Phototropic Products from the Reactions of Aril Monoazines with Bases

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Treatment of benzil monoazine with sodium methoxide gives 5-methoxy-1,2,5-triphenyl-3,4-diaza-2,4-pentadien-1-one (**2**), 5-benzoyl-4,5-dihydro-3,4,5-triphenylpyrazol-4-ol (**3**), and simple cleavage products. Compound **3** is hydrolyzed to 3,4,5-triphenylpyrazole and benzoic acid. It is phototropic, being reversibly converted on exposure to sunlight to a red product, which is readily autoxidized to benzil monoazine. Analogous phototropic products are formed on reaction of *p*-anisil monoazine and *p*-tolil monoazine with sodium methoxide. Reduction of the azines to the phototropic products may occur by cleavage to α-keto imine anions followed by their dimerization; such a pathway can also account for the formation of the cleavage products. Alternatively, reduction may proceed by hydride or electron transfer; that hydride transfer need not necessarily be involved is established by the observation that treatment of *p*-tolil monoazine with potassium *t*-butoxide also gives the corresponding phototropic product. It is proposed that the phototropic transformations involve intramolecular hydrogen abstraction to give enolic isomers of **3** and its analogs in which the heterocyclic ring has been cleaved.

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Le traitement de la monoazine du benzile avec du méthylate de sodium conduit au méthoxy-5 triphényl-1,2,5 diaza-3,4 pentadien-2,4 one-1 (**2**) aux côtés du benzoyl-5 dihydro-4,5 triphényl-3,4,5 pyrazolol-4 (**3**) et d'autres composés de clivages simples. Le composé **3** peut être hydrolyzé pour fournir de l'acide benzoique et de la triphényl-3,4,5 pyrazole. C'est un composé phototropique qui se transforme d'une façon réversible sous l'action de la lumière du jour en un composé rouge qui est facilement autooxydé en un monoazine de benzile. D'autres composés phototropiques analogues sont formés par réaction des monoazines de *p*-anisile et de *p*-tolile avec le méthylate de sodium. La réduction des azines en produits phototropiques peut s'effectuer par clivage conduisant aux anions des α-céto imines qui peuvent alors se dimérisés; un tel processus peut aussi expliquer la formation des produits de clivage. La réduction peut aussi être effectuée par un hydrure ou un transfert d'électrons; le fait que le transfert d'hydrure n'est pas nécessairement impliqué est démontré par l'observation que le traitement de la monoazine du *p*-tolile avec du *t*-butylate de potassium donne aussi le produit phototropique correspondant. On propose donc que les transformations phototropiques impliquent un enlèvement d'hydrogène moléculaire conduisant aux isomères énoliques de **3** ainsi qu'à ses analogues dans lesquels l'hétérocycle a été coupé. [Traduit par le journal]

The reaction of benzil monoazine (**1**) with sodium methoxide was first investigated by Yates and Shapiro in connection with their studies of the reactions of α-diazo ketones with bases (1).

When a suspension of **1** and excess sodium methoxide in ether was boiled under reflux, the amount of suspended solid slowly decreased and the mixture acquired a deep purple color. The intensity of this color was not diminished after 15 days at reflux. Treatment of the mixture with water rapidly destroyed this color, giving an intensely yellow orange ethereal phase. Methyl benzoate, benzonitrile, and benzamide, together with unconsumed **1**, were isolated from the ethereal solution. In addition, two new crystalline compounds were obtained, each in *ca.* 10% yield; these are assigned structures **2** and **3** (Scheme 1).

Compound **2** is a very pale yellow substance, $C_{22}H_{18}N_2O_2$, that contains a methoxyl group and shows a strong band at 5.95 μ in its i.r. spectrum (*cf.* **1**, 5.95 μ) but no band in the 2.8–3.2 μ region. On hydrolysis in acid medium it gave **1**, benzil (**4**), benzoic acid, and hydrazine; basic hydrolysis gave deoxybenzoin (**5**), deoxybenzoin azine (**6**), and benzoic acid (Scheme 2). These hydrolysis products can be envisaged as arising via hydrolysis of the imino ether system of **2** to give **7** and hydrolysis of this

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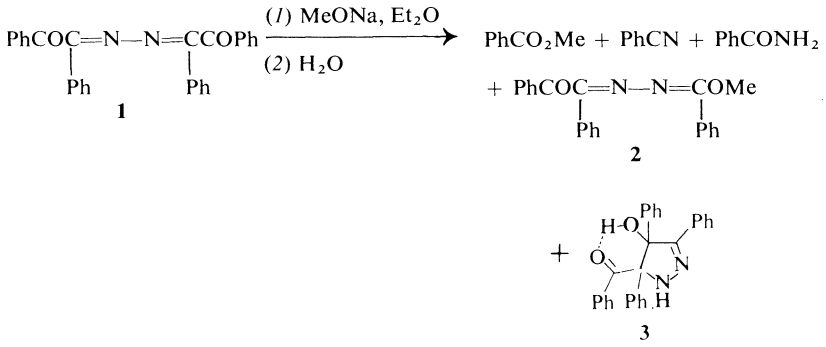
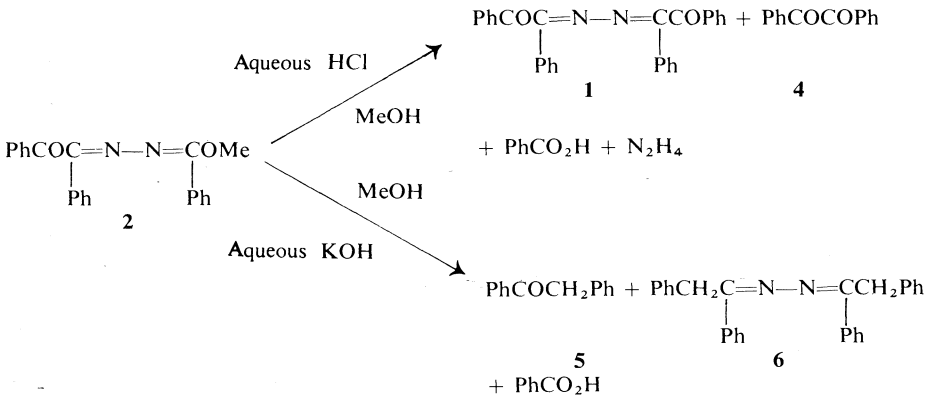
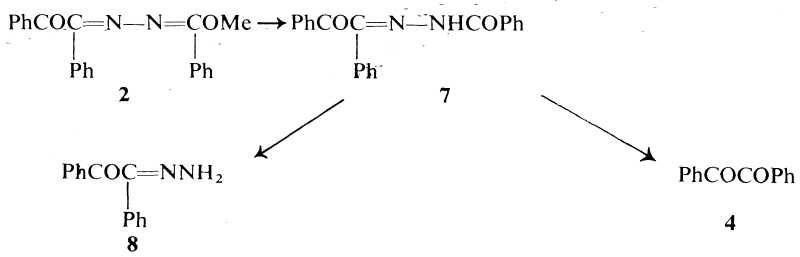


SCHEME 1



SCHEME 2

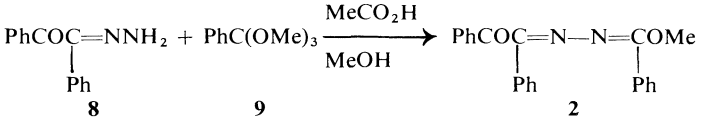


SCHEME 3

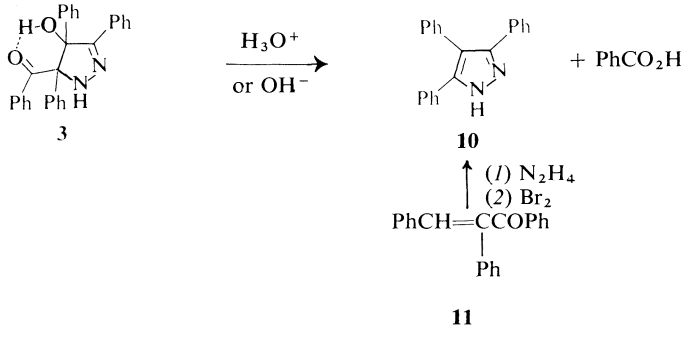
to benzil (**4**) or benzil monohydrazone (**8**) (Scheme 3). Facile Wolff-Kishner reduction of the monohydrazone of an α-diketone under mildly basic conditions has ample precedent (2).

The structural assignment **2** was confirmed by the independent synthesis of this compound in good yield from benzil monohydrazone (**8**) and trimethyl orthobenzoate (**9**) (Scheme 4).

Compound **3** is a yellow crystalline substance, $C_{28}H_{22}N_2O_2$, that undergoes decomposition on attempted recrystallization. Its most striking property is its phototropism; on exposure to light it is reversibly converted to a red substance that in turn is converted to **1** in the presence of air. For this reason it is necessary to carry out the reaction of **1** with sodium methoxide and the isolation of **3** in the dark or in subdued light. The i.r. spectrum of **3** shows a complex, medium intensity band at 3.01 μ and a single band in the carbonyl-stretching region at 6.03 μ. Its ^1H n.m.r. spectrum shows, in addition to signals corresponding to 20 aromatic protons, 2 one-proton singlets at δ 6.01 and 7.32 that are absent after treatment with D_2O. Compound **3** was



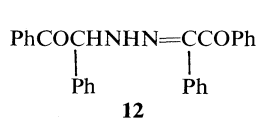
SCHEME 4



SCHEME 5

hydrolyzed in either acidic or basic medium to give benzoic acid and 3,4,5-triphenylpyrazole (**10**), which was identified by comparison with an authentic sample prepared by treatment of α-phenylchalcone (**11**) with hydrazine followed by oxidation with bromine (Scheme 5).

The reconversion of the phototropic product to **1** in good yield under mild conditions suggests strongly that it retains the skeleton of **1** and this, together with its spectra and its hydrolysis to **10**, leads to the structural assignment **3**. This assignment requires that strong hydrogen bonding in the β-ketol system shifts the carbonyl-stretching band in the i.r. spectrum of **3** to an unusually long wavelength; such shifts have been observed previously for related β-ketols (3). Structure **3** is related by ring closure to the acyclic dihydroazine **12**; an alternative structure **13**, similarly related to **12**, cannot be absolutely excluded at this juncture,[2] although it seems very unlikely that hydrogen bonding in this structure would be sufficiently strong to account for the i.r. spectrum (*vide supra*).



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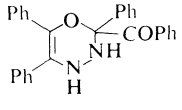


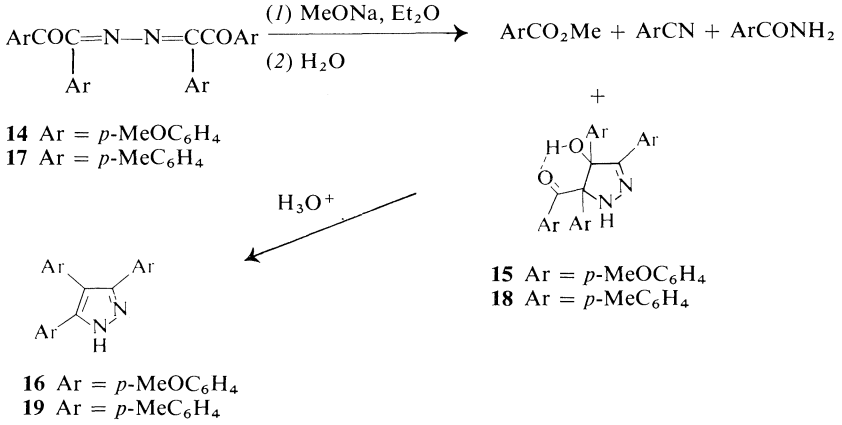
13

In order to obtain further spectroscopic data on which to base a definitive distinction between structures **3** and **13**, attempts were made to form an alkyl or acyl derivative of the phototropic compound. These were unsuccessful, and attention was turned to the reaction of sodium methoxide with other aril monoazines.

Reaction of *p*-anisil monoazine (**14**) gave methyl *p*-anisate, *p*-anisonitrile, *p*-anisamide, and a phototropic dihydro product that gave 3,4,5-tri-*p*-anisylpyrazole (**16**) on hydrolysis and is assigned structure **15** (Scheme 6); no product analogous to **2** was isolated, but no significance is attached to this circumstance since the weight balance of the products isolated was poor. Compound **15**, however, is more sensitive to oxidation than is **3** and was not investigated further.

Reaction of *p*-tolil monoazine (**17**) with sodium methoxide gave methyl *p*-toluate, *p*-tolunitrile, *p*-toluamide, and a phototropic dihydro product that gave 3,4,5-tri-*p*-tolylpyrazole (**19**) on hydrolysis and is assigned structure **18**; again no analog of **2** could be isolated. Compound **18** was isolated in 25% yield and formed a monoacetyl derivative on treatment with acetyl chloride. This derivative shows a single one-proton signal in its ^{1}H n.m.r. spectrum that is absent after D_2O treatment in contrast to its parent compound, which shows two such signals. Its i.r. spectrum shows a weak broad band at 2.8–3.1 μ and a strong band at 6.00 μ. The latter spectrum clearly indicates that, in terms of structure **18**, acylation has occurred on nitrogen to give **20**. In terms of structure **21**, the analog of

[2]The formation of **10** could be accommodated by the postulation of the intermediacy of **12** in the hydrolyses.



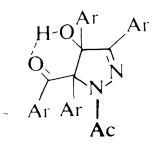
14 Ar = *p*-$MeOC_6H_4$
17 Ar = *p*-MeC_6H_4

15 Ar = *p*-$MeOC_6H_4$
18 Ar = *p*-MeC_6H_4

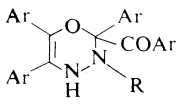
16 Ar = *p*-$MeOC_6H_4$
19 Ar = *p*-MeC_6H_4

SCHEME 6

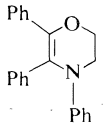
13, the acetylation product would have structure **22**.



20 Ar = *p*-MeC_6H_4



21 Ar = *p*-MeC_6H_4; R = H
22 Ar = *p*-MeC_6H_4; R = Ac



23

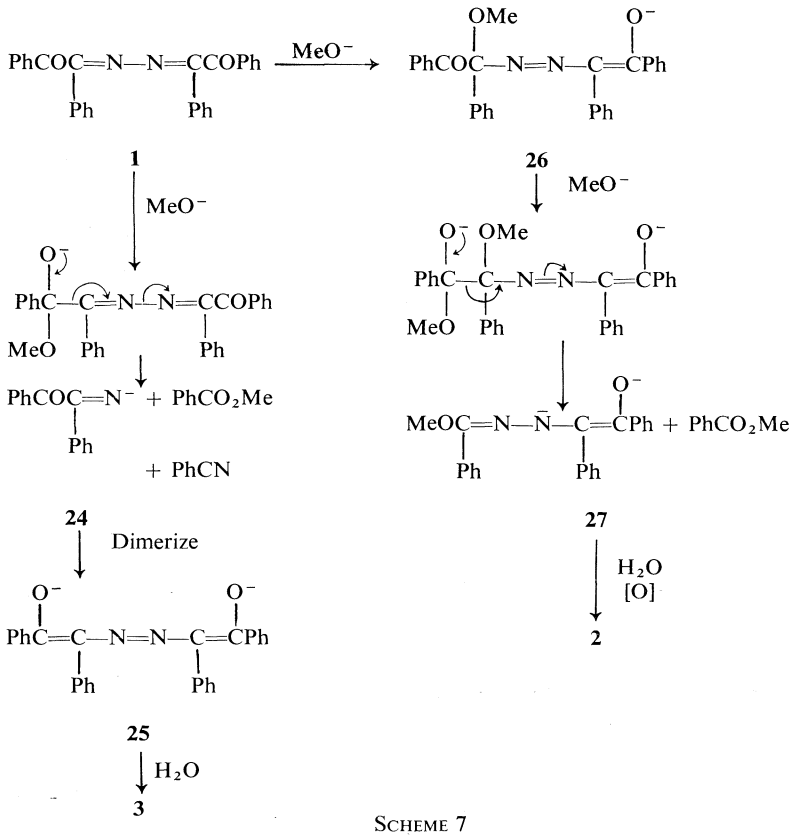
A definitive distinction could be made between these structures on the basis of ^{13}C n.m.r. spectroscopy. The ^{13}C spectrum of the acetylation product shows, in addition to signals attributable to methyl, aryl, and carbonyl carbons, signals at δ 83.9, 94.8, and 156.0. The first two of these can be assigned to the two sp^3 carbon atoms of the pyrazoline ring of **20** and the third to the pyrazoline C=N carbon atom (4). Structure **22** possesses only a single sp^3 carbon atom in addition to methyl carbon atoms and no carbon atom that would be expected to give rise to a signal at δ 156.0. The remote possibility that one of the ethylenic carbon atoms might give rise to a signal at δ < 100 was eliminated by examination of the ^{13}C spectrum of compound **23** (5); this showed only two methylene signals in the region δ < 120. Thus **22** can be excluded as the structure of the acetyl derivative.

One interpretation of the origin of compounds **2** and **3** from **1** is shown in Scheme 7. Here **3** arises from the dianion **25**, which is formed by dimerization of the anion **24**, itself formed together with methyl benzoate and benzonitrile by nucleophilic attack of methoxide ion on a carbonyl group of **1**. It may be noted that the anion **24** can be represented as the hybrid **24***a* with nitrenoid character. The origin of **2** is represented as involving initial attack by methoxide ion on an azomethine group of **1** to give an anion **26**, which is again attacked by methoxide ion to give methyl benzoate and the dianion **27**, which undergoes protonation and oxidation to **2** during the aqueous work-up. Alternatively, oxidation might occur before protonation by electron transfer from **27** to **1**, giving **2** and **25**. It is possible that the purple color of the reaction mixture arises from the dianions **25** and/or **27**; thus, treatment of **3** in ether with sodium hydride also generated this color.

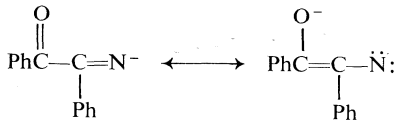
A different interpretation of the origin of **3** is shown in Scheme 8. Here reduction of **1** is postulated to occur by hydride transfer from methoxide ion in a Meerwein-Ponndorf process, for which analogy exists (6), giving the monoanion **28**.

This view of the formation of **3** as involving a simple reduction process led us to investigate the possibility of preparing compounds of type **3** by the hydrogenation of aril monoazines. In the event, this has proved to be successful and to provide the best method for the preparation of such compounds (7).

The conception of Scheme 8 also led us to examine the reaction of an aril monoazine with



SCHEME 7

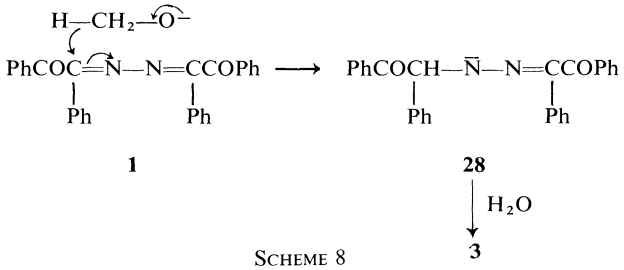


24*a*

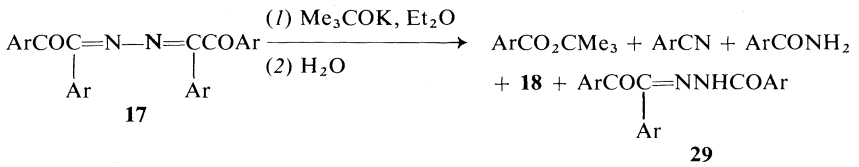
potassium *t*-butoxide, an alkoxide without the potentiality for hydride ion transfer. Treatment of *p*-tolil monoazine (**17**) with potassium *t*-butoxide in boiling ether led to more rapid development of a deep-purple coloration than in the case of sodium methoxide. Aqueous work-up gave *t*-butyl *p*-toluate, *p*-tolunitrile, *p*-toluamide, the phototropic compound **18**, and *p*-tolil *p*-toluylhydrazone (**29**) (Scheme 9). The structure of **29** was established by its independent preparation from *p*-tolil monohydrazone and *p*-toluyl chloride; this product may well arise from compound **30**, the analog of **2**.

The formation of **18** by reaction of **17** with potassium *t*-butoxide demonstrates that reduction of **17** by an alkoxide can occur without the involvement of hydride ion transfer, although it does not, of course, exclude this as a possible pathway in the reaction of **17** with methoxide ion. Recent evidence that both methoxide and *t*-butoxide ion can react by electron transfer to systems with high electron affinity (8) leaves open the possibility that reduction of the aril monoazines occurs by such a pathway. However, we presently favor the process postulated in Scheme 7 since it provides an economical interpretation of the formation of both the phototropic compounds and the fragmentation products from the azines.

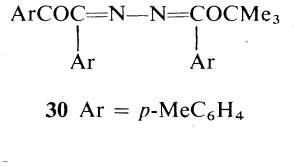
Finally we comment on the phototropism f **3** and its analogs. Exposure of **3** in the solid state or solution to light led to the formation of a red compound which reverted to **3** in the dark and gave **1** in the presence of air. This red compound could not be isolated, but it was shown to possess a strong i.r. band at 6.50 μ (see Experimental). Prolonged exposure of **3** to light and air led to its complete conversion to **1**. Similar observations were made in the case of compound **18**; however, its *N*-acetyl derivative, **20**, did not undergo these transformations. It is suggested



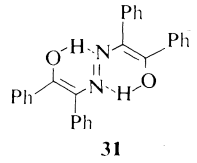
SCHEME 8



SCHEME 9
(Ar = p-MeC_6H_4)



30 Ar = p-MeC_6H_4



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that the structure of the red intermediate is **31** and that it is formed via intramolecular hydrogen abstraction by the carbonyl oxygen atom in an excited state of **3**. It may be noted that **31** is the dienol corresponding to the dianion **25**.

Experimental

Hydrolysis of **2**

In Acid Medium

A solution of **2** (180 mg) (1) in a mixture of concentrated hydrochloric acid (10 ml), water (10 ml), and methanol (10 ml) was boiled under reflux for 5 h. The mixture was cooled, made basic with sodium hydroxide, and extracted with chloroform. The dried extract gave benzil monoazine (105 mg) and benzil (trace). Acidification of the aqueous phase and extraction gave benzoic acid (32 mg). The aqueous phase was again made basic with sodium hydroxide and the presence of hydrazine was established by the addition of a few drops of benzaldehyde; the pale yellow solid that separated after several hours was filtered, washed with water and a small amount of ice-cold 95% ethanol; m.p. 90–92°, undepressed on admixture with authentic benzalazine, m.p. 93–94° (lit.(9) m.p. 93°).

In Basic Medium

A solution of **2** (500 mg) and potassium hydroxide (20 g) in water (20 ml) and methanol (40 ml) was boiled under reflux for 26 h under nitrogen. The mixture was cooled, diluted with water, and extracted with dichloromethane. Evaporation of the extract and crystallization of the residue from 95% ethanol gave deoxybenzoin azine (**6**; 51 mg) as bright yellow crystals; three recrystallizations from ethanol–benzene gave material, m.p. 163–164°, undepressed on admixture with authentic deoxybenzoin azine, m.p. 163–164° (lit. (10) m.p. 164°). The mother liquor from the original crystallization of the azine was treated with 2,4-dinitrophenylhydrazine and hydrochloric acid to give deoxybenzoin 2,4-dinitrophenylhydrazone (120 mg) as pale orange crystals; three recrystallizations from chloroform–methanol gave shiny, orange prisms, m.p. 202–203°, undepressed on admixture with authentic deoxybenzoin 2,4-dinitrophenylhydrazone, m.p. 202–203° (lit. (11) m.p. 204°). Acidification of the original basic aqueous solution gave benzoic acid (265 mg).

Independent Synthesis of **2**

A solution of benzil monohydrazone (1.68 g), trimethyl orthobenzoate (3.08 g), and a few drops of acetic acid in anhydrous methanol (70 ml) was boiled under reflux for 72 h. The mixture was evaporated and the residue was taken up in benzene and chromatographed on neutral alumina. Evaporation of eluates obtained with benzene and 5% ether–benzene gave **2** (1.87 g; 73%) as a pale yellow crystalline solid; three recrystallizations from ether gave material, m.p. 124–125°, that was shown by mixture melting point and i.r. spectral comparison to be identical with the product, m.p. 124.5–125.5°, obtained from the reaction of **1** with sodium methoxide.

Hydrolysis of **3**: *Formation of* ***10***

In Acid Medium

A solution of **3** (450 mg) (1) in a mixture of methanol (50 ml), concentrated hydrochloric acid (15 ml), and benzene (15 ml) was boiled under reflux in the dark for 3.5 h. The solution was concentrated by evaporation to *ca.* 40 ml, cooled to room temperature, made basic with sodium hydroxide, and cooled at 0° overnight. The white needles that were deposited were collected, washed with a little cold aqueous sodium hydroxide and with water, and dried to give 3,4,5-triphenylpyrazole (**10**; 316 mg; 99%), m.p. 258–259.5°. Four recrystallizations from methanol gave material, m.p. 261–262°. The melting point of this product

was not depressed on admixture with authentic 3,4,5-triphenylpyrazole, m.p. 261–263° (*vide infra*).

Anal. Calcd. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.26; H, 5.22; N, 9.34.

Acidification of the original aqueous filtrate gave benzoic acid (118 mg; 90%).

In Basic Medium

Hydrolysis of **3** with boiling 20% aqueous methanolic potassium hydroxide for 14 h also gave 3,4,5-triphenylpyrazole (**10**) but in considerably lower yield (16%); the major product was benzil monoazine (55%).

*3,4,5-Triphenylpyrazole (**10**)*[3]

A solution of α-phenylchalcone (**11**; 5.68 g) (13), 95% hydrazine (750 mg), and two drops of acetic acid in ethanol (60 ml) was boiled under reflux for 12 h. The solution was cooled in an ice bath to give 3,4,5-triphenyl-2-pyrazoline as a white crystalline solid, which was filtered and washed with a little cold ethanol; concentration of the mother liquor gave a second crop of the same product (total yield, 95%). Four recrystallizations from ethanol (with minimal contact with the air) and drying *in vacuo* at room temperature gave an analytical sample, m.p. 166–168° (dec.); λ_{max} (CH_2Cl_2) 3.01 μ.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.41; H, 6.06; N, 9.27.

A solution of 3,4,5-triphenyl-2-pyrazoline (unrecrystallized: 4.50 g) in chloroform (50 ml) was treated with a solution of bromine in chloroform until the bromine color was no longer destroyed. A small additional portion of bromine solution was added and the mixture was boiled under reflux for 4 h. The mixture was evaporated with chloroform twice to dryness, the residue was taken up in hot 95% ethanol, and the solution was boiled under reflux for 30 min with aqueous 10% sodium hydroxide (50 ml). The resulting copious white precipitate was brought into solution by the addition of hot ethanol (400 ml) and the solution was filtered hot, allowed to cool slowly to room temperature, and then chilled in an ice bath to give 3,4,5-triphenylpyrazole (**10**), m.p. 259–261° (3.57 g; 80%). Three recrystallizations from methanol gave material, m.p. 261–263° (lit. (12) m.p. 265°).

*Irradiation of **3***

On exposure to visible light, compound **3** in the solid state or in solution rapidly acquired a very intense red color. A solution of **3** in dichloromethane in an i.r. cell was irradiated with strong sunlight for 5 min and the i.r. spectrum of the solution was immediately recorded three times in succession (20 min). The spectrum of the freshly irradiated solution showed a diminution of *ca.* 5% in the intensities of the bands of **3** and the appearance of a new band at 6.50 μ, together with weaker new bands in the 6.0–12.0 μ region. The second trace showed a marked decrease in intensity of the 6.50 μ band, and in the third trace this was almost entirely absent; the intensities of the bands of **3** increased in the second and third traces. During the recording of these three spectra the red color of the irradiated solution had faded almost completely, restoring the original color. Similar behavior was observed when the same solution was exposed to light for additional periods of 15 and 30 min. However, at the end of the third exposure, the 6.03 μ band of **3** had a distinct shoulder on the lower wavelength side that did not decrease in intensity with time. On prolonged exposure to sunlight (*ca.* 12 h) the red color faded gradually and the i.r. spectra showed the growth of the shoulder into the band of benzil monoazine at 5.95 μ and the eventual disappearances of the band of **3** at 6.03 μ. The solution was then bright yellow in color (perceptibly more intensely colored than the original pale yellow solution of **3**) and its i.r. and u.v. spectra showed the presence of benzil monoazine alone, which was recovered in essentially quantitative yield from the solution.

Addition of a small amount of hydroquinone to a solution of **3** before irradiation did not affect the rate of appearance of the red color. When a solution of **3** in dichloromethane was degassed by freezing in liquid nitrogen, pumping at 2×10^{-5}mm, thawing and refreezing five times, the rate of appearance of the red color was perceptibly faster than in the case of an undegassed solution.

*Reaction of p-Anisil Monoazine (**14**) with Sodium Methoxide: Formation of **15***

p-Anisil monoazine (**14**) was prepared from *p*-anisil and hydrazine dihydrochloride in aqueous ethanol; recrystallization from benzene – acetic acid gave yellow plates, m.p. 162–163.5° (lit. (14) m.p. 165°); λ_{max} ($CHCl_3$) 6.01 μ; λ_{max} (CH_2Cl_2) 293 nm (log ε 4.60), 347 nm (log ε 4.54); $^{H}\delta(CDCl_3)$ 3.71 (s, 6H), 3.81 (s, 6H), 6.73 (d, J = 8 Hz, 4H), 6.95 (d, J = 8 Hz, 4H), 7.48 (d, J = 8 Hz, 4H), 7.93 (d, J = 8 Hz, 4H); *m/e* (%) 536(4), 136(16), 135(100), 105(10), 77(16).

The azine **14** (6.43 g, 0.012 mol), sodium methoxide (2.22 g, 0.041 mol), and dry ether (300 ml) were placed in a dry, nitrogen-preswept, three-necked flask. The mixture was heated under reflux with stirring under a blanket of dry nitrogen. After *ca.* 2 h a faint red tinge was observed in the reaction mixture; after 16 h the reaction mixture was pink, after 1 day it was faint purple, and after 2 days it was dark purple. After 12 days the cooled reaction mixture was shaken with water (250 ml) at night under subdued light giving a dark orange ethereal solution and a pale yellow aqueous solution containing suspended yellow solid. This solid (1.99 g), m.p. 159–164°, was shown by i.r. spectroscopy to be *p*-anisil monoazine. The aqueous solution was extracted with ether, and the combined ethereal solutions were dried, filtered, and concentrated to 50 ml. Compound **15** separated as a yellow crystalline solid (690 mg, 11%),[4] m.p. 177–178°(dec.); λ_{max} ($CHCl_3$) 2.98 (complex), 6.05 μ; λ_{max} (CH_2Cl_2) 289 nm (log ε 4.39), 368 nm (log ε 3.47); *m/e* (%), 538(1), 536(9), 520(2), 510(13), 390(44), 386(10), 375(19), 358(11), 240(15), 227(100), 211(25), 137(11), 136(98), 135(100), 134(47), 133(17).

Anal. Calcd. for $C_{32}H_{30}N_2O_6$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.13; H, 5.67; N, 5.19.

The residual ethereal solution was evaporated to give an orange oil; this was taken up in petroleum ether –

[3]The preparation of **10** by this route has also been reported by Parham and Hasek (12); we include the details of our procedure here since it appears to have some advantage.

[4]In another run with **14** (6.43 g), sodium methoxide (3.33 g), and ether (500 ml) the yield of **15** was increased to 1.26 g (20%).

benzene, and the solution was chromatographed on alumina. Elution with petroleum ether – benzene (3:2) gave a colorless oil (771 mg) which had bands in its i.r. spectrum at 4.47 and 5.82 μ. Rechromatography of these fractions gave methyl *p*-anisate as a white solid (220 mg), m.p. 44–46° (lit. (11) m.p. 49°), λ_{max} (CCl_4) 5.82, 6.22 μ, eluted with petroleum ether, and a white solid, eluted with benzene – petroleum ether (1:3), which crystallized from petroleum ether to give *p*-anisonitrile (150 mg), m.p. 57–58.5°, λ_{max} (CCl_4) 4.47 μ, mixture m.p. 58–59° with an authentic sample (m.p. 59–60°). Elution of the original chromatographic column with petroleum ether – benzene (2:3) gave a yellow oil (630 mg) containing mainly *p*-anisil monoazine. Elution with methanol–chloroform (1:1) gave an oil (170 mg) which crystallized from water to give *p*-anisamide, m.p. 163–164° (lit. (11) m.p. 167°), identified by its i.r. spectrum.

The aqueous solution from work-up of the original reaction mixture was acidified to give *p*-anisic acid (240 mg), m.p. 184–185°, identified by mixture melting point and i.r. spectral comparison with an authentic sample (m.p. 182–185°).

*Hydrolysis of **15**: Formation of **16***

Compound **15** (263 mg) and a mixture of methanol, concentrated hydrochloric acid and benzene, (10:3:3; 64 ml) were heated under reflux. After *ca.* 30 min the original yellow color had faded. After 11 h the solution was concentrated under reduced pressure until crystals separated. Aqueous sodium hydroxide was added to neutralize the acid and the mixture was cooled at 0° overnight. Compound **16** separated as a white crystalline solid (186 mg; 99%), m.p. 211–220°. Four recrystallizations from methanol gave white needles, m.p. 225–225.5°; λ_{max} (KBr) 2.88, 6.21 μ; $^{H}\delta$ ($CDCl_3$) 3.42 (s, 2H; absent after D_2O treatment), 3.70 (s, 6H), 3.77 (s, 3H), 6.97 (m, 13H; 12H after D_2O treatment).[5]

Anal. Calcd. for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.17; H, 5.87; N, 7.23.

This product was shown to be **16** by mixture m.p. 224.5–225° with an authentic sample (m.p. 224–225.5°; *vide infra*). The i.r. and ^{1}H n.m.r. spectra of the two samples were indistinguishable.

The remaining aqueous solution was acidified and extracted with chloroform (100 ml); the chloroform extracts were dried and evaporated to give a white solid (85 mg) which crystallized from water to give *p*-anisic acid, m.p. 181–182°; mixture m.p. 182–185° with an authentic sample (m.p. 182–185°); the i.r. spectra of the two samples were indistinguishable.

*3,4,5-Tri-p-anisylpyrazole (**16**)*

Hydrogen chloride was passed through a cooled solution (ice bath) of deoxy-*p*-anisoin (14.0 g) and *p*-anisaldehyde (10 g) in ether (50 ml) for 30 min. The red solution was cooled at −20° overnight. The resulting cake was broken up under ethanol, filtered, washed with ice-cold ethanol, and dried, to give 3-chloro-1,2,3-tri-(*p*-anisyl)-1-propanone as a white solid (18.6 g), m.p. 134–139°; $^{H}\delta$($CDCl_3$) 3.67 and 3.70 (two s, 9H), 5.20 (d, J = 11 Hz, 1H), 5.72 (d, J = 11 Hz,1H), 6.7–7.0 (m, 8H), 7.48 (d, J = 9 Hz, 2H), 7.87 (d, J = 9 Hz, 2H). It was not further purified.

A suspension of 3-chloro-1,2,3-tri-(*p*-anisyl)-1-propanone (10 g), potassium acetate (8 g), and sodium carbonate (3 g) in methanol (100 ml) was boiled under reflux with stirring for 2 days. The methanol was evaporated, the residue was taken up in carbon tetrachloride, and the solution was filtered to remove suspended inorganic material and evaporated to give 1,2,3-tri-(*p*-anisyl)-2-propen-1-one as a yellow oil (7.5 g). The oil was taken up in benzene and chromatographed on silica gel. The purified material, eluted with ether–benzene (1:99), failed to crystallize; λ_{max} (CCl_4) 6.07 μ; $^{H}\delta$(CCl_4) 3.62 (s, 3H), 3.67 (s, 3H), 3.70 (s, 3H), 6.5–7.5 (m, 11H), 7.75 (d, J = 9 Hz, 2H).

A solution of 1,2,3-tri-(*p*-anisyl)-2-propen-1-one (as an oil; 6.92 g, 0.018 mol) and 95% hydrazine (620 mg, 0.018 mol) in absolute ethanol (60 ml) containing 2 drops of acetic acid was boiled under reflux for 2 days. The reaction mixture was cooled at −20° for 2 days and the supernatant decanted. The residual white solid was dissolved in chloroform (50 ml) and a solution of bromine in chloroform was added until the solution remained red colored. An additional 1 ml of the bromine solution was added and the resulting solution was boiled under reflux for 2 h. The chloroform was evaporated and the solid residue was taken up in hot 95% ethanol. Aqueous 10% sodium hydroxide (50 ml) was added, and the solution was cooled, to give 3,4,5-tri-(*p*-anisyl)pyrazole (**16**) as off-white needles (4.0 g). Four recrystallizations from 95% ethanol gave needles, m.p. 224–225.5°.

*Irradiation of **15***

Exposure of compound **15** to visible light in the solid state or in solution led rapidly to a red coloration. A solution of **15** in chloroform was exposed to light and air for three days. The i.r. spectrum of the irradiated solution showed that quantitative conversion of **15** to *p*-anisil monoazine (**14**) had occurred; this was confirmed by isolation of the product, m.p. 162–163°, which showed no depression on admixture with **14**.

*Reaction of p-Tolil Monoazine (**17**) with Sodium Methoxide: Formation of **18***

p-Tolil monoazine (**17**) was prepared from *p*-tolil and hydrazine dihydrochloride in aqueous ethanol. The crude product was dissolved in boiling benzene and the hot solution was filtered into boiling acetic acid; the benzene was removed by azeotropic distillation and the acetic acid solution was cooled to give **17**, m.p. 253–254° (lit. (15) m.p. 248°); λ_{max} ($CHCl_3$) 5.97 μ; λ_{max} (CH_2Cl_2) 266 nm (log ε 4.52), 327 nm (log ε 4.49); $^{H}\delta$ ($CDCl_3$) 2.37 (s, 6H), 2.25 (s, 6H), 7.03 (d, J = 8 Hz, 4H), 7.35 (m, 8H), 7.87 (d, J = 8 Hz, 4H).

p-Tolil monoazine (11.34 g, 0.024 mol), dry sodium methoxide (6.66 g, 0.12 mol), and dry ether (*ca.* 1 l) were placed in a dry, nitrogen-preswept flask. The mixture was boiled under reflux with stirring under a blanket of dry nitrogen. After *ca.* 2 h the reaction mixture had acquired a deep purple color. Reflux was continued for 15 days. The cooled reaction mixture was shaken with water (500 ml) at night under subdued light, to give a deep orange ethereal solution and a pale yellow aqueous solu-

[5]This material is considered to be the monohydrate of **16**; the analytical sample was subjected to intensive drying (at 100° and 6×10^{-4} mm for 45 h).

tion with discharge of the purple color. The aqueous solution was extracted with ether (3 × 100 ml) and the combined, dried ethereal solutions were concentrated under reduced pressure (at *ca.* 40°) to *ca.* 35 ml. Compound **18** separated as a pale yellow crystalline solid (2.50 g; 22%), m.p. 172–175°(dec.). This was treated with ether on a Hirsch funnel under slightly reduced pressure; insoluble azine contaminant remained on the filter paper and the filtrate was evaporated to give **18**, m.p. 173–175°(dec.) (very dependent on the rate of heating); λ_{max} ($CHCl_3$) 2.99 (complex), 6.05 μ; λ_{max} (CH_2Cl_2) 262 nm (log ε 4.22), 291 nm (log ε 4.23), 370 nm (log ε 3.29); $^{H}\delta$ ($CDCl_3$) 2.17 (s, 3H), 2.20 (s, 3H), 2.30 (s, 6H), 6.01 (s, broad, 1H; absent after D_2O treatment), 6.85–7.18 (m, 12H), 7.37 (s, sharp, 1H; absent after D_2O treatment), 7.50 (d, J = 8 Hz, 2H), 7.72 (d, J = 8 Hz, 2H); *m/e* (%), 474(3), 355(76), 238(15), 120(30), 119(95), 118(91), 117(100), 91(44).

Anal. Calcd. for $C_{32}H_{30}N_2O_2$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.89; H, 6.75; N, 6.01.

The ethereal mother liquor from the original crystallization of **18** was evaporated to an orange oil, which was taken up in benzene and chromatographed on alumina (500 g). Elution with benzene gave an oil (450 mg) whose i.r. spectrum, with bands at 4.50 and 5.80 μ, indicated the presence of a nitrile and an ester. *p*-Tolunitrile and methyl *p*-toluate were detected by comparison of v.p.c. retention times; they were separated by preparative v.p.c. and identified by i.r. spectral comparison with authentic samples; the estimated yields of nitrile and ester are 250 mg (8%) and 200 mg (6%), respectively. Further elution with benzene gave *p*-tolil monoazine (1.36 g). Elution with methanol–chloroform (1:1) gave an oil (1.36 g), which crystallized from benzene to give *p*-toluamide, m.p. 159–160°, identified by i.r. spectral comparison with an authentic sample, m.p. 158.5–160°.

The aqueous solution from the work-up of the original reaction mixture was acidified to give *p*-toluic acid (1.8 g), identified by i.r. spectral comparison with an authentic sample.

*Hydrolysis of **18**: Formation of **19***

Compound **18** (238 mg) and a mixture of methanol, concentrated hydrochloric acid, and benzene (10:3:3; 64 ml) were heated under reflux for 12 h; the yellow color of the solution faded within 30 min. The mixture was concentrated to 40 ml, neutralized with concentrated aqueous sodium hydroxide, and cooled to 0° to give **19** as a white crystalline solid (136 mg; 80%), m.p. 244–249°. Two recrystallizations from methanol gave white needles, m.p. 253–254°; λ_{max} ($CHCl_3$) 2.88 μ; λ_{max} (EtOH) 250 nm (log ε 4.38); *m/e* (%) 338(100), 337(25).

Anal. Calcd. for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.10; H, 6.69; N, 8.32.

This compound was identified as **19** by mixture m.p. 253–254° with an authentic sample (m.p. 253–254°; *vide infra*).

The aqueous solution was acidified and extracted with ether to give *p*-toluic acid, identified by i.r. spectral comparison with an authentic sample.

*3,4,5-Tri-(p-tolyl)pyrazole (**19**)*

Hydrogen chloride was passed through a cooled solution of deoxy-*p*-toluoin (10.2 g) in *p*-tolualdehyde (8.0 g) until the solution set to a solid cake; this was then cooled at −20° overnight. The cake was broken up under ethanol, filtered, and washed with ice-cold ethanol and with ether, and dried to give 3-chloro-1,2,3-tri-(*p*-tolyl)-1-propanone as a white solid (12.0 g), m.p. 153–155°; $^{H}\delta$ ($CDCl_3$) 2.13 (s, 3H), 2.23 (s, 3H), 2.35 (s, 3H), 5.23 (d, J = 11 Hz, 1H), 5.73 (d, J = 11 Hz, 1H), 6.7–7.3 (m, 10H), 7.97 (d, J = 9 Hz, 2H).

A suspension of 3-chloro-1,2,3-tri-(*p*-tolyl)-1-propanone (10 g), potassium acetate (8 g), and sodium carbonate (3 g) in methanol (100 ml) was boiled under reflux for 1 day. The methanol was cooled and evaporated, and the residue was taken up in ether. The solution was filtered and cooled to give 1,2,3-tri-(*p*-tolyl)-2-propen-1-one (4.2 g). This was recrystallized from methanol to give greenish tinged needles, m.p. 116–117°; λ_{max} (CCl_4) 6.04 μ; $^{H}\delta$ (CCl_4) 2.23 (s, 3H), 2.43 and 2.45 (two s, 6H), 6.8–7.2 (m, 11H), 7.70 (d, J = 9 Hz, 2H).

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.28; H, 6.84.

A solution of 1,2,3-tri-(*p*-tolyl)-2-propen-1-one (2.30 g) and 95% hydrazine (200 mg) in ethanol (20 ml) containing 2 drops of acetic acid was boiled under reflux for 26 h. The solvent was evaporated to give an oil. This was taken up in chloroform, and a solution of bromine in chloroform was added until the bromine color persisted; a few additional drops of the bromine solution were then added. The resulting solution was boiled under reflux for 4 h. The chloroform was evaporated, and the solid residue was taken up in hot ethanol. Aqueous 10% sodium hydroxide was added and the solution was cooled to give 3,4,5-tri-(*p*-tolyl)pyrazole (**19**) as a white solid (2.0 g). This was recrystallized five times from methanol to give material, m.p. 253–254°.

*Acetylation of **18**: Formation of **20***

Compound **18** (1.20 g) was added to freshly distilled acetyl chloride (60 ml) in an aluminum foil-wrapped flask that had been preswept with nitrogen. The solution was boiled under reflux for 20 h under nitrogen. The red solution was stripped of acetyl chloride and the residue was taken up in chloroform (100 ml). The solution was washed with saturated aqueous sodium bicarbonate, dried, and evaporated. The residue was taken up in hot methanol, the solution was filtered from a yellow solid, and the filtrate was cooled to give **20** as a white crystalline solid (500 mg; 38%) that was recrystallized several times from methanol to give material, m.p. 196–198°; λ_{max} ($CHCl_3$) 2.8–3.1 (w), 6.00 μ; λ_{max} (MeOH) 260 nm (sh, log ε 4.23), 290 nm (log ε 4.30); $^{H}\delta$ ($CDCl_3$) 2.01 (s, 6H), 2.27 (s, 6H), 2.52 (s, 3H), 5.01 (br s, 1H; absent after D_2O treatment) 6.5–7.2 (m, 12H), 7.45 (d, J = 8 Hz, 2H), 7.63 (d, J = 8 Hz, 2H); *m/e* (%) 516(8), 397(20), 356(25), 355(83), 338(14), 280(23), 263(19), 238(50), 208(13), 146(14), 120(16), 119(100), 118(67), 91(54), 65(14).

Anal. Calcd. for $C_{34}H_{32}N_2O_3$; C, 79.04; H, 6.24; N, 5.42. Found: C, 79.14; H, 6.23; N, 5.51.

*Irradiation of **18***

Exposure of compound **18** in the solid state or solution to visible light led to a red coloration and eventual conversion to *p*-tolil monoazine. The development of the red color was more rapid than in the case of compounds **3** and **15**; however, in the solid state, the red intermediate appeared to be less sensitive to air oxidation since the

red color remained after exposure of a sample to light and air for 1 week.

Two solutions of compound **18** were prepared (*ca.* 60 mg/ml). One was preswept with oxygen and the other with nitrogen. The solutions were exposed to radiation from a Mineralite lamp (maximum emission at 254 nm). A red color appeared in the nitrogen-preswept solution in *ca.* 5 min while *ca.* 10 min were required for its appearance in the oxygen-preswept solution.

Two solutions of concentrations similar to that described above were exposed to a sunlamp. One solution was preswept with nitrogen, and the other was swept with oxygen throughout the irradiation, which was carried out for 30 min. Both solutions developed a red coloration within 1 min. After cessation of irradiation, the red color of the oxygen-swept solution disappeared within 2 min, while the color of the nitrogen-preswept solution faded more slowly, and could still be detected after 20 min. The i.r. spectrum of the oxygen-swept solution showed distinct bands due to *p*-tolil monoazine, whereas that of the nitrogen-preswept solution showed little conversion to azine.

*Reaction of p-Tolil Monoazine (**17**) with Potassium t-Butoxide*

p-Tolil monoazine (5.68 g, 0.012 mol), dry potassium *t*-butoxide (5.10 g, 0.045 mol), and dry ether (600 ml) were placed in a dry, nitrogen-preswept, 1-l two-necked flask. The suspension was boiled under reflux with stirring under a blanket of dry nitrogen. A deep purple color appeared within 2 min of mixing the reagents. After 7 days at reflux, the mixture was cooled and shaken with water (400 ml) at night under subdued light. The purple color was discharged, and an orange ethereal solution and a pale yellow aqueous solution were obtained. The aqueous solution was extracted with ether (250 ml) and the ethereal extract was dried, filtered, and evaporated to give compound **18** (1.21 g). Material recrystallized from ether and dried had an i.r. spectrum indistinguishable from that of material isolated from the reaction of *p*-tolil monoazine with sodium methoxide.

The ethereal mother liquor was evaporated and the residue was taken up in benzene. The solution was chromatographed on silica gel; elution with benzene gave (*i*) *t*-butyl *p*-toluate (100 mg), identified by spectral and v.p.c. comparison with an authentic sample prepared from *p*-toluyl chloride and *t*-butyl alcohol in pyridine; b.p. 126–128° (16 mm); λ_{max} (CCl_4) 5.86 μ; $^{H}\delta$ (neat) 1.58 (s, 9H), 2.27 (s, 3H), 7.07 (d, J = 8 Hz, 2H), 7.92 (d, J = 8 Hz, 2H); (*ii*) an oil (470 mg) containing *p*-tolunitrile (97%) and *t*-butyl *p*-toluate (3%) as shown by n.m.r. spectroscopy and v.p.c.; (*iii*) *p*-tolunitrile (170 mg), identified by i.r. and n.m.r. spectroscopy and v.p.c. Further elution with benzene and elution with ether–benzene mixtures (1:99, 1:49, and 3:97) gave *p*-tolil monoazine (970 mg). Further elution with ether–benzene mixtures (3:47 and 3:22) gave *p*-tolil *p*-toluylhydrazone, as a white solid (240 mg). Crystallization from ethanol gave material, m.p. 150–151°; λ_{max} ($CHCl_3$) 5.92, 6.05 μ; $^{H}\delta$ ($CDCl_3$) 2.40 (s, 3H), 2.47 (s, 6H), 7.1–7.4 (m, 8H, with a peak at 7.33), 7.62 (d, J = 8 Hz, 2H), 8.07 (d, J = hz, 2H), 9.33 (s, 1H; absent after D_2O treatment); *m/e* (%), 370(0.1), 369(0.1), 368(0.1), 367(0.1), 251(100), 208(12), 119(95), 118(11), 91(49).

Anal. Calcd. for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 78.15; H, 5.67; N, 7.63.

This compound was identified by i.r. spectral comparison and mixture m.p. 149–150° with an authentic sample of *p*-tolil *p*-toluylhydrazone, m.p. 149–150°, prepared from *p*-tolil monohydrazone and *p*-toluyl chloride in pyridine.

Elution with chloroform–ether mixtures gave *p*-toluic acid (290 mg). Elution with methanol–chloroform (3:22) gave a dark oil (260 mg) whose i.r. spectrum with bands at 2.89, 3.00, 6.02, and 7.35 μ indicated the presence of *p*-toluamide. In another run *p*-toluamide, m.p. 159–160°, was isolated and identified by i.r. spectral comparison with an authentic sample.

The aqueous solution from work-up of the original reaction mixture on acidification gave *p*-toluic acid (1.88 g), identified by i.r. spectral comparison with an authentic sample.

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