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Reactions with 3,5-Dioxoanilides. I Reactions with 5-Phenylcyclohexane-1,3-dione-4-carboxanilide

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34

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TURQUIE

Reactions with 3,5-Dioxoanilides. I Reactions with 5-Phenylcyclohexane-1,3-dione-4-carboxanilide

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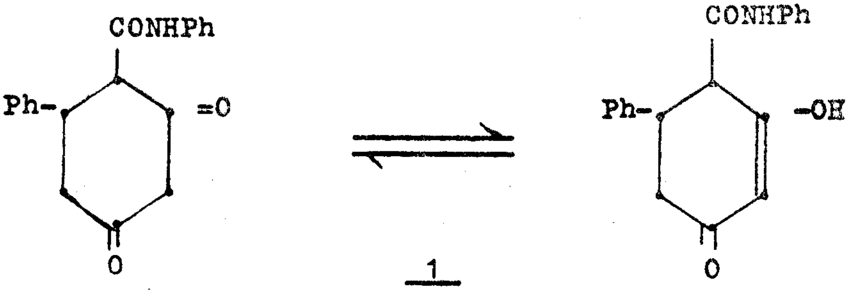
The title compound was found to react with aldehydes to give, according to conditions, the 2-arylmethylene 2 and xanthene 4, derivatives; with 2-nitrostyrene to give the benzofuran 5; with phenyl isocyanate to give phenylcarbamoyl derivative 6; with diazonium salts to give the hydrazone compounds 7; with aromatic amines to give anils 8; and with bromine to give the 2-bromo derivative 10. Compounds 1 and 10 were cyclised with sulphuric acnid to yield the quinoline derivatives 9 and 11. The bromo compound 10 also gave a thiazolo derivative 12.

A number of cyclohexane-1,3-dione derivatives have found application in clinical medicine [1-7] because of their antibacterial activity, also as effective herbicides [8-12], insecticides [13,14], and as plant growth regulators [15]. This work was undertaken to prepare cyclic 3,5-dioxoanilides to study the effect of extending betacarbonyl groups with respect to the anilide group and to examine the biological behaviour of such compounds.

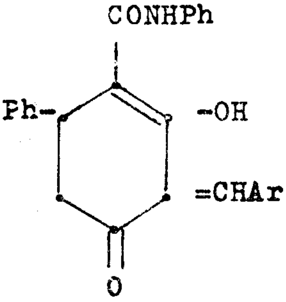
5-Phenyl-cycholexane-1,3-dione-4-carboxanilide (5-phenyl-3-hydroxy-cyclohexan-1-one-4- carboxanilide) 1 has been obtained by the addition reaction between ethyl cinnamate and acetoacetanilide in presence of sodium ethoxide [16].

The IR spectrum of compound 1 shows two carbonyl absortion bands at 1670 $cm^{-1}$and at 1725 cm^{-1}, NH band at 3100 cm^{-1}, and OH band at 3300 cm^{-1}



1

Compound 1 condensed with equimolecular amounts of aromatic aldehydes in refluxing acetic anhydride to give the 2-aryl-metylene derivatives 2a-e.

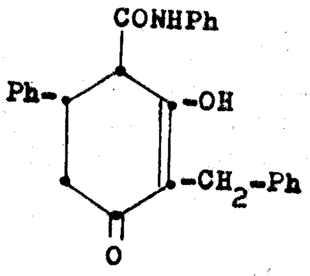


2

2	Ar
a,	C_6H_5
b,	$C_6H_4OCH_3$-p
c,	C_6H_4Cl-o
d,	$C_6H_4NO_2$-p
e,	$C_6H_4NO_2$-p

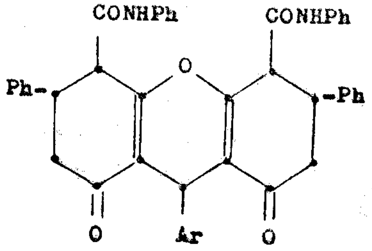
This structure is based on elemental analysis and IR data, also by analogy with the condensation product of 5-phenylcyclohexane -1,3-dione and benzaldehyde [17]. The IR spectrum of 2e shows two carbonyl absorption bands at 1675 cm^{-1}(CONH) and at 1705 cm^{-1} (CO); bands at 3100 cm^{-1}(NH) and 3400 cm^{-1}(OH). The shift of the second carbonyl band to a lower frequency compared with the starting material is due to conjugation with the exo-cyclic double bond.

Reduction of 2a with zinc dust and acetic acid gave the 2-benzyl derivative 3, which also could be obtained by the action of benzyl chloride on 1 in presence of sodium ethoxide.



3

When two molecules of compound 1 were allowed to react with one molecule of aromatic aldehydes in absolute ethanol or acetic acid at 70°C, two molecules of water were lost and the products formulated as 4a-f were obtained. Compounds 4a,b were obtained by reacting compound 1 with each of 2a,b in hot absolute ethanol.

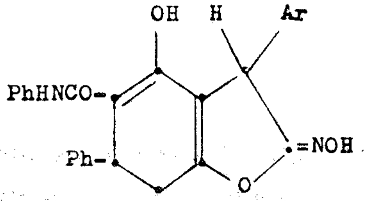


4	Ar
a ,	C_6H_5
b ,	$C_6H_4OCH_3$-p
c ,	$C_6H_4NO_2$-m
d ,	$C_6H_4NO_2$-p
e ,	piperonyl
f ,	furfuryl

The formation of 4 is analogy to the formation of the xanthene structure in the case of dimedone and aldehydes [18,19].

The IR spectrum of 4a shows two carbonyl absorption bands at 1675 cm^{-1}(CONH) at 1720 cm^{-1}(unconjugated CO), NH band at 3030 cm^{-1}, and no absorption bands in the OH region. The absence of colouration with ferric chloride solution corroborates the absence of hydroxyl groups.

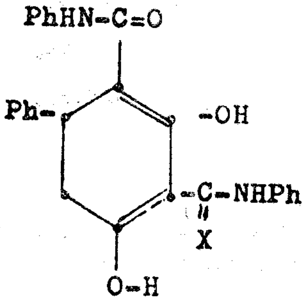
Attempts to react compound 1 with 2-nitrostyrene resulted in the formation of coloured crystaline compound which did not analyse for 1:1 adduct, indicating the possibility of abnormal reaction. An abnormal adduct during the Michael addition of cyclohexane 1,3-dione to 2-nitrostyrene was reported [20-24] and a similar formula is assigned to the products 5.



5	Ar
a,	C_6H_5
b,	$C_6H_4OCH_3$-p
c,	piperonyl

Compounds 5a-c gave deep violet colour with ferric chloride solution. The IR spectra of 5a,b show a carbonyl absorption broad band at ca. 1660 cm^{-1}(CONH), and a broad peak centered at 3100 cm^{-1}(NH, OH).

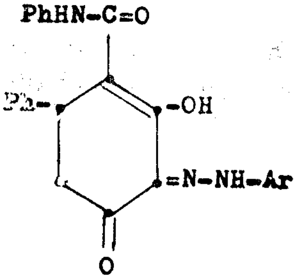
Compound 1 underwent Michael addition with phenyl-isocyanate and phenyl-isothiocyanate to give 6a,b (or possible tautomers).



6	X
a,	O
b,	S

The IR spectrum of 6a reveals one band at 1660 cm^{-1}(CONH), one at 3060 cm^{-1}(NH), and OH band at 3280 cm^{-1}shifted to lower frequency. The IR spectrum of 6b shows carbonyl absorption band at 1665 cm^{-1}, NH band at 3140 cm^{-1}, and OH band at 3300 cm^{-1}.

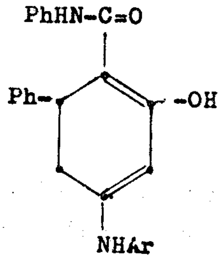
The presence of an active methylene group in 1 renders the compound susceptible to coupling arene-diazonium salts to give 7a-g (and/or possible tautomers).



7	Ar
a,	C_6H_5
b,	$C_6H_4OCH_3$-m
c,	$C_6H_4OCH_3$-p
d,	$C_6H_4CH_3$-m
e,	$C_6H_4CH_3$-p
f,	$C_6H_4NO_2$-m
g,	$C_6H_4NO_2$-p

The UV spectrum of 7a shows a maximum band at 340 nm, favouring the hydrazone structure [25]. The IR spectrum of 7a shows carbonyl absorption band at 1675 cm^{-1}, and NH and OH bands at 3080 cm^{-1}and at 3360 cm^{-1} respectively.

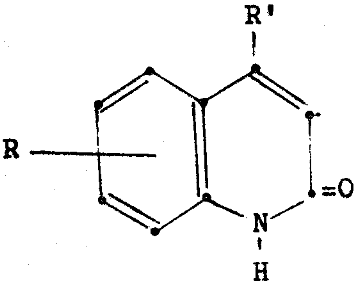
Compound 1 reacted with aromatic amines (in ethanol and in acetic acid) to give anils formulated as 8.



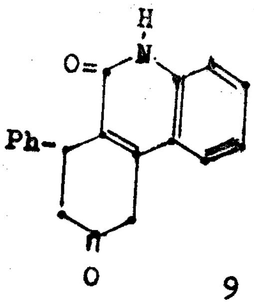
8	Ar
a,	C_6H_5
b,	$C_6H_4OCH_3$-m.
c,	$C_6H_4OCH_3$-p
d,	$C_6H_4CH_3$-m
e,	$C_6H_4CH_3$-p
f,	$C_6H_4NO_2$-m
g,	$C_6H_4NO_2$-p

The IR spectrum of 8a shows a carbonyl absorption band at 1660 cm^{-1}(CONH), NH band at 3180 cm^{-1}, and OH band at 3250 cm^{-1}. The PMR of 8a (in MeOH-d_4) shows signals at 2.85 ppm (m, 2, CH_2); 3.8 ppm (m, 1, CH); 5.6 ppm (s, 1, ethylenic CH), and 7.3 ppm(m, 15, Ar-H).

It is well known that β-ketoanilides such as acetoacetanilides and aroyl-acetanilides undergo cyclisation to 2-quinolone [26-28].



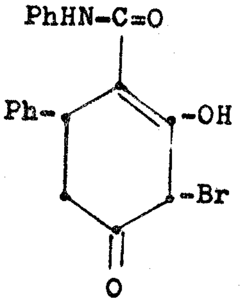
Similarly, cyclisation of compound 1 with concentrated sulphuric acid (at 90-100°C) yields compound 9.



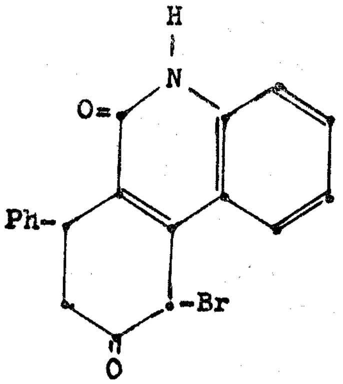
9

The PMRof 9 (in TFA) shows signals at 3.15 ppm (m, 2, CH_2) 4.1 ppm (m, 2, CH_2); 6.32 ppm (s, 1, CH); 7.1-7.4 (m,9, Ar-H) and 8.55 ppm (s, 1, NH).

Bromination of 1 with one mole of bromine in $CHCl_3$ or in aqueous sodium hydroxide gave 2-bromo-derivative 10, which was cyclised with concentrated sulphuric acid affording compound 11.

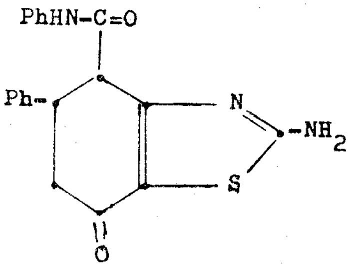


10

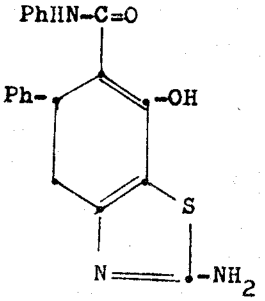


11

On refluxing compound 10 with thiourea in absolute ethanol it gave a compound which can be formulated as 12A or 12B.



12A



12B

Since the product did not give any colour with ferric chloride solution and its IR spectrum of 12 showed peaks at 3300, 3200, 3140 cm^{-1} (NH_2, NH) with broad peak at 1640–1665 cm^{-1}, it is most likely to be 12A rather than 12B.

Experimental:

Melting points are not corrected. IR spectra were recorded on an Infrared Recording Spectrophotometer IR 4220. The UV spectrum was recorded on a Beckman Spectrophotometer model 26. NMR spectra were recorded on a Varian A 60 A Spectrophotometer.

5- Phenylcyclohexane-1,3-dione-4-carboxanilide (1):

5-Phenylcyclohexane-1,3-dione-4-carboxanilide 1 was prepared after the method of Diechmann et al. [16].

Analysis : $C_{19}H_{17}NO_3$
requires : C, 74.24; H, 5.58; N, 4.56
Found : C, 74.3 ; H, 5.5 ; N, 4.7

2-Arylmethylene-3-hydroxy-5-phenylcyclohex-3-en-1-one-4-carboxanilides (2a-e):

A mixture of 1.5 g (0.005 mole) of 1, and 0.005 mole of the aromatic aldehydes was refluxed in 10 ml of acetic anhydride for 5 hr, cooled and poured into water. The product 2a e formed was collected and crystallised from the proper solvent (see Table 1).

Table 1: 2-Arylmethylene-derivatives (2a-e)

Compound	m.p. (°C) (Solvent)	Yield (%)	Formula (Mol. Wt.)	Analysis Calcd. / Found		
				Carbon	Hydrogen	Nitrogen
2a	164	55	$C_{26}H_{21}NO_3$	78.96	5.35	3.54
	EtOH		(395.5)	79.2	5.5	3.2
2b	149	67	$C_{27}H_{23}NO_4$	76.22	5.45	3.29
	AcOH		(425.5)	76.5	5.3	3.2
2c	168	63	$C_{26}H_{20}ClNO_3$	72.64	4.69	Cl= 8.25
	C_6H_1		(429.91)	72.8	4.4	Cl= 8.1
2d	181	64	$C_{26}H_{20}N_{2}0_{5}$	70.89	4.58	6.36
	Dioxan		(440.5)	70.6	4.5	6.2
2e	175	72	$C_{26}H_{20}N_{2}0_{5}$	70.89	4.58	6.36
	AcOH		(440.5)	70.8	4.4	6.5

2-Benzyl-3-hydroxy-5-phenylcyclohex-3-en-1-one-4-carboxanilide (3):

a) A mixture of 2 g of compound 2a and 0.5 g zinc dust was boiled in 20 ml acetic acid for 20 min. The solution was filtered while hot, cooled then the filtrate was poured into water. The product formed, was collected and crystallised from ethanol m.p. 137°C; yield 63 %.

Analysis : $C_{26}H_{23}NO_3$
requires : C, 78.56; H, 5.83; N, 3.52
Found : C, 78.3 ; H, 5.9 ; N, 3.6

b) 1.5 Grams of 1 were dissolved in 30 ml of absolute ethanol containing 0.12 g of sodium metal and treated with 0.6 ml of benzyl chloride. The solution was refluxed for 1 hr, then worked up as above to give the same product 3.

Xanthene derivatives (4a-f):

a) A mixture of 0.01 mole of 1, 0.005 mole of the appropriate aromatic aldehydes, and 2 drops of piperidine was heated at 70°C in 20 ml absolute ethanol (or acetic acid) for 15 min and cooled. The products separated (after pouring into water if necessary) were collected and crystallised from the proper solvend (see Table 2).

Table 2: Xanthen-derivatives (4a-f)

Compound	m.p. (°C) (Solvent)	Yield (%)	Formula (Mol. Wt.)	Analysis Calcd./Found		
				Carbon	Hydrogen	Nitrogen
4a	236 AcOH	73	$C_{45}H_{36}N_20_5$ (684.8)	78.93 79.1	5.30 5.1	4.09 4.0
4b	213 AcOH	76	$C_{46}H_{38}N_20_6$ (714.8)	77.30 77.0	5.36 5.5	3.92 3.8
4c	264 $Ph\text{-}NO_2$	70	$C_{45}H_{35}N_30_7$ (729.8)	74.06 74.2	4.83 5.0	5.76 5.5
4d	253 Dioxan	71	$C_{45}H_{35}N_30_7$ (729.8)	74.06 73.9	4.83 5.1	5.76 5.6
4e	224 AcOH	67	$C_{46}H_{35}N_20_7$ (728.8)	75.81 75.6	4.98 5.0	— —
4f	215 C_6H_6	71	$C_{43}H_{34}N_20_6$ (674.8)	76.54 76.7	5.08 5.0	— —

b) A mixture of 0.005 mole of 2a or 2b and 0.005 mole of 1 was heated in 20 ml absolute ethanol for 15 min, cooled, and poured into water. The solid obtained was proved to be 4a and 4b, respectively.

3- **Aryl - 2 - hydroxyimino**-6-**phenyl**-5 **phenylcarbamoyl** 2,3,6,7-**tetrahydro**-4 (5**H**)-**benzofuranones** (**5a-c**):

a) 0.005 Mole of 1 and 0.005 mole of 2-nitrostyrene were dissolved in 30 ml dry benzene, treated with few drops triethylamine, and left overnight. The solid that separated (or obtained by evaporation of the solvent) was collected and crystallised (see Table 3).

b) A mixture of 0.005 mole of 2a or 2b and 0.005 mole nitromethane in 20 ml absolute ethenaol was cooled below 5°C. A cold

Table 3: Benzofuranone derivatives 5 and 2-arylhyrazino-3-hydroxy-5-phenylcycloheaxn 1-one-4-carboxanilides (7a-g)

Compound	m.p. (°C) (Solvent)	Yield (%)	Formula (Mol. Wt.)	Analysis Calcd./Found		
				Carbon	Hydrogen	Nitrogen
5a	157	55	$C_{27}H_{22}N_20_4$	73.96	5.06	6.39
	AcOH		(438.5)	74.1	5.2	6.3
5b	142	58	$C_{28}H_{24}N_20_5$	71.78	5.16	—
	MeOH		(468.5)	72.0	5.1	—
5c	168	50	$C_{28}H_{22}N_20_6$	69.70	4.60	—
	AcOH		(482.5)	69.4	4.4	—
7a	152	78	$C_{25}H_{21}N_30_3$	72.97	5.14	10.21
	EtOH		(411.5)	72.7	5.3	10.0
7b	139	70	$C_{26}H_{23}N_30_4$	70.73	5.25	9.52
	AcOH		(441.5)	71.0	5.1	9.4
7c	142	74	$C_{26}H_{23}N_30_4$	70.73	5.25	9.52
	EtOH		(441.5)	70.9	5.0	9.2
7d	145	65	$C_{26}H_{23}N_30_3$	73.39	5.45	—
	AcOH		(425.5)	73.5	5.7	—
7e	136	67	$C_{26}H_{23}N_30_3$	73.39	5.45	9.88
	AcOH		(425.5)	73.1	5.4	9.6
7f	172	58	$C_{25}H_{20}N_40_5$	65.78	4.42	12.27
	Dioxan		(456.5)	66.0	4.3	12.5
7g	183	60	$C_{25}H_{20}N_40_5$	65.78	4.42	—
	AcOH		(456.5)	65.9	4.5	—

solution of sodium ethoxide (0.12 g sodium metal in 10 ml absolute ethanol) was gradually added with stirring. The reaction mixture was left in icecold water for 2 hr, poured onto crushed ice and acidified with acetic acid. The formed precipitates were filtered off, washed with water and crystallised to 5a or 5b.

5-Phenyl-5, 6-**dihydroresorcinol**-2,4-**dicarboxanilide** (6**a**):

A mixture of 1 (0.005) mole) and 0.6 of ml phenyl-isocyanate (0.005 mole) in 25 ml dry benzene was treated with few drops of triethylamne, refluxed for 2 hr. The precipitate separated by cooling was filtered off and crystallised from acetic acid m.p. 235°C; yield 65 %.

Analysis : $C_{26}H_{22}N_20_4$
requires : C, 73.22; H, 5.20; N, 6.56
Found : C, 73,5 ; H, 5.0 ; N, 6,4

5-Phenyl - 2 - **thio** - **carbamoyl** - 5,6-**dihydroresocinol**-4-**carboxanilide** (6**b**):

By the above procedure 1 reacted with phenyl-isothiocyanate to give 6b which was crystallised from ethanol m.p. 165°C; yield 57 %.

Analysis : $C_{26}H_{22}N_{2}0_{3}S$
requires : C, 70.57; H, 5.01; N, 6.33; S, 7.25
Found : C, 70.8; H, 4.8 ; N, 6.5; S, 7.2

Coupling products of 1 (7a-g):

0.005 Mole of 1 was dissolved in ca. 15 ml pyridine and cooled in ice bath. The cold solution was treated dropwise with a cold solution of the diazonium salt (from 0.005 mole of the appropriate aromatic amine in the usual way) and left for sometime in the ice bath with stirring. The solution was poured into water, and acidified with with 50 % hydrochloric acid solution. The products 7a-g formed were collected, wasted with water, and crystallised from the proper solvent (see Table 3).

Formation of 1-arylamino-derivatives (8a-g):

A solution of 0.005 mole of 1 in 20 ml absolute ethanol or aceticacid was treated with 0.005 mole of aromatic amine and heated at 60° for 5 min, then left to cool. The products 9a-g that separated (after pouring into water if necessary) were filtered off and crystallised from the proper solvent (see Table 4).

Table 4: 1-Anilino-3-hydroxy-5-phenylcyclohexan-4-carboxanilides (8a-g)

Compound	m.p. (°C) (Solvent)	Yield (%)	Formula (Mol. Wt.)	Analysis Calcd./Found		
				Carbon	Hydrogen	Nitrogen
8a	215 EtOH	85	$C_{25}H_{22}N_{2}0_{2}$ (382.5)	78.50 78.2	5.80 5.6	7.32 7.5
8b	222 AcOH	82	$C_{26}H_{24}N_{2}0_{2}$ (396.5)	78.76 79.0	6.10 6.3	7.06 6.9
8c	227 AcOH	87	$C_{26}H_{24}N_{2}0_{2}$ (396.5)	78.76 78.6	6.10 6.4	7.06 7.3
8d	233 Dioxan	66	$C_{26}H_{24}N_{2}0_{3}$ (412.5)	75.71 76.0	5.86 6.0	— —
8e	224 C_6H_6	74	$C_{26}H_{24}N_{2}0_{3}$ (412.5)	75.71 75.6	5.86 6.1	6.79 6.6
8f	257 AcOH	55	$C_{25}H_{21}N_{3}0_{4}$ (427.5)	70.24 70.5	4.95 5.0	9.83 10.0
8g	248 AcOH	67	$C_{25}H_{21}N_{3}0_{4}$ (427.5)	70.24 70.4	4.95 5.1	9.83 9.6

7,8,9,10-**Tetrahydro**-9-**oxo**-7-**phenl-benzo** [c] **quinolin**-6 (5**H**) **one** (9):

2 Grams of 1 were dissolved in 12 ml concentrated sulphuric acid and heated in an oil bath at 90-100°C for 1 hr, cooled and poured into crushed ice. The product formed was filtered off, washed with water and crystallised from ethanol m.p. 182°C; yield 68 %.

Analysis : $C_{19}H_{15}NO_2$
requires : C, 78.87; H, 5.23; N, 4.84
Found : C, 79.0 ; H, 5.1 ; N, 4.6

2-**Bromo** - 3 - **hydroxy** - 5 - **phenylcyclohex** - 3-**en**-1-**one** - 4 - **carboxanilide** (10):

a) A solution of 0.5 ml (1.6 g, 0.01 mole) bromine in 10 ml chloroform was added portionwise with stirring to a solution of 3 g (0.01 mole) of 1 in 30 ml chloroform, and left overnight. The solvent was evaporated on water bath. The product formed was collected and crystallised from dilute ethanol m.p. 139°C; yield 77 %.

Analysis : $C_{19}H_{16}BrNO_3$
requires : C, 59.08; H, 4.18; N, 3.63
Found : C, 59.3 ; H, 4.4 ; N, 3.8

b) A cold solution of 0.005 mole bromine in 30 ml acqueous methanol (1:1) was added portionwise to a cold solution of 0.005 mole of 1 in 30 ml water-methanol mixture (1:1) containing 0.2 g sodium hydroxide. The reaction mixture was left for 1 hr in the the ice bath. The product formed was filtered off, and washed with water to give 10.

10-**Bromo** - 7,8,9,10 - **tetrahydro** - 9 - **oxo** - 7 - **phenyl-benzo** [c] **quinolin**-6 (5**H**):

2 Grams of 10 were dissolved in 12 ml concentreted sulphuric acid, heated in an oil bath at 90-100°C for 1 hr, and cooled. The reaction mixture was poured into crushed ice. The product formed was filtered off, washed with water, and crystallised from ethanol m.p. 246°CC; yield 72 %.

Analysis : $C_{19}H_{14}BrNO_2$
requires : C, 61.98; H; 3.83; Br, 21.70
Found : C, 62.1; H, 3.7 ; Br, 21.9

Reaction of compound 10 with thiourea (12):

A mixture of 1.9 g (0.005 mole) of compound 10 and 0.4 g (0.005 mole) of thiourea in 30 ml absolute ethanol was refluxed for 2 hr and cooled. The reaction mixture was poured into water and made alkaline with ammonium hydroxide solution. The resulting solid was filtered off, washed with water and crystallised from acetid acid p.0. 166°C; yield 78 %.

Analysis : $C_{20}H_{17}N_3O_2S$
requires : C, 66.10; H, 4.72; N 11.56; S, 8.82
Found : C, 65.9 ; H, 4.8 ; N, 11.7 ; S, 8.6

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