($CCl_4$): $\delta$ = 1.31-1.90 (br m, 8 H, ring-$CH_2$-), 2.08 (s, 3 H, $CH_3$), 4.02 (s, 2 H, -$CH_2$-), 4.63 ppm (br s, 1 H, methine).

***6-Methyl-6-(hydroxymethyl)fulvene (5).*** Optimized conditions for preparing alcohol **5** from the tetrahydropyranyl ether **4** are the following: In a 500-mL flask under $N_2$ was placed 5.4 g of **4** and a mixture of 142 mL of methanol, 36 mL of water, 0.7 mL of concentrated HCl, and 0.5 g of diphenyl ether (present as GLC reference). The resulting cloudy mixture was stirred, and periodically aliquots were removed for GLC analysis (10% SE-30 on Chromosorb W, 5 ft column). The maximum yield (GLC) of alcohol formed after 3 h at room temperature. Significant losses were noted for longer reaction times. The reaction mixture was extracted into ether, and the organic layer was washed with water and with brine. After drying of the mixture over anhydrous sodium sulfate, solvent was removed giving 4.8 g of crude, orange oil. Purification by dry column chromatography on grade III alumina (chloroform eluent), gave 2.2 g (69%) of pure **5**, which solidified on standing to give yellow needles, mp 54.0-54.5 °C (pentane). IR (neat): 3623, 3413, 3118, 3083, 3008, 2958, 2923, 2883, 1811, 1648, 1618, 1481, 1442, 1381, 1373, 1261, 1194, 1151, 1123, 1094, 1014, 998, 919, 860, 773, 661, 619 $cm^{-1}$.

***6-Methyl-6-(methoxymethyl)fulvene (6).*** Fulvene **6** was prepared by method B in 40% yield from cyclopentadiene and methoxyacetone. **6** had bp 68-70 °C (3.2 mm). IR (neat): 3117, 3080, 2990, 2937, 2825, 1660, 1645, 1617, 1478, 1453, 1372, 1322, 1282, 1255, 1194, 1153, 1098, 1070, 1030, 995, 958, 920, 903, 862, 810, 770, 740, 670, 622 $cm^{-1}$.

***6-Phenyl-6-(methoxymethyl)fulvene (7).*** Fulvene **7** was prepared by method A in 35% yield from cyclopentadiene and 2-methoxyacetophenone. The product was purified by column chromatography on silica gel by using 70:30 hexane/benzene as eluent. On removal of solvent, an orange-red oil was obtained. IR (neat liquid): 3100, 3082, 3045, 3010, 2945, 2920, 2882 (sh), 2843, 1630, 1615 (sh), 1505, 1482, 1455, 1376, 1200, 1140, 1108, 1038, 965, 908, 790, 780, 715, 650 $cm^{-1}$.

***6-Phenyl-6-(tetrahydropyran-2-yloxy)fulvene (8).*** Fulvene **8** was prepared by method A in 33% yield from cyclopentadiene and 2-(tetrahydropyran-2-yloxy)acetophenone. Purification was accomplished by column chromatography on activity IV alumina, 70:30 hexane/benzene as eluent. A red-orange oil was obtained on removal of solvent. IR (neat): 3070, 3060, 2950, 2870, 2850, 1640, 1610, 1495, 1480, 1465, 1450, 1395, 1375, 1330, 1290, 1285, 1270, 1210, 1190, 1170, 1145 (sh), 1130, 1280, 1045, 1035, 980, 915, 880, 813, 775, 710, 645 $cm^{-1}$.

***2-(Tetrahydropyran-2-yloxy)acetophenone.*** In a flame-dried flask under $N_2$ was placed 0.18 mol of 2-hydroxyacetophenone in 500 mL of anhydrous ether. To the yellow-tinted slurry was added 0.52 mol of dihydropyran (distilled from sodium) and 1.5 mL of concentrated HCl. The mixture became homogeneous on stirring for 10 min. Stirring was continued overnight at which time the reaction was quenched by addition of aqueous sodium bicarbonate. The ether layer was washed with water and brine and was dried over anhydrous $Na_2SO_4$. On removal of solvent, a yellow oil was recovered which crystallized from hexane. On recrystallization from hexane, an 86% yield of white crystals, mp 50-53 °C, was obtained.

***6-Phenyl-6-(hydroxymethyl)fulvene (9).*** Fulvene **9** was prepared in 35% yield by hydrolysis of tetrahydropyranyl ether **8** using conditions that were similar to those employed in the hydrolysis of **4**. To an orange-red solution of 0.0048 mol of **8** in 26 mL of methanol under $N_2$ was added 7 mL of water. The resulting mixture was not completely homogeneous. To this mixture was added 0.2 mL of concentrated HCl. After being stirred for 5 min, the mixture became homogeneous. Stirring was continued for 3 h, at which time 500 mL of water was added. Product was extracted into ether and washed with water to remove methanol. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Removal of solvent left an orange-red oil which was chromatographed on silica gel, deactivated by the addition of 10% water, using chloroform as eluent. IR (neat): 3580 (sh), 3425 (br), 3100, 3082 (sh), 3045, 2980, 2950, 2910, 1630, 1610, 1583, 1505, 1485, 1455, 1380, 1335, 1300, 1130, 1105, 1070, 1045, 1015, 940, 905, 820, 798, 780, 715, 650 $cm^{-1}$.

***Formation of Tetracyanoethylene Adducts of Fulvenes 2-7.*** Fulvenes **2-7** were converted to Diel-Alder adducts by reaction with tetracyanoethylene (TCNE). Typically, 0.5 g of fulvene dissolved in 5 mL of toluene was added at room temperature to solutions containing equivalent amounts of TCNE dissolved in 5-10 mL of toluene. In all cases a transient dark green or black color formation was observed which quickly vanished, leaving yellow-orange solutions. Approximately equal volumes of hexane were added to the reaction mixtures, and crystals were observed, either immediately or on standing in a freezer. The solid adducts were collected and recrystallized from 1:1 hexane/toluene. Physical constants and NMR spectra in acetone-$d_6$ are recorded in Table II.

***Formation of Adducts of Maleic Anhydride and Fulvenes 8 and 9.*** Approximately 0.5 g of fulvenes **8** and **9** dissolved in benzene were added to a solution of a slight excess of maleic anhydride in about 5 mL of benzene. The mixtures were stirred under $N_2$ at 40 °C for about 3 h. Dry column chromatography (alumina adsorbent, benzene eluent) was employed to purify the products. On removal of the solvent, the residue was crystallized from benzene/hexane. Physical constants and NMR spectra in acetone-$d_6$ are recorded in Table II.

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# Preparation and Properties of Nickel(II) Complex Dyes

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**The preparation and properties of five new dyes derived from nickel(II) ions and aromatic azo derivatives of ethylenebis(β-ketoesters) are reported.**

Metal complexes containing phenylazo functionalities have been potentially used as pigments and dyes (*1*). We have been investigating the properties of the metal complexes derived from

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Table I. IR, Visible, and $^1$H NMR Spectral Data for the Dyes[a]

| R | X | ν(C=O) | ν(C=N) + ν(C=C) | λ, nm (ε) | $^1$H NMR chemical shifts (multiplicity, no. of protons) |
|---|---|---|---|---|---|
| $CH_3CH_2$ | H | 1680 | 1580 | 510 (17 200) | 1.4 (t, 6), 2.10 (s, 6), 3.4 (m, 4), 7.4 (m, 10) |
| $CH_3CH_2$ | $CH_3$ | 1688 | 1570 | 515 (16 000) | 1.4 (t, 6), 2.4 (s, 6), 2.23 (s, 6), 3.4 (m, 4), 4.2 (q, 4), 7.1 (m, 8) |
| $CH_3CH_2$ | $OCH_3$ | 1680 | 1575 | 510 (16 300) | 1.4 (t, 6), 2.4 (s, 6), 3.4 (m, 4), 3.70 (s, 6), 4.30 (q, 4), 7.25 (q, 8) |
| $CH_3CH_2$ | $NO_2$ | 1700 | 1595 | 534 (18 700) | 1.40 (t, 6), 2.51 (s, 6), 3.5 (m, 4), 4.40 (q, 4), 7.62 (q, 8) |
| $CH_3$ | $NO_2$ | 1700 | 1590 | 530 (19 100) | 2.50 (s, 6), 3.4 (m, 4), 3.80 (s, 6), 7.00 (q, 8) |

[a] Chemical shift represented in ppm, δ units. Key: s = singlet; t = triplet; q = quartet; m = multiplet.

the phenylazo derivatives of tricyclic tetradentate ligands (*2–4*). These molecules incorporate metal ions in their easily accessible cavities forming intensily colored stable pigments. We have found that similar metal complexes could be prepared from the phenylazo derivatives of the imine derived from β-ketoesters and ethylenediamine. The preparative route discussed in this report replaces the general method we adopted before, namely, the azo coupling reactions of the coordinated ligands by a simple recombination of the phenylazo derived ligands and the metal ions.

The preparation of the phenylazo derivatives of the imines derived from β-ketoesters and ethylenediamine was done by the procedure discussed below: 50 mmol of the imine was dissolved in 50 mL of 95% ethanol to which an excess of an aqueous saturated solution of sodium acetate was added. This solution was kept cooled at 0 °C. To this an aqueous solution of arenediazonium chloride (prepared from 100 mmol of an aromatic amine and neutralized with sodium acetate) was added slowly with gentle stirring. The reaction mixture was stirred at 0–5 °C till the coupling reaction was complete (10–15 min). The product formed was precipitated by adding about 100 mL of water. The precipitate was filtered, washed with water, and dried under vacuum. It was recrystallized from methanol.

A solution of 2 mmol of the ligand in 30 mL of methanol was stirred magnetically with 2 mmol of nickel(II) acetate in the same solvent for 2 h. A deep red dye was precipitated gradually. This was filtered and washed with a 1:1 water/methanol mixture and recrystallized from a 1:1 methanol/chloroform mixture. Yields were always more than 80% on the basis of the ligand.

All the isolated compounds gave elemental analysis for C, H, N, and Ni which were in good agreement with the represented structure. They are freely soluble in organic solvents but insoluble in aqueous media. They are nonelectrolytes in solution whereas magnetic susceptibility studies show them to be diamagnetic. The structure of these dyes was confirmed by IR, $^1$H NMR, and electronic spectroscopic methods (Table I). In the IR spectra, all the compounds showed two strong absorption bands in the region 1550–1750 cm$^{-1}$, arising from the C=O, C=N, and C=C stretching vibrations (*2*, *3*).

The $^1$H NMR spectra of these complexes (in $CDCl_3$) were consistent with the assigned structure. Detailed $^1$H NMR assignments of the different protons in related compounds are discussed previously (*2–4*).

All the nickel compounds reported here were found to impart a reddish yellow color to cellulose which was reasonably stable toward light. The recombination method adopted here for the synthesis of metal dyes presents a wide choice of testing the properties of pigments with different azo functionalities and metal ions.


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# Synthesis of *N*-Aryl-*N'*-2-(4-*p*-anisyl-5-arylazothiazolyl)thiocarbamides


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**Different *N*-aryl-*N'*-2-(4-*p*-anisyl-5-arylazothiazolyl)thiocarbamides have been synthesized by the condensation of the corresponding 2-amino-4-*p*-anisyl-5-arylazothiazoles and appropriate aryl isothiocyanates. The intermediates required in these syntheses were prepared according to the methods reported in the literature.**


In view of the little amount of work done on 5-arylazothiazoles and related compounds, and also in the pursuit of new potential antineoplastic drugs,[1-7] it was considered worthwhile to synthesize some title compounds and to study their antitumor properties. These compounds have been submitted for biological screening and results will be reported elsewhere.

The present communication deals with the syntheses of *N*-aryl-*N'*-2-(4-*p*-anisyl-5-phenylazothiazolyl)-, *N*-aryl-*N'*-2-(4-

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