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Note

Synthesis of azo compounds containing thymol moiety

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The present work includes the synthesis of azo compounds containing thymol moiety.

Keywords: Thymol, azo compounds, monoterpenoids

It is well known for many years that azo dyes have been most widely used in fields such as dyeing textile fibers, biomedical studies, advanced applications in organic synthesis and high technology areas like lasers, liquid crystalline displays, electrooptical devices and ink-jet printers[1-3].

Before advent of the sulphonamide and antibiotics, it was found that certain dyes could stain certain tissue and not others. Hence it was believed that certain dyes can be found, which could selectively combine and destroy the bacteria without damaging the tissue. Extensive investigations were resulted in the discovery of certain dyes like acridine, thiazine triphenylmethane and azo dyes. The azo dyes posses antiseptic and antiprotozoal properties and also promote wound healing. The cationic dyes are more active in acidic medium and preferably attack gram-positive bacteria as compared to anionic dyes. Most common azo dyes used as antiseptics are scarlet red and dimazon[4].

Many of essential volatile oils contain C_{10} hydrocarbons or related alcohols, ketones, aldehydes, carboxylic acids, phenols etc, which are collectively called as monoterpenoids[5]. Monoterpenoids are naturally occurring substances and secondary metabolites of plants, which are generally considered as self-defense tactics against plant enemies. The biological activity of monoterpenoids[6,7] against insects, nematodes, phytopathogenic fungi and other pest species are believed to be related to the nature and position of specific groups or substituent. The chemical modifications of natural monoterpenoids to various ether and ester derivatives[8-12] have been reported to result in modification of biological activity. These medicinal properties of azo compounds and thymol prompted us to undertake the synthesis of azo compounds containing thymol moiety (**Scheme I**).

Experimental Section

All chemicals were of synthetic grade (S.D. Fine Chem. Ltd, Mumbai, India). The products were characterized by ^{1}H NMR and IR. The m.p.s were determined by open capillary method and are uncorrected. The IR spectra were recorded on a Perkin-Elmer spectrum-one FTIR instrument in the form of KBr pallet. ^{1}H NMR spectra (**Table I**)were recorded in $CDCl_3$ on a Varian Mercury-YH-300 spectrometer using TMS as an internal standard. The purity of compounds were checked by TLC. The crude products were recrystallized from ethanol.

General procedure for synthesis of 2-isopropyl-5-methyl-4-(2-nitrophenyl)diazenyl]phenol 3 a-j

o-Nitroaniline (1.38 g, 0.01 mole) was mixed with Conc. HCl (2.5 mL) To the resultant suspension crushed ice (25 g) and $NaNO_2$ (2.5 mL, 4*N*) was added with stirring. Diazotization was carried out over 0.5 hr at 5°C and then diazonium salt solution was added dropwise at 5 to 10°C to the alkaline solution of thymol. The coupling reaction was stirred for 0.5 hr and the *p*H of the resultant mixture was adjusted to *p*H 7. The formed dye was filtered, washed with water and dried. Crude products were recrystallised with proper solvent.

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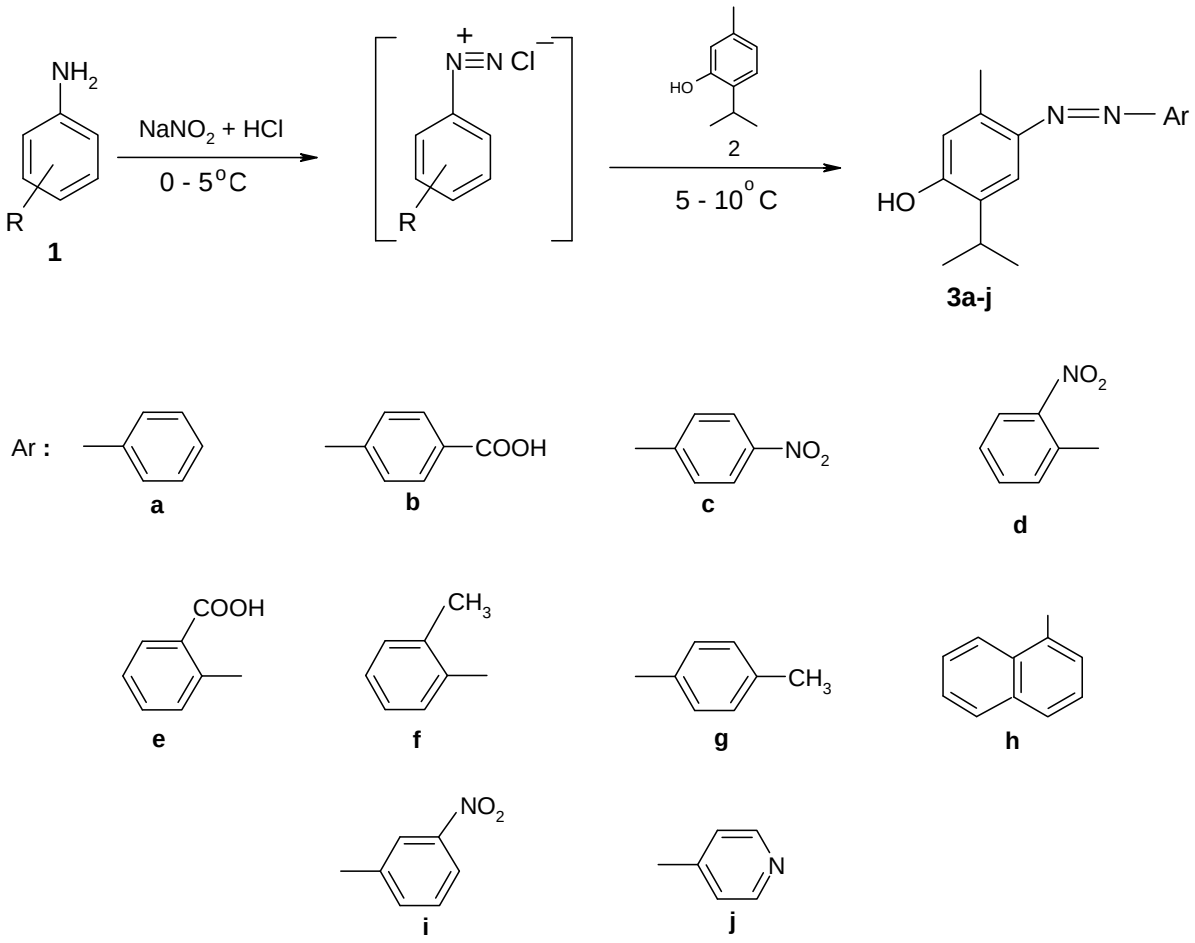

Scheme I

Table I — Spectroscopic data of compounds **3a-j**

Compd	m.p. (°C)	yield (%)	Mol.Formula	^{1}H NMR (δ, ppm)
a	150-56	71	$C_{16}H_{18}ON_2$	1.25 (d, 6H, $2CH_3$, gem), 2.63 (s, 3H, Ar-CH_3), 3.40 (m, 1H, CH), 5.25 (bs, 1H, OH), 6.65 (s, 1H, Ar-H of thymol), 7.20 (s, 1H, Ar-H of thymol), 7.45 (m, 3H, Ar-H), 7.90 (m, 2H, Ar-H).
b	234-38	67	$C_{17}H_{18}O_3N_2$	1.25 (d, 6H, $2CH_3$, gem) , 2.64 (s, 3H, Ar-CH_3), 3.20 (m, 1H, CH), 5.15 (bs, 1H, OH), 6.67 (s, 1H, Ar-H of thymol), 7.27 (s, 1H, Ar-H of thymol), 7.92 (d, 2H, Ar-H), 8.24 (d, 2H, Ar-H), 11.30 (bs, 1H, COOH).
c	160-64	90	$C_{16}H_{17}O_3N_3$	1.26 (d, 6H, $2CH_3$, gem), 2.62 (s, 3H, Ar-CH_3), 3.19 (m, 1H, CH), 5.20 (bs, 1H, OH), 6.68 (s, 1H, Ar-H of thymol), 7.22 (s, 1H, Ar-H of thymol), 7.90 (d, 2H, Ar-H), 8.33 (d, 2H, Ar-H)
d	120-23	93	$C_{16}H_{17}O_3N_3$	1.25 (d, 6H, $2CH_3$, gem), 2.38 (s, 3H, Ar-CH_3), 3.20 (m, 1H, CH), 5.20 (bs, 1H, OH), 6.40 (s, 1H, Ar-H of thymol), 7.20 (s, 1H, Ar-H of thymol), 7.45 - 8.30 (m, 4H, Ar-H).
e	220-26	65	$C_{17}H_{18}O_3N_2$	1.21 (d, 6H, $2CH_3$, gem) 2.23 (s, 3H, Ar-CH_3), 3.17 (m, 1H, CH), 5.23 (bs, 1H, OH), 6.55 (s, 1H, Ar-H of thymol), 6.70 (d, 1H, Ar-H of anthranilic acid), 7.20 (s, 1H, Ar-H of thymol), 7.40 - 8.00 (m, 2H, Ar-H of anthranilic acid), 7.65 (d, 1H, Ar-H of anthranilic acid), 11.50 (bs, 1H, of COOH)
f	130-32	45	$C_{17}H_{20}ON_2$	1.26 (d, 6H, $2CH_3$, gem), 2.63 (s, 3H, Ar-CH_3 of thymol), 2.70 (s, 3H, ArCH_3), 3.17 (m, 1H, CH), 5.19 (bs,1H, OH), 5.60 (s, 1H, Ar-H of thymol), 7.21 (m, 1H, Ar-H of thymol & 2H, Ar-H), 7.60 (m, 2H, Ar-H)

— *Contd*

Table I — Spectroscopic data of compounds **3a-j** — *Contd*

Compd	m.p. (°C)	yield (%)	Mol.Formula	^{1}H NMR (δ, ppm)
g	98-100	65	$C_{17}H_{20}ON_2$	1.20 (d, 6H, $2CH_3$, gem), 2.40 (s, 3H, Ar-CH_3), 2.60 (s,3H, ArCH_3 of thymol), 3.20 (m, 1H, CH), 5.24 (bs, 1H, OH), 6.58 (s, 1H, Ar-H thymol), 6.78 (d, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.60 (s, 1H, Ar-H of thymol).
h	60-64	80	$C_{20}H_{20}ON_2$	1.25 (d, 6H, $2CH_3$, gem), 2.63 (s, 3H, Ar-CH_3), 3.20 (m, 1H, CH), 5.24 (bs, 1H, OH), 6.70 (s, 3H, Ar-H of thymol), 7.20 (s, 1H, Ar-H of thymol), 7.90-8.00 (m, 6H, Ar-H), 8.80 (d, 1H, Ar-H)
i	110-12	64	$C_{16}H_{17}O_3N_3$	1.25 (d, 6H, $2CH_3$, gem), 2.40 (s, 3H, Ar-CH_3), 3.20 (m, 1H, CH)), 5.20 (bs, 1H, OH), 7.20 (s, 1H, Ar-H of thymol), 7.20-8.00 (m, 4H, Ar-H) 7.60 (s, 1H, Ar-H of thymol)
j	120-24	61	$C_{15}H_{17}ON_3$	1.25 (d, 6H, $2CH_3$, gem), 2.63 (s, 3H, Ar-CH_3), 3.32 (m, 1H, CH)), 4.20 (bs, 1H, OH) , 6.50 (s, 1H, Ar-H of thymol), 7.00-8.00(m, 1H, Ar-H of thymol & 4H of pyridine)

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