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Chemical and Spectral Study of 6- and 7-Nitro-2-Methyl, 2-Benzyl, 2-Styryl and 2-(1-Phenylstyryl)-3*H*-4-Ketoquinazolines and Their 3-Me and 3-Ph Derivatives

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6- and 7-Nitro-2-benzyl-3*H*-4-ketoquinazolines and their 3-Me and 3-Ph derivatives were prepared by condensing the 6-nitro (III) and 7-nitro (XII) derivatives of -4*H*-3,1-benzoxazin-4-one with ammonia, methylamine and aniline, respectively. The compounds III and XII were formed on refluxing 5- and 4-nitro-*N*-phenylacetylanthranilic acids with acetic anhydride. 6- and 7-Nitro-2-benzyl-3*H*-4-ketoquinazolines (IV and XIII) were also prepared by condensing 5- and 4-nitro-*N*-phenylacetylanthranilic acids with formamide, respectively, in very low yields. The compounds IV and XIII yielded the corresponding 2-benzoyl derivatives on oxidation and the corresponding 2-(1-phenylstyryl) derivatives on reaction with benzaldehyde. 6- and 7-Nitro-2-styryl and 2-(1-phenylstyryl)-3*H*-4-ketoquinazolines were not oxidized by alkaline permanganate. UV spectra of these compounds have been studied.

Quinazoline has proved to be a very stable ring-system. Unlike quinoline and isoquinoline, a quinazoline does not undergo a ring-cleavage when subjected to an oxidation reaction which normally brings about such a cleavage. Simple quinazoline yields 4-ketoquinazoline on oxidation.[1] 2-Methyl-3-phenyl-3,4-dihydroquinazoline affords 2-methyl-3-phenyl-4-ketoquinazoline on oxidation with alkaline permanganate.[2] 2-Methyl-3*H*-4-keto-quinazoline remains unchanged on treatment with this reagent.[1]

Patel and coworkers have reported that 2-benzyl and 2-(1-phenylstyryl)-3*H*-4-ketoquinazolines on oxidation yield 2-benzoyl-3*H*-4-ketoquinazoline, but 2-styryl-3*H*-4-ketoquinazoline remains uneffected.[3] 2-(1-Phenylstyryl)-3*H*-4-ketoquinazoline was formed on condensing 2-benzyl-3*H*-4-ketoquinazoline with benzaldehyde.[4] In continuation of this, the syntheses and the study of the oxidation reactions of various 6- and 7-nitro-2-R-3*H*-4-ketoquinazoline derivatives were undertaken. UV spectra of these compounds have been studied with a view to studying the spectra-structure correlation. Because of the interesting aspect of the tautomeric behaviour of 6- and 7-nitro-3*H*-4-ketoquinazolines, their

1) H. Yamanaka, *Chem. and Pharm. Bull.* (Tokyo), **7**, 152 (1959); *Chem. Abstr.*, **54**, 22672 (1960).

2) C. Paal and Krecke, *Ber.*, **23**, 2634 (1890).

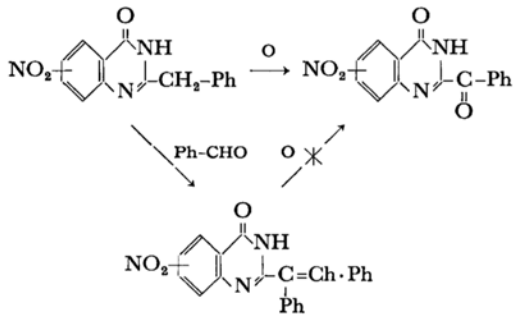
3) V. K. Mehta, Ph. D. thesis, Gujarat University, Ahmedabad (1965).

4) M. T. Bogert and R. A. Gortner, *J. Am. Chem. Soc.*, **32**, 1657 (1910); **57**, 729 (1935).

spectra were compared with those of the corresponding 3-methyl and 3-phenyl derivatives which have fixed amide-structures. With this aim in view, the 3-methyl and 3-phenyl derivatives of 6- and 7-nitro 2-benzyl-3*H*-4-ketoquinazolines were also prepared.

5-Nitro-*N*-phenylacetylanthranilic acid (II) was formed on reaction of 5-nitroanthranilic acid (I) with phenylacetyl chloride. 6-Nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (III), synthesized by refluxing II with acetic anhydride, afforded 6-nitro-2-benzyl-3*H*-4-ketoquinazoline (IV) on reaction with liquid ammonia at 100°C. The compound IV was also synthesized in about 15% yield by condensing II with formamide following the modified Niementowski 4-ketoquinazoline synthesis.[5] Patel has reported that condensation of 5-nitro-*N*-acetylanthranilic acid with formamide yields a mixture of 6-nitro-3*H*-4-ketoquinazoline and its 2-methyl derivative, while its condensation with acetamide affords pure 6-nitro-2-methyl-3*H*-4-ketoquinazoline.[6] The condensation of 6-nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one III with methylamine and with aniline at 100°C afforded 6-nitro-2-benzyl-3-methyl and 3-phenyl-4-ketoquinazolines (V and VI) respectively.

6-Nitro-2-methyl-3*H*-4-ketoquinazoline was not oxidized on treatment with alkaline permanganate at 100°C. 6-Nitro-2-benzyl-3*H*-4-ketoquinazoline (IV) on oxidation with alkaline potassium permanganate at 100°C afforded 6-nitro-2-benzoyl-3*H*-4-ketoquinazoline (VII) in very low yield.



Chart

Most of the original compound (IV) was recovered unchanged. The same product (VII) was also formed in good yield when the oxidation of IV was carried out with selenium dioxide in isoamyl alcohol. The oxidation reaction of IV leading to the formation of a ketone is a characteristic property of a benzylic methylene group. Selenium dioxide has been reported to be a specific oxidizing agent for an alkyl group attached to an *ortho* or a *para* position to ring-nitrogen of a heterocyclic system.[7] 6-Nitro-2-methyl-3*H*-4-ketoquinazoline (VIII) on reaction with benzaldehyde afforded the corresponding 2-styryl derivative (IX). Compound IV likewise afforded 6-nitro-2-(1-phenylstyryl)-3*H*-4-ketoquinazoline (X) on reaction with benzaldehyde. Both 2-styryl (IX) and 2-(1-phenylstyryl) (X) derivatives did not undergo oxidation reaction when treated with alkaline permanganate solution at 100°C even on prolonged heating with excess of the reagent. As indicated previously, 2-(1-phenylstyryl)-3*H*-4-ketoquinazoline is reported to be oxidized to the corresponding 2-benzoyl derivative on treatment with permanganate in acetone solution in cold.

7-Nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (XII), formed on treating 4-nitro-*N*-phenylacetylanthranilic acid (XI) with boiling acetic anhydride, afforded 7-nitro-2-benzyl-3*H*-4-ketoquinazoline (XIII) and their 3-methyl (XVIII) and 3-phenyl (XIX) derivatives on reaction with ammonia, methylamine and aniline solutions, respectively. The compound (XIII) was also formed on condensing 4-nitro-*N*-phenyl acetylanthranilic acid (XI) with formamide in about 23% yield. Compound XIII was oxidized by heating it with a large excess of alkaline permanganate solution at 100°C for twenty four hours to 7-nitro-2-benzoyl-3*H*-4-ketoquinazoline (XIV) in very poor yield. Most of compound XIII was recovered from precipitated manganese dioxide on extracting it with boiling acetone. Compound XIV was formed in very good yield on oxidation of XIII with selenium dioxide in isoamyl alcohol solution. 7-Nitro-2-methyl-3*H*-4-ketoquinazoline (XV) and its 2-benzyl analog (XIII) on reaction with benzaldehyde afforded 7-nitro-2-styryl-3*H*-4-ketoquinazoline (XVI), and 7-nitro-2-(1-phenylstyryl)-3*H*-4-ketoquinazoline (XVII). Both these 2-styryl (XVI) and 2-(1-phenylstyryl) (XVII) derivatives were not oxidized on treatment with alkaline permanganate solution at 100°C. Even 7-nitro-2-methyl-3*H*-4-ketoquinazoline was not oxidized by the same reagent.

These results suggest that owing to the presence of the nitro group, the permanganate oxidation reaction of nitro-substituted 2-benzyl-3*H*-4-ketoquinazolines becomes difficult and that of the correspondingly substituted 2-(1-phenylstyryl)-3*H*-4-ketoquinazoline is completely prevented. The fact that the presence of a nitro group makes oxidation reaction of so-substituted compound difficult is well known.[8]

5) V. S. Patel and S. R. Patel, *J. Indian Chem. Soc.*, **42**, 531 (1965); **45**, 167 (1968).

6) V. S. Patel, Ph. D. thesis, Sarder Patel University, Vallabh Vidyanagar (1967).

7) a) W. Borsche and W. Doeller, *Ann.*, **39**, 537 (1938); *Ber.*, **76**, 1176 (1944); A. Kjaer, *Acta. Chem. Scand.*, **2**, 455 (1948). b) H. D. Law and F. M. Perkin, *J. Chem. Soc.*, **93**, 1633 (1908); Weiler, *Ber.*, **32**, 1050 (1899).

8) M. J. S. Dewar and P. M. Maitlis, *J. Chem. Soc.*, **1957**, 2521.

TABLE 1. ULTRAVIOLET SPECTRAL DATA FOR 6- AND 7-NITRO-(2-R-3-R′-)-4-KETOQUINAZOLINES

NO_2	R	R′	β-Band		*Para*-band	
			mμ	log ε	mμ	log ε
6	$-CH_3$	H	255 (i)	4.02	320	4.01
6	$-CH_2-Ph$	H	260 (s)	3.90	325	4.01
6	$-CO-Ph$	H	258	4.41	325 (i)	3.86
					370	4.06
6	$-CH=CH-Ph$	H	255 (i)	4.12	360 (i)	4.2
			310 (i)	4.14		(Broad band)
6	$-C(H)=C(Ph)-Ph$	H	260	4.30	305 (i)	4.20
					375	4.17
6	$-CH_2-Ph$	$-CH_3$	260 (s)	4.00	335	4.14
6	$-CH_2-Ph$	$-C_6H_5$	260 (i)	4.06	320	4.21
7	$-CH_3$	H	255	4.34	340	3.47
7	$-CH_2-Ph$	H	253	4.44	350	3.47
7	$-CO-Ph$	H	258	4.43	320 (i)	3.68
					340 (i)	
7	$-CH=CH-Ph$	H	*210 to 323	*4.7 to 4.29	*323—380	*4.29—3.7
7	$-C(H)=C(Ph)-Ph$	H	216	4.59	323	4.23
			256	4.16		
7	$-CH_2-Ph$	$-CH_3$	248	4.38	326	3.56
7	$-CH_2-Ph$	$-C_6H_5$	250	4.55	320	3.53
					345	3.59

* Indicates a change in log ε value over the indicated range of spectrum.
(i) = Inflexion; (s) = Shoulder.

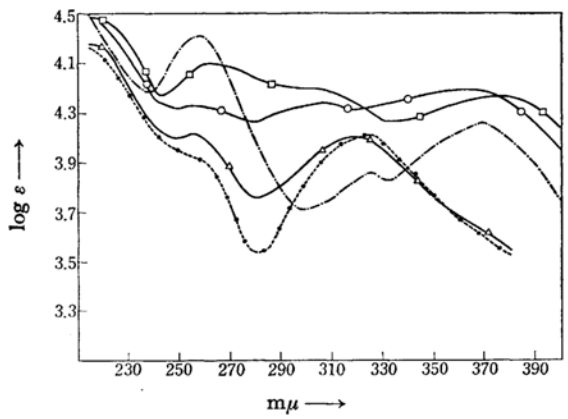


Fig. 1

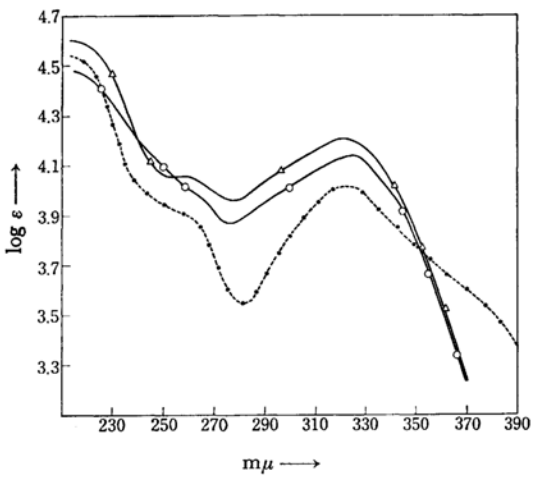
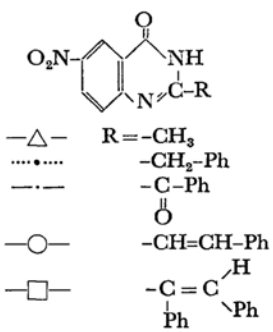
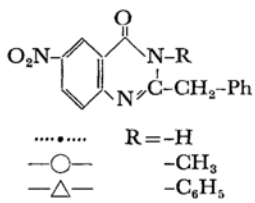


Fig. 2





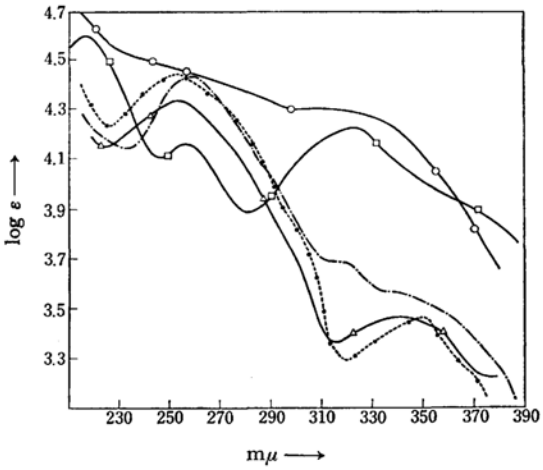
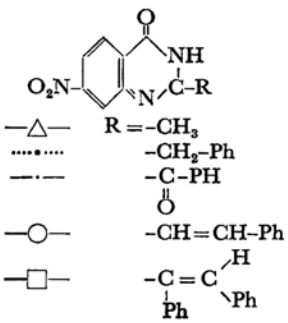


Fig. 3



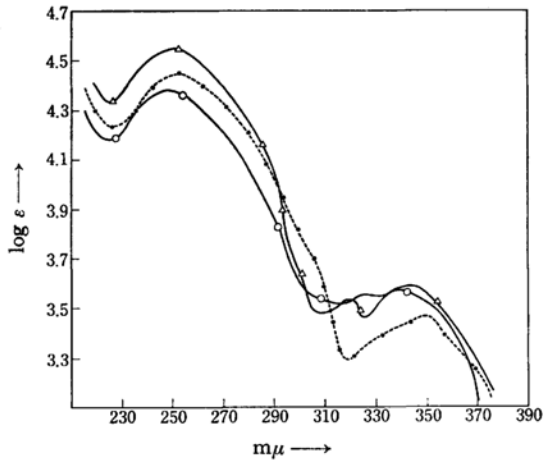
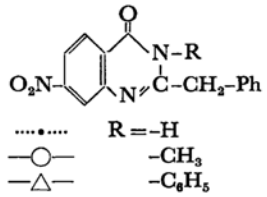


Fig. 4



The ultraviolet spectra of the compounds described in this communication have been studied on Beckmann DU Spectrophotometer in ethanol solution. The sepctral data have been reported in Table 1 and the spectral curves have been shown in Figs. 1—4. 2-Alkyl-3*H*-4-ketoquinazoline normally exhibits a three band spectrum characteristic of a bicyclic aromatic hydrocarbon with the only difference that the long wavelength band does not show a much finer structure.[9] The spectra of all the 2,3-disubstituted 6- and 7-nitro-4-ketoquinazolines described in the present communication comprise only two bands. They have been designated as β and *para* bands.[10] The disappearance of the long wave length α band in the spectrum of the nitrosubstituted 2-alkyl-3*H*-4-ketoquinazoline seems most probably due to the presnece of the nitro group which is known to be a very strong chromophore.

The β and *para* bands in the spectrum of 6-nitro-2-methyl-3*H*-4-ketoquinazoline appear at 255 mμ ($\log \varepsilon = 4.02$) and 320 mμ ($\log \varepsilon = 4.01$) (Fig. 1). The corresponding bands appear at relatively longer wavelengths ($\Delta\lambda \approx +5$ mμ) in the spectrum of 6-nitro-2-benzyl-3*H*-4-ketoquinazoline (IV). In the spcctrum of 6-nitro-2-benzoyl-3*H*-4-ketoquinazoline (VII) the β band is much more intense ($\log \varepsilon = 4.41$) and the *para* band appears at a much longer wavelength, 370 mμ ($\log \varepsilon = 4.06$), than the corresponding bands in the spectrum of its parent compound, 6-nitro-2-benzyl-3*H*-4-ketoquinazoline (IV). This seems to be due to the -C-Ph group acting as a strong chromophore.
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Attachment of a styryl group in 2-position increases the length of the conjugated system. This is reflected in the spectrum of 6-nitro-2-styryl-3*H*-4-ketoquinazoline (IX) which exhibits a strong absorption over the whole of the spectrum range with the value of log ε ranging around the value of 4.0. In the spectrum of 6-nitro-2(1-phenylstyryl)-3*H*-4-ketoquinazoline (X) the short wavelength β band is slightly stronger probably owing to an extra phenyl group while the long wavelength *para* band is somewhat weaker than the corresponding band in the spectrum of its 2-styryl compound (IX). Similar differences in the spectral trends have been observed in the spectra of stilbene and α-phenylstibene by Suzuki.[11] According to this author, the difference in the spectral trend is due to the fact that all the three phenyl groups in α-phenylstilbene are not accomodated in a strain-free planar configuration around the ethylenic bond, but have

9) J. B. Koepfli, J. F. Mead and J. A. Brockman, *J. Am. Chem. Soc.*, **71**, 1048 (1949).

10) E. Clar, "Aromatische Kohlenwasserstoffe," 2. Auflage., Julius Springer, Berlin (1952).

11) H. Suzuki, This Bulletin, **33**, 389 (1960).

been possibly tilted slightly away from the main plane. By analogy 6-nitro-2-(1-phenylstyryl)-3*H*-4-ketoquinazoline (X) may be supposed to have a similar configuration for the quinazolone moiety and the two phenyl groups around the styryl double bond. Had only the α-phenyl group been tilted away from the main plane and the other two groups left remaining in the same plane, the spectra of 2-(1-phenylstyryl) and 2-styryl compounds would have probably been almost exactly the same in the long wavelength part of their spectra. The spectra of 6-nitro-2-benzyl-3*H*-4-ketoquinazoline (IV), and its 3-methyl and 3-phenyl derivatives (V and VI) exhibit mainly the same trends (Fig. 2). The *β* and *para* bands in the spectra of both the 3-methyl and 3-phenyl compounds (V and VI) appear respectively at almost the same positions as, but more intense than, the corresponding bands in the spectrum of their parent 3*H* compound (IV). The spectral similarity is an indication of the fact that compound IV exists mostly in the amide-form like its 3-methyl and 3-phenyl derivatives (V and VI) which have fixed keto-structures.

The ultraviolet spectra of 7-nitro-2-methyl-3*H*-4-ketoquinazoline (XV) and its 2-benzylanalog (XIII) comprise only two bands (Fig. 3). The *β* band appears near about 255 mμ but is more intense in the spectrum of XIII than that in the spectrum of XV; the *para* band appears round about 350 mμ in the spectra of both these compounds. The spectrum of the 7-nitro-2-benzoyl compound (XIV) also comprises two bands; its long wavelength *para* band is almost featureless and is more intense than the corresponding band in the spectrum of XIII in the region beyond 310 mμ as expected, owing to the presence of the 2-benzoyl group acting as a stronger chromophore. The UV spectrum of 7-nitro-2-styryl 3*H*-4-ketoquinazoline (XVI) exhibits a strong absorption over a range from 210 to 323 mμ with log ε value decreasing slowly from 4.7 to 4.2; the only feature in the spectrum of XVI seems to be a broad shoulder near about 323 mμ, beyond which the intensity of absorption decreases comparatively more rapidly. The broadening, the increased intensity and the disappearance of the fine structure of the constituent bands are the usual effects of increased conjugation which in this case is due to the presence of styryl group in 2-position. The spectrum of 7-nitro-2(1-phenylstyryl)-3*H*-4-ketoquinazoline (XVII) exhibits an arm at 261 mμ (log ε=4.59) and a peak at 256 mμ (log ε=4.16) and a broad band at 256 mμ (log ε=4.16) and a broad band at about 323 mμ (log ε=4.23). However the intensity of all the bands in the spectrum of the 7-nitro-2-(1-phenylstyryl) compound (XVII) is less than that of the corresponding bands in the spectrum of its parent compound (XVI) almost over the whole spectral range. It seems to be due to the steric effect exerted by the α-phenyl group which would not allow all the three groups to remain in a strain-free planar configuration. The spectra of 7-nitro-2-benzyl-3-methyl and phenyl (XVIII and XIX) derivatives are very closely similar to that of their parent compound (XIII) (Fig. 4), indicating that XIII exists mostly in the keto-form.

Experimental

5-Nitro-*N*-phenylacetylanthranilic Acid (II). The compound was prepared by heating 5-nitroanthranilic acid (2.58 g) with phenylacetyl chloride (4.2 g) in dry benzene (20 m*l*) containing a drop of pyridine for two hours. Excess of benzene was removed by steam distillation and the residual solid product was collected, washed with hot water and crystallized from a mixture of chloroform and benzene (2 : 1) in white long needles, mp 187—189°C. Yield: 2.5 g.

Found: N, 9.40%. Calcd for $C_{15}H_{12}O_5N_2$: N, 9.33%.

4-Nitro-*N*-phenylacetylanthranilic Acid (XI). The compound was prepared as described above from 4-nitroanthranilic acid and crystallized from aqueous ethanol in white needles, mp 206—208°C.

Found: N, 9.28%. Calcd for $C_{15}H_{12}O_5N_2$: N, 9.33%.

6-Nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (III). A mixture of 5-nitro-*N*-phenylacetylanthranilic acid (0.660 g) and acetic anhydride (1.5 m*l*) was refluxed for forty five minutes. The solution was clarifide with activated charcoal, filtered hot and cooled to room temperature to give yellowish crystalline solid. It was filtered and washed with dry petroleum ether, mp 177—179°C. Yield: 0.550 g.

Found: N, 9.85%. Calcd for $C_{15}H_{10}O_4N_2$: N, 9.92%.

7-Nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (XII). The compound was synthesised from 4-nitrophenylacetylanthranilic acid (0.5 g) and acetic anhydride as described above in the form of yellowish white needles, mp 125—126°C. Yield: 0.390 g.

Found: N, 9.82%. Calcd for $C_{15}H_{10}O_4N_2$: N, 9.92%.

6-Nitro-2-benzyl-3*H*-4-ketoquinazoline (IV). 6-Nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (0.550 g) was suspended in liquid ammonia and heated for three hours at 100°C. The reaction mixture was acidified and the solid product was stirred in dilute bicarbonate solution. The residual solid was then filtered, washed and crystallized from glacial acetic acid (carbon) in pale yellow crystalline solid, mp 258—260°C. Yield: 0.405 g.

Found: N, 15.02%. Calcd for $C_{15}H_{11}O_3N_3$: N, 14.95%.

7-Nitro-2-benzyl-3*H*-4-ketoquinazoline (XIII). The compound was prepared as described above from 7-nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (0.380 g). It was crystallized from ethanol (carbon) in white cottony needles, mp 262—264°C. Yield: 0.315 g.

Found: N, 14.85%. Calcd for $C_{15}H_{11}O_3N_3$: N, 14.95%.

6-Nitro and 7-Nitro-2-benzyl-3*H*-4-ketoquinazolines (IV and XIII) by Modified Niementowski Method. A mixture of 4- or 5-nitro-*N*-phenylacetylanthranilic acid (1.3 g) and formamide (2.0 g) was heated to 160—165°C for two hours. The solid product was powdered and stirred in bicarbonate solution,

filtered, and washed with water. It was crystallized from glacial acetic acid. Yield 22.9% for the 7-nitro isomer and 15.5% for 6-nitro isomer, respectively. They were compared (mixed mp) with corresponding products prepared by an alternate method describeed earlier.

6-Nitro-2-benzyl-3-methyl-4-ketoquinazoline (V). The compound was formed on heating a suspension of 6-nitro-4*H*-3,1-benzoxazin-4-one (0.350 g) and methylamine (2.0 m*l*; 10%) for an hour on a water bath. The dark orange coloured solution was decomposed with dilute hydrochloric acid (10 m*l*) and the solid product was collected, washed with bicarbonate solution and crystallized from ethanol (carbon) in white amorphous powder, mp 180—182°C. Yield: 0.275 g.

Found: N, 14.13%. Calcd for $C_{16}H_{13}O_3N_3$: N, 14.25%.

7-Nitro-2-benzyl-3-methyl-4-ketoquinazoline (XVIII). The compound was prepared from 7-nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (0.4 g) and methylamine and was crystallized from ethanol (carbon) in light amorphous powder, mp 155—158°C. Yield: 0.330 g.

Found: N, 13.78%. Calcd for $C_{16}H_{13}O_3N_3$: N, 14.25%.

6-Nitro-2-benzyl-3-phenyl-4-ketoquinazoline (VI). The compound was prepared by reacting 6-nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (0.4 g) with 20% alcoholic solution of aniline (3.0 m*l*). It was crystallized from glacial acetic acid in yellowish white plates, mp 231—233°C. Yield: 0.365 g.

Found: N, 11.92%. Calcd for $C_{21}H_{15}O_3N_3$: N, 11.76%.

7-Nitro-2-benzyl-3-phenyl-4-ketoquinazoline (XIX). The compound was synthesised from 7-nitro-2-benzyl-4*H*-3,1-benzoxazin-4-one (0.5 g) and aniline. The product was crystallized from ethanol (carbon) in silvery plates, mp 171—173°C. Yield: 0.420 g.

Found: N, 11.69%. Calcd for $C_{21}H_{15}O_3N_3$: N, 11.76%.

6-Nitro-2-styryl-3*H*-4-ketoquinazoline (IX). A suspension of 6-nitro-2-methyl-3*H*-4-ketoquinazoline (0.3 g) in freshly distilled benzaldehyde (2 m*l*) was heated for an hour at 180°C. The reaction mixture was steam distilled to remove excess benzaldehyde. The brownish orange product was collected, treated with bicarbonate solution and crystallized (carobn) from glacial acetic acid in orange yellow powder, mp 322—323°C. Yield: 0.405 g.

Found: N, 14.20%. Calcd for $C_{16}H_{11}O_3N_3$: N, 14.33%.

7-Nitro-2-styryl-3*H*-4-ketoquinazoline (XVI). The compound was synthesised from 7-nitro-2-methyl-3*H*-4-ketoquinazoline (0.420 g) and benzaldehyde (2.0 m*l*). The product was crystallized from glacial acetic acid in light yellow powder, mp 298—300°C. Yield: 0.575 g.

Found: N, 13.96%. Calcd for $C_{16}H_{11}O_3N_3$: N, 14.33%.

6-Nitro-2-(1-phenylstyryl)-3*H*-4-ketoquinazoline (X). The compound was prepared from 6-nitro-2-benzyl-3*H*-4-ketoquinazoline (0.570 g). The product was crystallized from glacial acetic acid in yellowish short needles, mp 274—276°. Yield: 0.600 g.

Found: N, 11.59% Calcd for $C_{22}H_{14}O_3N_3$: N, 11.41%.

7-Nitro-2-(1-phenylstyryl)-3*H*-4-ketoquinazoline (XVII). The compound was prepared from 7-nitro-2-benzyl-3*H*-4-ketoquinazoline and benzaldehyde. The brownish sticky mass was dissolved in a minimum amount of acetone and the acetone extract was poured in dilute bicarbonate solution and left overnight at room temperature. The solid product was collected, washed and crystallized from aqueous ethanol in light yellow short needles, mp 242—244°C. Yield: 98.5%.

Found: N, 11.18%. Calcd for $C_{22}H_{14}O_3N_3$: N, 11.41%.

7-Nitro-2-benzoyl-3*H*-4-ketoquinazoline (XIV). The compound was formed on, oxidation of 7-nitro-2-benzyl-3*H*-4-ketoquinazoline by the following two methods.

a) Oxidation with Alkaline Permanganate. 6-Nitro-2-benzyl-3*H*-4-ketoquinazoline (1.0 g) was suspended in a mixture of sodium hydroxide solution (5.0 m*l*; 4%) and potassium permanganate solution (50.0 m*l*; 2%). The reaction mixture was heated on a boiling water bath for six hours with continuous stirring. As the violet colour disappeared, extra permanganate (1.0 g) was added and heating was continued for two more hours. Excess permanganate was destoryed by adding required amount of ethanol to the hot reaction mixture. The latter was then filtered hot and the precipitates were washed with boiling water. The combined filtrate was concentrated and acidified with acetic acid. The product which separated was collected and crystallized from ethanol in pale yellow short needles, mp 235—237°C. The precipitated manganese dioxide was extracted with boiling acetone. Acetone was evaporated to dryness to give a major portion of the unreacting original compound (XIII).

Found: 13.96%. Calcd for $C_{15}H_9O_4N_3$: N, 14.23%.

b) Oxidation with Selenium Dioxide. A mixture of 7-nitro-2-benzyl-3*H*-4-ketoquinazoline (0.6 g) and selenium dioxide (0.6 g) in isoamyl alcohol (15.0 m*l*) was refluxed for fifteen hours. The yellowish brown solution was filtered hot and the residual solid was washed with a minimum amount of hot isoamyl alcohol. The combined filtrate was steam distilled to remove isoamyl alcohol. The residual brownish yellow product was collected, washed and crystallized from ethanol (charcoal) in light yellow short needles, mp 235—237°C.

Found: N, 14.12%. Calcd for $C_{15}H_9O_4N_3$: N, 14.23%.

6-Nitro-2-benzoyl-3*H*-4-ketoquinazoline (VII). The compound was formed on oxidation of 6-nitro-2-benzyl-3*H*-4-ketoquinazoline by the two methods described above. In the permanganate oxidation reaction major part of the starting substance (IV) was recovered unchanged. The product was crystallized from ethanol in yellowish white tiny needles, mp 230—233°C.

Found: N, 14.15%. Calcd for $C_{15}H_9O_4N_3$: N, 14.23%.