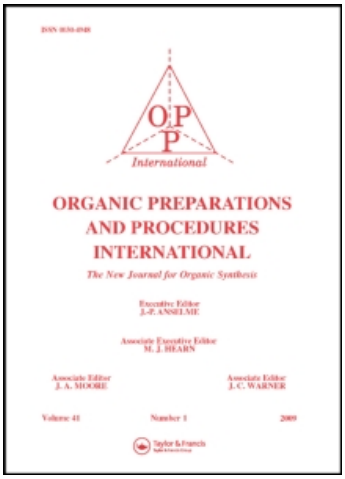

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SYNTHESIS OF 3-ARYL AZO-3-PENTENE-4-OL-2-ONES

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SYNTHESIS OF 3-ARYL AZO-3-PENTENE-4-OL-2-ONES

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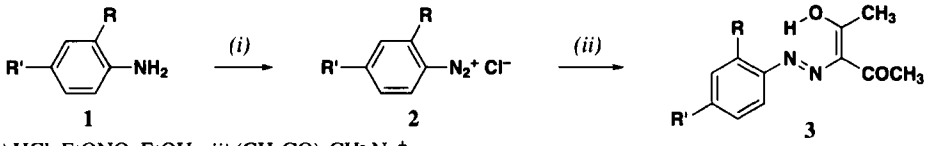
A large number of compounds which possess active methylene groups have been subjected to diazonium-coupling conditions.[1-9] Aryl azo compounds have been shown to possess significant biological activities[2], including apparent antineoplastic activity.[10] Some azo compounds are used as starting materials in the synthesis of some potential antitumor drugs.[7]

We now describe the reaction of arenediazonium salts prepared in an anhydrous medium with sodio acetylacetone leading to a novel series of 3-phenylazo-3-pentene-4-ol-2-ones. The enol form of the azo-β-dicarbonyl compounds which have far greater stability than keto form leads to the exclusive formation of azo-conjugated enol type compounds **(3)** as yellow solids. Although it is possible that our products could exist as the arylhydrazones of 2,3,4-pentanetriones, we assigned the azo enol structure on the basis of the following data. The ^{1}H NMR spectra of these compounds display two signals (3H) of equal intensity near δ 3 corresponding to the methyl hydrogens. A singlet (1H) about δ 15 is assigned to the enol protons. The NH peaks of hydrazones have been observed[11] at δ 10-12 and appear as a sharp band at 3400 cm^{-1} while the IR peaks for our compounds in this area are broad. The 2,4-dinitrophenylhydrazones of these compounds **(3)** were prepared and their melting points are reported in *Table 2*.



1 2 3

i) HCl, EtONO, EtOH *ii)* $(CH_3CO)_2CH^-$ Na^+

a) R, R' = H b) R = Cl, R' = H c) R = H, R' = Cl d) R = Br, R' = H e) R = H, R' = Br f) R = I, R' = H g) R = H, R' = I h) R = NO_2, R' = H, i) R = H, R' = NO_2 j) R = CH_3, R' = H k) R = H, R' = CH_3

EXPERIMENTAL SECTION

The substituted anilines and other chemicals were purchased from Merck Co. All melting points were determined in sealed capillaries and are uncorrected. FT-IR spectra were recorded on a Matson 1000 spectrometer as KBr pellets. ^{1}H NMR spectra were obtained on a Varian Gemini 200 (200 MHz) NMR spectrometer in $CDCl_3$. Elemental analyses were carried out on a Leco-CHNS 600 instrument.

3-Phenylazo-3-pentene-4-ol-2-on (3a). Typical Procedure.- Aniline (9 mL, 0.1 mole) and 27 mL (0.2 mole) of conc. HCl were mixed slowly. The formed anilinium chloride was filtered and

air dried and this salt was dissolved in 20 mL of absolute alcohol. The mixture was cooled to –5-0°C and diazotized by the careful dropwise addition (over a period of 30 minutes) of ethyl nitrite (15 mL, 0.1 mole) with stirring. Both the mixture and ethyl nitrite (bp 17°C) must be kept cold (–5-0°C) during the addition *because ethyl nitrite evaporates rapidly and the reaction does not occur efficiently as the diazotized solution decomposes.*

Table 1. Yields, mps ^{1}H NMR and IR Spectral Data of **3**

Cmpd	mp (°C)	Yield (%)	^{1}H NMR (δ)	IR (cm^{-1}) O-H,	C=O,	=CH,	CH
3a	85-86	47	14.94 (s, 1H); 7.45-7.62 (m, 5H); 2.81 (s, 3H); 2.70 (s, 3H)	3416,	1683,	3056,	2928
3b	120-124	66	14.95 (s, 1H); 8.10-7.60 (m, 4H); 2.90 (s, 3H); 2.70 (s, 3H)	3450,	1676,	3082,	2928
3c	128-130	45	14.93 (s, 1H); 7.60-7.40 (s, 4H); 2.95 (s, 3H); 2.80 (s, 3H)	3442,	1676,	3063,	2945
3d	132-134	71	14.92 (s, 1H); 7.88-7.10 (m, 4H); 2.71 (s, 3H); 2.58 (s, 3H)	3428,	1676,	3089,	2928
3e	136-138	39	14.91 (s, 1H); 7.80-7.50(m, 4H); 2.85 (s, 3H); 2.75 (s, 3H)	3416,	1676,	3070,	2935
3f	164-166	20	14.94 (s, 1H); 8.30-7.80 (m, 4H); 2.95 (s, 3H); 2.80 (s, 3H)	3416,	1676,	3075,	2993
3g	106-108	35	14.94 (s, 1H); 7-90-7.40 (m, 4H); 2.85 (s, 3H); 2.70 (s, 3H)	3416,	1683,	3063,	2935
3h	182-184	72	14.92 (s, 1H); 7-80-7.70 (m, 4H); 2.95 (s, 3H); 2.80 (s, 3H)	3428,	1689,	3114,	2979
3i	220-222	53	14.93 (s, 1H); 7.85-7.70 (m, 4H); 2.85 (s, 3H); 2.75 (s, 3H)	3448,	1683,	3121,	2928
3j	108-110	55	14.94 (s, 1H); 8.10-7.40 (m, 4H); 2.90 (s, 3H); 2.75 (s, 3H); 2.65 (s, 3H)	3423,	1670,	3031,	2935
3k	89-92	38	14.94 (s, 1H); 7.60-7.30 (s, 4H); 2.90 (s, 3H); 2.70 (s, 3H); 2.68 (s, 3H)	3429,	1670,	3085,	2921

Table 2. Elemental Analyses of **3** and mps of their 2,4-Dinitrophenylhydrazones

Cmpd	C(Found)	H(Found)	N(Found)	mp (°C) 2,4-DNPH
3a	64.69(64.55)	5.92(5.87)	13.72(13.73)	224-227
3b	55.35(55.46)	4.64(4.69)	11.74(11.67)	180
3c	55.35(55.49)	4.64(4.58)	11.74(11.65)	166-168
3d	46.67(46.71)	3.92(3.95)	9.89(9.80)	148-150
3e	46.67(46.61)	3.92(3.88)	9.89(9.81)	162-165
3f	40.02(39.95)	3.36(3.39)	8.48(8.55)	170-172
3g	40.02(39.97)	3.36(3.32)	8.48(8.41)	160-163
3h	53.01(53.08)	4.45(4.49)	16.86(16.92)	155-156
3i	53.01(52.97)	4.45(4.51)	16.86(16.82)	196-198
3j	66.03(66.07)	6.47(6.55)	12.84(12.84)	148-150
3k	66.03(66.09)	6.47(6.42)	12.84(12.89)	154-156

To a stirred solution of sodium ethoxide, prepared by the careful addition of pieces of sodium (2.1 g, 0.1 mole) to absolute alcohol (60-75 mL), was added in one portion, 2,4-pentanedione (9.5 mL, 0.1 mole) and the solution was heated to about 60°C for 1 hr. Then, the diazotized amine solution in alcohol was added cautiously and slowly to a warm (about 40°C) solution of

the carbanion with stirring. The mixture was then heated at reflux for 30 min. The reaction mixture was then allowed to become ambient and the product was precipitated by addition of 30 mL of water. The precipitate was recrystallized from EtOH-water (yellow needles, 9.6 g, 47%).

Preparation 2,4-Dinitrophenylhydrazones. Typical Procedure.- 3-Phenylazo-3-pentene-4-ol (1.02 g, 0.005 mole) was added into solution of 2,4-dinitrophenylhydrazine (1 g, 0.005 mole) in 50 mL of ethanol and 5 mL conc. HCl. The reaction mixture was refluxed for 5 minutes. The mixture was cooled to room temperature. The solid formed was filtered and recrystallized from alcohol (0.86 g, yield 45%, mp 224-227°C; IR(cm^{-1}, KBr) 3307 sharp singlet, N-H of hydrazone; 3400-3200 broad band, O-H of enol).

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