxide. An oil separated which was extracted with ether. Removal of the ether by distillation gave 2.90 g. (80.5%) of crude product, m.p. 80–83°. After several recrystallizations from 1:1 aqueous ethanol, 1.5 g. (41.7%) of the colorless base was obtained, m.p. 82–83°.

Anal. Calcd. for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.58. Found: C, 82.05; H, 8.46; N, 9.95.

Method B. The bis-formyl derivative was converted directly to IV by heating a mixture containing 3.60 g. of III (0.0125 mole), 40 ml. of 88% formic acid, and 16.5 g. of 40% formalin at the reflux temperature for 12 hr. The product was isolated as described under method A. After recrystallization 0.98 g. (27.2%) of IV was obtained, m.p. 83–84.5°.

*Dimethiodide of 9,12-*Bis*dimethylaminodiphensuccindane* (VI). A solution of 4.5 g. (0.0125 mole) of IV in 100 ml. of methanol was heated under reflux with 8.7 g. (0.061 mole) of methyl iodide for 24 hr. The pale yellow salt which precipitated during this period was recrystallized from 2:1 aqueous ethanol to yield 6.1 g. (69.3%) of the dihydrate of VI, m.p. 270° (decomp.).

Anal. Calcd. for $C_{22}H_{30}N_2I_2{\cdot}2H_2O$: C, 43.13; H, 5.60; N, 4.58. Found: C, 43.39; H, 5.87; N, 4.56.

Dibenzopentalene(I). To a mixture of 700 ml. of benzene and 50 ml. of saturated aqueous sodium hydroxide, 4.0 g. (0.007 mole) of VI dissolved in 30 ml. of water was added with stirring. An atmosphere of nitrogen was maintained in the flask. The hydrocarbon layer became blood red. After 2 hr. the benzene layer was separated and dried. On removal of the bulk of the benzene, red crystals of I separated. The product after recrystallization from 95% ethanol weighed 0.4 g. (28.2%). The compound softened at 270° and decomposed at 285°. Identity of this material was established by comparison of x-ray powder patterns, ultraviolet and infrared spectra with those of a sample prepared by the method of Blood and Linstead.[3]

When 0.09 g. (0.00044 mole) of VI, 20 ml. boiling acetic acid was treated with zinc dust, a colorless solution was obtained from which 0.07 g. (77%) of 10-diphensuccindene, m.p. 204–208° was isolated. A mixture of this material with an authentic sample of 10-diphensuccindene[6] melted at 204–208°.

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(6) Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected.

(7) W. Roser, *Ann.*, **247**, 153 (1888).

(8) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **83**, 995 (1903).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Absorption Spectra of Tetracyclones. V[1]

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Four *p*-phenoxy-, four *p*-phenylthio, and four *o*-fluoro-substituted tetracyclones (tetraphenylcyclopentadienones) have been prepared in order to study their electronic spectra. When referred to the spectrum of the parent compound, the maxima at 342 mμ and at 512 mμ shift in accordance with the previous correlations: a substituent in the 3- and/or 4-phenyl ring affects principally the band at 342 mμ while a substituent in the 2- and/or 5-phenyl ring affects principally the band at 512 mμ. Electron-releasing phenoxy and phenylthio groups shifted their bands bathochromically.

Substitution in the ortho position by fluorine affected the substituted path most, but in this case the shift was to shorter wave lengths with lower intensity. The shift was accompanied by an intensification of the band associated with the unsubstituted path.

The purpose of this investigation was to test the previously published interpretation of the absorption spectrum of tetracyclone (tetraphenylcyclopentadienone) using the following groups: phenoxy and phenylthio in the para positions and fluoro in the ortho positions. First the syntheses and then the spectra are discussed.

Synthesis of tetracyclones. Most of the desired

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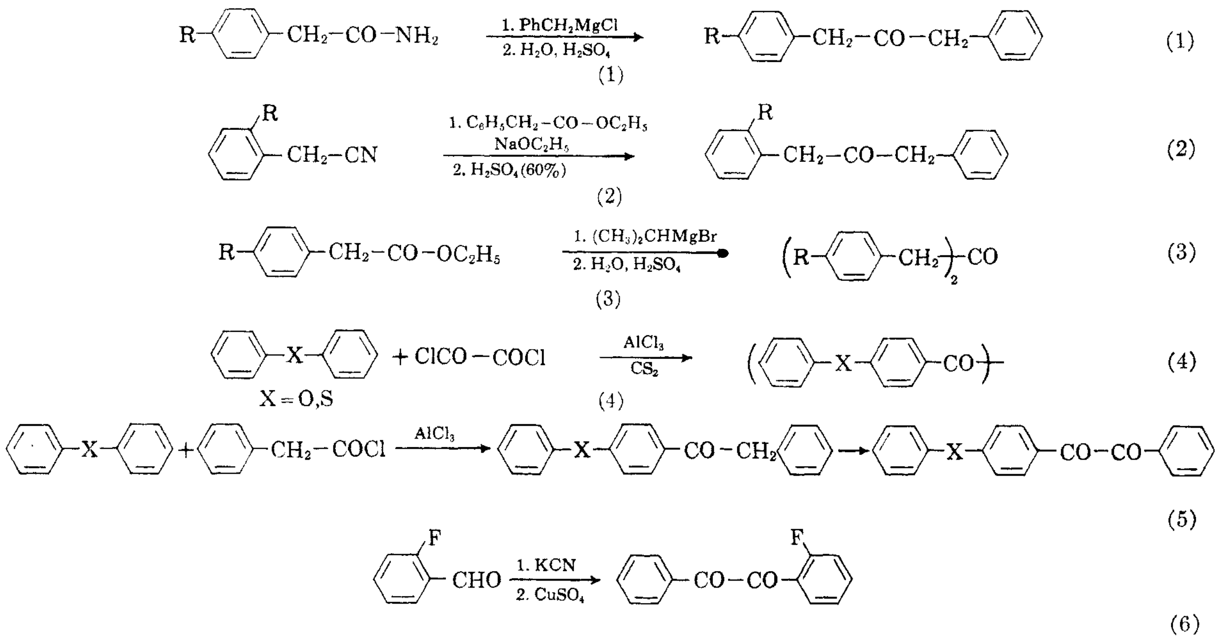
(1) Part IV: *J. Am. Chem. Soc.*, **77**, 60 (1955).

(2) From the M.S. theses of V. F. D. (1957), M. J. D. (1955), and A. E. E. (1955).

(3) To whom inquiries should be directed.

intermediates were prepared according to literature procedures or by methods analogous to those in the literature. The desired monosubstituted phenylthio and phenoxy benzylketones were easily prepared using the method of Shapiro and Becker[4] (Equation 1). Synthesis of the same unsymmetrical benzyl ketones by a Claisen-type condensation proved to be less satisfactory.[5] In preparing the monosubstituted 1-(2′-fluorophenyl)-3-phenyl-2-propanone, however, no difficulty was encountered using the Claisen-type condensation—the reaction gave a 70% yield (Equation 2). The symmetrical 1,3-bis-(4′-phenylthio- and -4′-phenoxy)phenyl-2-propanones were synthesized using the procedure of Conant and Blatt (Equation 3).[6] The symmetrical 1,3-bis(2′-fluorophenyl)-2-propanone was prepared satisfactorily by means of a Claisen condensation using the appropriately substituted ethyl phenylacetate in place of the unsubstituted compound (Equation 2).



The 4,4′-bis(phenoxy)benzil[7] and the 4,4′-bis-(phenylthio)benzil[8] were prepared by a Friedel-Crafts reaction between oxalyl chloride and either phenyl ether or phenylthio ether (Equation 4). The unsymmetrical phenylthio- and phenoxybenzils were prepared by acylating the appropriate ether with phenylacetyl chloride in a Freidel-Crafts reaction[9] and oxidizing the resulting 4′-phenoxy-(or phenthio)α-phenylacetophenone with selenium (Equation 5). During the preparation of these compounds it was found that if an excess of phenylacetyl chloride was used with the phenthio ether in the Friedel-Crafts reaction the product obtained could be oxidized with selenium dioxide to give a bisbenzil. The 2,2′-difluorobenzil was prepared by the procedure given in Organic Syntheses[10] as modified by M. Koral[11] (Equation 6).

Using the appropriately substituted benzil and benzyl ketone the tetracyclones were easily prepared by the procedure of Dilthey and Quint[12] as modified by Johnson and Grummitt[13] and also by using Triton B[4] or sodium methoxide as catalyst. When preparing 3,4-diphenyl-2,5-bis(2′-fluorophenyl)cyclopentadienone, it was found that using potassium hydroxide gave only a 10% yield while a 60% yield was obtained using Triton B. The syntheses and properties of the tetracyclones are shown in Tables II and III.

Absorption spectra. Parasubstituted tetracyclones. Table IV gives the spectral characteristics for the various tetracyclones at the three peaks observed in the substituted and unsubstituted compounds. The three structures Ia,b,c have been used to depict the principal resonance structures for tetracyclone. In accordance with previous work (see Parts I–IV) an unhindered substituent in the 2-phenyl ring will affect primarily the 512 mμ peak, while an unhindered substituent in the 3-phenyl ring will affect principally the peak at 343 mμ. Thus, substitution

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(4) E. L. Shapiro and E. I. Becker, *J. Am. Chem. Soc.*, **75**, 4769 (1953).

(5) S. B. Coan, D. E. Trucker, and E. I. Becker, *J. Am. Chem. Soc.*, **75**, 900 (1953).

(6) J. B. Conant and A. H. Blatt, *J. Am. Chem. Soc.*, **51**, 1227 (1929).

(7) A. Schönberg and O. Kraemer, *Ber.*, **55**, 1174 (1922).

(8) W. Dilthey, O. Trösken, K. Plum, and W. Schommer, *J. prakt. Chem.*, **141**, 331 (1934).

(9) H. Kipper, *Ber.*, **38**, 2490 (1905).

(10) R. Adams and C. S. Marvel, *Org. Syntheses*, **Coll. Vol. I**, 94 (1941).

(11) M. Koral, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1956.

(12) W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930).

(13) J. R. Johnson and O. Grummitt, *Org. Syntheses*, **Coll. Vol. III**, 806 (1955).

TABLE I

PHYSICAL CONSTANTS AND ANALYSES FOR INTERMEDIATES

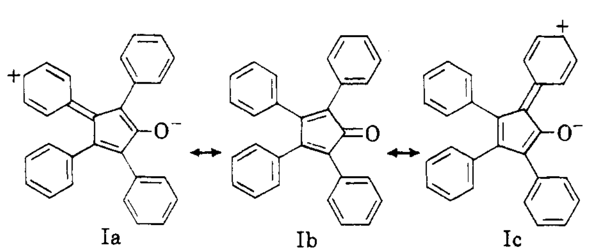
Sub-stituent	M.P. or B.P., °C. (Mm. of Hg)	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
			Substituted α-Phenylacetophenones						
p-C_6H_5O	87.3– 87.5	82	$C_{20}H_{16}O_2$	83.31	83.42	5.59	5.65		
p-C_6H_5S	105 –106	76	$C_{20}H_{16}OS$	78.91	79.02	5.3	5.3[a]		
			Substituted Phenylacetamides						
4-C_6H_5O	173.5–174.0	95	$C_{14}H_{13}NO_2$	73.99	73.61	5.76	6.06	6.06	6.12
4-C_6H_5S	175.5–176.0	90	$C_{14}H_{13}NOS$	69.10	68.71	5.38	5.28[b]	5.76	5.91
2-F	157.2–159.2	89	C_8H_8FNO	62.74	62.52	5.26	5.18	9.15	9.21
			o-Fluorophenylacetic Acid						
	63.5– 64.6	95	$C_8H_7FO_2$	62.34	62.34	4.58	4.70		

Substituted Acetoacetonitriles

Substituents	M.P. or B.P., °C. (Mm. of Hg)	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
α-(o-Fluorophenyl)-γ-phenyl	66.6–67.8	54	$C_{16}H_{12}FNO$	75.87	75.84	4.78	4.89	5.53	5.37
α,γ-bis(o-Fluorophenyl)	87.9–88.5	74	$C_{16}H_{11}F_2NO$	70.83	70.78	4.09	4.22	5.16	5.21

Substituents	M.P. or B.P., °C. (Mm. of Hg)	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
			Substituted Dibenzylketones				
p-phenoxy	155 –158 (0.5–1 mm.)	28	$C_{21}H_{18}O_2$	83.42	83.41 83.36	6.00	6.54 6.44
p,p′-diphenoxy	93.5– 94	95	$C_{27}H_{22}O_3$	82.21	82.22	5.62	5.63
p-phenylthio	185 –188 (1 mm.)	14	$C_{21}H_{18}OS$	79.21	79.34	5.70	6.08[c]
p,p′-diphenylthio	90.5– 91	89	$C_{27}H_{22}OS_2$	76.02	76.35	5.20	5.32[d]
o-fluoro	36 – 37.2	70	$C_{15}H_{13}FO$	78.93	78.73	5.74	5.87
o,o′-difluoro	71.1– 71.2	68	$C_{15}H_{12}F_2O$	73.16	73.18	4.91	5.03
			Substituted Benzils				
p-phenoxy	65.0– 65.7	26	$C_{20}H_{14}O_3$	79.45	79.57	4.67	4.68
p,p′-diphenoxy	116 –117[e]	28					
p-phenylthio	58.5– 59.5	60	$C_{20}H_{14}O_2S$	75.45	75.07	4.43	4.13[f]
p,p′-diphenylthio	104 –105[g]	15					
o,o′-difluoro	95.5– 96.6[h]	49					

[a] Calcd.: S, 10.53. Found: S, 10.53. [b] Calcd.: S, 13.18. Found: S, 13.53. [c] Calcd.: S, 10.07. Found: 9.63. [d] Calcd.: S, 15.03 Found: 14.62. [e] Footnote 7 reported m.p. 116–117°. [f] Calcd.: S, 10.07. Found: 10.37. [g] Footnote 8 reported m.p. 104–105°. [h] Footnote 11 reported m.p. 95.3–96.3°.



Ia Ib Ic

of phenoxy at the p-position of the 2-phenyl ring has caused a bathochromic and hyperchromic shift of the substituted (512 mμ) path while simultaneously a hypsochromic and hyperchromic shift of the unsubstituted (342 mμ) peak has been effected. Substitution of phenylthio in the p-position of the 2-phenyl ring caused a more pronounced bathochromic and hyperchromic shift than noted in the phenoxy-substituted compound. The 342 mμ peak has been completely eliminated.

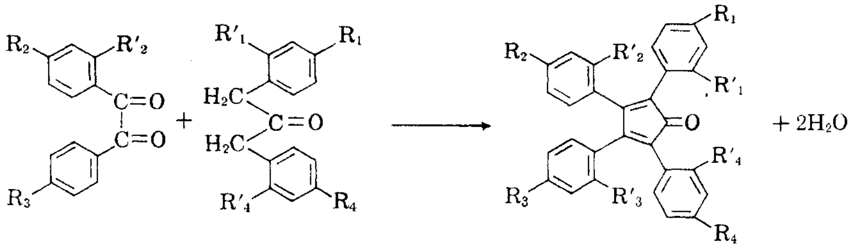
Disubstitution increased the effect noted for the monosubstituted compounds at the 512 mμ peak. The 342 mμ peak, however, shows a fairly strong hypsochromic and hyperchromic shift for the bis-2,5(4′-phenoxyphenyl)-3,4-diphenylcyclopentadienone (IV), and a very small hypsochromic but sizable hyperchromic shift for the bis-2,5-(4′-phenylthiophenyl)-3,4-diphenylcyclopentadienone.

It appears that the total increase of electron availability to the conjugated systems with the diphenoxy and diphenylthio compounds is more than sufficient to overcome the added importance of the electronic structure Ic.

With substitution of the phenoxy and phenylthio groups into the p-position of the 3- and 4-phenyl rings, it is noted that the 342 mμ peak is shifted bathochromically and hyperchromically in all four compounds (VI–IX) while the 512 - mμ peak in (VI) is shifted weakly hypsochromically and hypochromically. The other three compounds (VII–IX), however, exhibit a hyperchromic and bathochromic shift, in spite of the fact that substitution is present in the 3- and 4-phenyl rings. This

TABLE II

SYNTHESIS OF SUBSTITUTED TETRACYCLONES



Benzils			1,3-Diphenyl-2-propanones				Products			
R_2	R_3	Mmoles	R_1	R_4	Mmoles	Catalyst[a,b]	No.	M.P., °C.	Solvent for Crystallization	Yield, %
H	H		H	H			I	218 -220		90
H	H	3.3	C_6H_5O	H	3.3	KOH	II	190.5–191.5	Ethanol-benzene Ethanol-chloroform	98
C_6H_5O	H	0.20	H	H	0.20	KOH	III	192.2–192.7	Ethanol-benzene	66
H	H	5.1	C_6H_5O	C_6H_5O	5.1	KOH	IV	183.5–184.5	Ethanol-benzene Ethanol-chloroform	86
C_6H_5O	C_6H_5O	1.0	H	H	0.95	KOH	V	217.5–218.5[c]	Acetic acid	70
H	H	2.35	C_6H_5S	H	2.35	KOH	VI	182 -182.5	Ethanol-benzene Ethanol-chloroform	87
C_6H_5S	H	2.0	H	H	2.0	KOH	VII	133 -134	Ethanol-benzene[d]	
H	H	2.3	C_6H_5S	C_6H_5S	2.3	KOH	VIII	142.5–143.5	Ethanol-benzene Ethanol-chloroform	78
C_6H_5S	C_6H_5S	1.8	H	H	1.9	$NaOCH_3$	IX	198.5–199.5[e]	Acetic acid	84
R_2^1	R_3^1		R_1^1	R_4^1						
H	H	6.1	F	H	6.1	Triton B	X	195.7–196.2	Ethanol[f]	70
H	H	6.1	F	F	6.1	Triton B	XI	194.0–195.0	Ethanol[f]	60
F	F	6.1	F	H	6.1	Triton B	XII	184.2–185.2	Ethanol[f]	60
F	F	6.1	F	F	6.1	Triton B	XIII	182.4–183.2	Ethanol[f]	54

[a] The solvent was absolute ethanol sufficient to dissolve the reactants at incipient reflux or a quantity proportional to that cited in footnote 13. [b] The quantity of catalyst taken was directly proportional to the ratio of benzil-to-catalyst cited in footnote 13. [c] Footnote 8 reported 219–220°. [d] Preceded by chromatography on alumina using benzene as eluant. [e] Footnote 8 reported 199°. [f] The crude product was placed on an alumina column from benzene solution and eluted with a mixture of benzene: petroleum ether (b.p. 60–70°): : 1:4.

TABLE III

ANALYSES FOR SUBSTITUTED TETRACYCLONES

		Carbon		Hydrogen		Sulfur	
Compound	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
II	$C_{35}H_{24}O_2$	88.21	88.23	5.08	5.08		
III	$C_{35}H_{24}O_2$	88.21	87.79	5.00	5.19		
IV	$C_{41}H_{28}O_3$	86.61	86.53	4.96	5.13		
VI	$C_{35}H_{24}OS$	85.33	84.92	4.91	4.89	6.51	6.58
VII	$C_{35}H_{24}OS$	85.33	85.51	4.92	5.00	6.51	6.45
VIII	$C_{41}H_{28}OS_2$	81.96	82.19	4.70	4.88	10.68	10.45
X	$C_{29}H_{19}FO$	86.54	86.37	4.76	5.05		
XI	$C_{29}H_{18}F_2O$	82.84	83.11	4.31	4.11		
XII	$C_{29}F_3H_{17}O$	79.44	79.65	3.91	4.05		
XIII	$C_{29}F_4H_{16}O$	76.31	76.11	3.53	3.73		

effect is obviously due to the greatly increased total electron availability in the compounds (VII–IX).

Orthosubstituted tetracyclones. With substitution of fluorine atoms in the *o*-position of the 2- and 2,5-phenyl rings the reverse effect is noted. Here the 512-mμ peak suffers a strong hypsochromic and hypochromic shift while the 342-mμ peak is shifted hypsochromically and hyperchromically. It is interesting to note that the shift observed for the 512-mμ peak with *o*-fluoro-substitution is intermediate in value for the wave length and extinction coefficient between the corresponding *o*-chloro-substituted compound and the unsubstituted compound.[4] This is most probably due to the size of the fluorine atom being intermediate between hydrogen and chlorine. The steric hindrance caused by the fluorine atom forces the phenyl rings out of the plane of the cyclopentadienone ring and destroys

TABLE IV

SPECTRAL CHARACTERISTICS OF TETRACYCLONES[a]

	λ_1	ϵ_1	λ_2	ϵ_2	λ_3	ϵ_3
I	260	28400	342	6670	512	1290
II			330	6680	524	1810
VI					532	2180
IV			330 (infl)	7720	538	2330
VIII			340 (infl)	7720	542	3240
III	265	27700	358	8480	509	1220
VII	256	31900	378	9305	516	1736
V	261	33300	363	11590	515	1590
IX	256	36800	380	13360	525	1717
X	260	29600	335	7700	490	1040
XI	260	24700	335	8400	460	860
XII	262	34400	325	8150	485	1700
XIII	260	17000	325	8240	460	1180

[a] The spectra of these compounds were carried out using a Beckman Model DU spectrophotometer with a Process Instrument Recorder and Photomultiplier or manually at a concentration of 1.5×10^{-4} molar. The peak at 260 mμ was determined in iso-octane at a concentration of 3×10^{-5} molar.

some of the resonance associated with the substituted ring.

EXPERIMENTAL

α-Phenyl-4-phenoxyacetophenone. A mixture of 31 g. (0.20 mole) of diphenyl ether was slowly added to a flask containing 26.7 g. (0.20 mole) of anhydrous aluminum chloride and about 100 ml. of dry carbon bisulfide. During the addition the flask was cooled in an ice bath. On completion of the addition, the mixture was allowed to stand at room temperature for about 1 hr. and was then refluxed 1.5 hr. or until hydrogen chloride had ceased to evolve. After cooling and pouring on to a mixture of 170 g. of ice and 70 g. of concentrated hydrochloric acid, the dark red reaction mixture changed to a pale yellow curdy product. After filtration and washing the precipitate with acidulated water (50 ml. hydrochloric acid to 1 liter of water) twice by suspending it and filtering again, the crude product was taken up with 250 ml. of benzene. The benzene solution was washed once with water and with 50 ml. of a 5% solution of sodium hydroxide, dried with anhydrous calcium chloride and concentrated to 100 ml. One hundred milliliters of absolute alcohol was added and the solution concentrated again to 100 ml. affording 53.1 g. of product, m.p. 85.8–87.6°. Recrystallization from 200 ml. of absolute alcohol gave 51.9 g. of white product, m.p. 87.1–88.2°. Recrystallization of 5.0 g. of this from 50 ml. of ether afforded 4.6 g. (0.17 mole, 83%) of white plate-like crystals, m.p. 87.3–88.2°.

4-Phenoxyphenylacetamide. A mixture of 35 g. (0.153 mole) of 4-phenoxyphenylacetic acid,[14] m.p. 75.5–77.0° (prepared from 4-phenoxyacetophenone without isolation of the intermediate thiomorpholide), and 60 g. (0.503 mole) of thionyl chloride were refluxed for 1 hr. The excess thionyl chloride was distilled on a water bath, the last traces being removed at aspirator pressure. The reaction mass was then poured into 400 ml. of ice cold concentrated ammonia with stirring. After filtering and washing the product with ice water, it was recrystallized from ethanol-water (Norit) to give 33 g. (0.149 mole, 95%) of colorless amide, m.p. 170–171°. One recrystallization from the same solvent and one from acetone raised the melting point to 173.5–174.0°.

4-Phenylthiophenylacetamide. This compound was prepared in the same manner as the analogous phenoxy compound. From 35 g. (0.143 mole) of 4-phenthiophenylacetic acid, m.p. 107–108° (reported:[15] m.p. 108–110°), also prepared without isolation of the thiomorpholide, there was obtained 31 g. (0.128 mole, 90%) of colorless 4-phenthiophenylacetamide, m.p. 172–174°. Recrystallization from ethanol and acetone raised the m.p. to 175.5–176.0°.

2-Fluorophenylacetamide. The general procedure of Wenner[16] for the preparation of aromatic amides was followed.

To 26 g. (0.19 mole) of 2-fluorophenylacetonitrile (b.p. 83–89°, 2–4 mm.) reported b.p. 122–126° 10 mm.),[17] was added to 100 ml. of concentrated hydrochloric acid. The mixture was stirred vigorously for 3 hr. and allowed to stand overnight. The reaction mixture was then diluted with 100 ml. of water and 100 g. of ice. On standing a short time a white precipitate formed, which was filtered, washed with water, and dried. After sublimation and recrystallization from benzene there remained 25.9 g. (0.17 moles, 89%) of 2-fluorophenylacetamide, m.p. 157.2–159.2°.

2-Fluorophenylacetic acid. A mixture of 25.9 g. (0.17 mole) of 2-fluorophenylacetamide and 150 ml. of 10% aqueous hydrochloric acid was refluxed for 24 hr. then cooled in an ice bath to give the crude acid. The product was recrystallized as follows: to 150 ml. of 10% hydrochloric acid was added 2–3 g. of impure product and the mixture was heated to incipient boiling. The solution was then decanted allowing none of the insoluble oils to come over. The decanted liquid was filtered and cooled in an ice bath. The process was repeated and in this manner 24 g. (0.16 mole 95%) of acid melting at 62.5–64.0° was obtained.

The analytical sample was further purified by sublimation, then recrystallization from petroleum ether (b.p. 60–70°) to give a product melting at 63.5–64.6°.

α-(2-Fluorophenyl)-γ-phenylacetoacetonitrile. The general procedure of Coan and Becker[18] for the preparation of unsymmetrical ketones was followed.

To a stirred and refluxing solution of sodium ethoxide in ethanol prepared from 11.5 g. (0.5 atom) of sodium and 150 ml. of absolute alcohol was slowly added a mixture of 33.8 g. (0.25 mole) of 2-fluorophenylacetonitrile and 50.8 g. (0.31 mole) of ethyl phenylacetate. The mixture was refluxed for 3 hr., cooled, and poured into 600 ml. of ice water. Extraction with ether, acidification with cold dilute hydrochloric acid, followed by three extractions with 150-ml. portions of ether gave a combined ether extract which was washed consecutively with water, sodium bicarbonate solution, and finally with water. The ether layer was then dried over anhydrous sodium sulfate, filtered and distilled to dryness affording 34 g. (0.13 mole, 54%) of crude product, m.p. 65–67°.

The product was purified by heating 100 ml. of petroleum ether (b.p. 60–70°) containing 2 g. of the crude product to incipient boiling, decanting the solvent, filtering, and cooling in a Dry Ice–acetone bath. After three crystallizations in this manner a pure white crystalline material was obtained by crystallization from petroleum ether (b.p. 60–70°) at room temperature, m.p. 66.6–67.8°.

Treatment with 2,4-dinitrophenylhydrazine according to a standard procedure[19] gave 1-(2′,4′-dinitrophenyl)-3-benzyl-4-(2″-fluorophenyl)-5-aminopyrazole. Recrystallization from ethanol gave the yellow product, m.p. 136.2–136.7°.

Anal. Calcd. for $C_{22}H_{16}FN_5O_4$: C, 60.97; H, 3.72; N, 16.16. Found: C, 60.81; H, 3.64; N, 16.00.

α,γ-Bis(2-fluorophenyl)acetoacetonitrile. This compound was prepared in the same manner as α-(2-fluorophenyl)-γ-

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phenylacetoacetonitrile. Starting with 20 g. (0.109 mole) of ethyl 2-fluorophenylacetate and 13.5 g. (0.10 mole) of 2-fluorophenylacetonitrile there was obtained 20 g. (0.074 mole, 74%) m.p. 86.2–87.2° of product. Two and one-half grams of the ester was recovered from the basic extract. The analytical sample was purified as described for the monofluoro analog, m.p. 87.9–88.5°.

1-(4'-Phenoxyphenyl)-3-phenyl-2-propanone. To a stirred solution of benzylmagnesium chloride prepared from 18 g. (0.74 atom) of magnesium and 110 g. (0.87 mole) of benzyl chloride in 500 ml. of ether was added 16 g. (0.071 mole) of 4-phenoxyphenylacetamide. Gentle reflux was maintained for two days. Hydrolysis with a mixture of 100 g. of ice and 50 g. of concentrated sulfuric acid was followed by separation of the aqueous phase, which was extracted with ether. The organic layers were combined, washed with water and 10% sodium carbonate, and then dried over sodium sulfate. After filtration and concentration, the residue was distilled at reduced pressure to give two fractions. The lower-boiling fraction [150–160° (2–3 mm.)] contained nitrogen and by analogy to the work of Shapiro and Becker[5] was assumed to be 4-phenoxyphenylacetonitrile. A second fraction of 6 g. (0.02 mole, 28%) of material distilling at 185–190° (2–3 mm.) was collected. Redistillation of this fraction gave a white oily product boiling at 155–158° (0.5–1.0 mm.).

1-(4'-Phenylthiophenyl)-3-phenyl-2-propanone. This compound was prepared in a manner analogous to that of the preceding oxygen analog starting with 16 g. (0.069 mole) of 4-phenylthiophenylacetamide. The lower boiling fraction [150–160° (0.8 mm.)] was also found to contain nitrogen. A second fraction of 3 g. (0.0095 mole, 14%) of material distilling at 185–190° (1 mm.) was collected and redistillation gave a yellow oil, b.p. 185–188° (1 mm.).

1,3-Bis(4'-phenoxyphenyl)-2-propanone. To an ice cold solution of isopropylmagnesium bromide [prepared from 3.2 g. (0.132 atom) of magnesium and 18 g. (0.146 mole) of isopropyl bromide in 250 ml. of ether] 20 g. (0.078 mole) of ethyl 4-phenoxyphenylacetate, b.p. 173–175° (1–2 mm.), [reported:[14] 173–174° (0.2 mm.)] was added over 0.5 hr. The reaction mixture was allowed to stand overnight and then was hydrolyzed with 20 g. of concentrated sulfuric acid in 400 ml. of ice water. The aqueous layer was separated and extracted with ether. The combined organic layers were washed with water, then 10% sodium carbonate, and dried over sodium sulfate. Concentration left a residue which was taken up in 250 ml. of glacial acetic acid. After adding 50 ml. of 18% hydrochloric acid, the mixture was refluxed until no carbon dioxide was evolved (about 2.5 hr.). About half of the solvent was then removed at the aspirator and a white product immediately crystallized. Recrystallization from ethanol (Norit) gave 14 g. (0.035 mole, 95%) of colorless ketone melting at 89–91°. Recrystallization from ethanol-water and then from acetone raised the melting point to 93.5–94°.

An oxime was prepared (88% yield), m.p. 115–117°. Recrystallization from ethanol-water raised the melting point to 117.5–118°.

Anal. Calcd. for $C_{27}H_{23}NO_3$: N, 3.42. Found: N, 3.53.

1,3-Bis(4'-phenylthiophenyl)-2-propanone. This product was prepared in an analogous manner to that of the phenoxy compound from 20 g. (0.074 mole) of ethyl *p*-phenylthiophenylacetate, b.p. 173–174° (2–3 mm.) [reported:[14] 163° (0.65 mm.)]. When, on concentration after decarboxylation, an oil separated, the mother liquid was decanted. The residue was crystallized from ethanol (Norit) to give 12 g. (0.028 mole, 89%) of a product melting at 89–90.5°. Recrystallization from ethanol and then acetone raised the melting point to 90.5–91°.

An *oxime* was prepared (85% yield), m.p. 117–119°. Recrystallization from ethanol-water raised the melting point to 118–119°.

Anal. Calcd. for $C_{27}H_{23}NOS_2$: N, 3.17. Found: N, 3.21.

1-(2'-Fluorophenyl)-3-phenyl-2-propanone. To 25 g. (0.099 mole) of crude α-(2'-fluorophenyl)-γ-phenylacetoacetonitrile, m.p. 65–67°, was added 75 ml. of 60% sulfuric acid. The reaction mixture was stirred at reflux for 4 hr. cooled, diluted with 200 ml. of water and extracted three times with 125-ml. portions of ether. The combined ether extracts were washed with two 100-ml. portions of 5% sodium bicarbonate solution and then with 100 ml. of water. The ether solution was dried over anhydrous sodium sulfate, filtered, and distilled. The crude product, b.p. 143–145° (1–2 mm.), was crystallized from petroleum ether (b.p. 60–70°) to give 16 g. (0.07 mole, 70%) of white product, m.p. 35.6–36.3°. The analytical sample was purified chromatographically on alumina using ether as solvent and eluant. A small yellow band remained at the top of the column. The desired compound did not fluoresce either in visible or ultraviolet light. The first 50 ml. of ether coming through the column contained the product. The ether was distilled to give a white compound, m.p. 36.0–37.2°.

A *2,4-dinitrophenylhydrazone* was prepared in the customary way[19] and crystallized from ethanol as orange platelets, m.p. 108.6–109.2°.

Anal. Calcd. for $C_{21}H_{17}FN_4O_4$: C, 61.76; H, 4.20; N, 13.72. Found: C, 62.13; H, 4.21; N, 13.55.

1,3-Bis(2'-fluorophenyl)-2-propanone. This ketone was prepared in the same manner as above using 16.3 g. (0.06 mole) of α,γ-bis(2-fluorophenyl)acetoacetonitrile. The product was recrystallized from ethanol to give 10 g. (0.041 mole, 68%), m.p. 71.1–72.1°. The analytical sample was further purified in the same manner as for the monofluoro compound.

The *2,4-dinitrophenylhydrazone*, prepared as described previously, crystallized from ethanol as orange platelets, m.p. 115.0–115.9°.

Anal. Calcd. for $C_{21}H_{16}F_2N_4N_4O_4$: C, 59.15; H, 3.78; N, 13.14. Found: C, 59.25; H, 3.92; N, 13.10.

4-Phenoxybenzil. A mixture of 7.5 g. (30 mmoles) of α-phenyl-4-phenoxyacetophenone, 5.2 g. (50 mmoles) of freshly prepared selenium dioxide and 34 ml. of acetic anhydride was refluxed for 4 hr. After cooling, the selenium was filtered and washed with a few milliliters of acetic anhydride. The filtrate and washings were then warmed with 150 ml. of water, cooled, and extracted with ether. The extract was washed with an equal volume of water and dried with anhydrous calcium chloride. Traces of selenium caused an oiling-out of the product and so it was chromatographed through alumina (F-20), the column being developed with chloroform. Concentration of the eluate gave 2.8 g. (9.3 mmoles) of yellow crystals, m.p. 61–63° and two recrystallizations from ether-chloroform gave 2.0 g. (6.6 mmoles, 25.5%) of pale yellow crystals, m.p. 65.0–65.7°.

2-Phenoxyphenyl-3-phenylquinoxaline. A mixture of 0.1 g. (3.5 mmoles) of 4-phenoxybenzil and 0.05 g. (4.6 mmoles) of *o*-phenylenediamine in ethyl alcohol was warmed for 10 min. The reaction mixture was allowed to cool and gave 0.1 g. (20 mmoles, 63%), of a tan compound, m.p. 216–217°.

Anal. Calcd. for $C_{26}H_{18}N_2O$: N, 7.48. Found: N, 7.45.

4-Phenylthiobenzil. This compound was prepared in a manner similar to that for 4-phenoxybenzil. A mixture of 2.1 g. (9.0 mmoles) of α-phenyl-4-phenthioacetophenone and 2.0 g. (18.0 mmoles) of freshly prepared selenium dioxide in acetic anhydride was refluxed until no further selenium precipitated. After separating the crude material, crystallization from ether gave 1.3 g. of light brown needles, m.p. 65–69°. Recrystallization from ethanol and ether gave 1.2 g. (3.6 mmoles, 60%) yellow crystals, m.p. 58.5–59.5°.

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