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SYNTHESIS AND TERMITICIDAL ACTIVITY OF BICYCLIC HETEROCYCLIC COMPOUNDS

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A novel series of bicyclic heterocyclic compounds namely N^1-(4-fluorobenzoyl)-5,5′-dimethyl cyclohexane-4-(sulpha/substituted phenylazo)-1,2-diazoles have been synthesized. The structure of the synthesized compounds was supported by elemental analysis, IR and NMR spectra data. The homogeneity and purity of the compounds were checked through TLC. They were screened for termiticidal activity against termites (*Microcerotermes beesoni*) at different concentrations. It was compared with Endosulfan and explained by graphical manner through regression equation $Y_{pc}=mX+C$.

The chemistry of five membered heterocyclic compounds having more than one hetero atom has gained importance recently as many of them exhibit pronounced bioactive nature. Diazole and its derivatives are known to have wide variety of biological activities such as antimicrobial, antiprotozoal, antifungal, pesticidal, orthopodicidal and nematocidal activity[1-7]. Keeping these facts in view and in continuation of our earlier work on a fused heterocyclic system[8-12], we have synthesized N^1-(4-fluorobenzoyl)-5,5′-dimethyl cyclohexane-4-(sulpha/substituted phenylazo)-1,2-diazoles by condensation of sulpha/substituted phenylazo-5,5′-dimethyl cyclohexane-1, 3-dione with 4-fluoro benzoic acid hydrazide using gl acetic acid as condensing agent (Scheme-1). They were tested for termiticidal activity.

Experimental

The melting points of the synthesized compounds were determined in open capillaries in a Ganson electrical melting apparatus and are uncorrected. The homogeneity and purity of the compounds were checked over thin layer chromatoplates coated with silica Gel-G (thickness 0.5 mm), developing solvent acetone/DMF (3:1), non-saturated chamber at room temp (20 + 1°). Infrared spectra (in cm^{-1}) were determined in KBr on a Perkin Elmer 577 Spectrophotometer and ^1H NMR spectra were recorded on Bruker WM-400 spectrophotometer at 200 MHz in $CDCl_3$ + DMSO-d_6 using TMS as an internal reference (Chemical shift δ ppm).

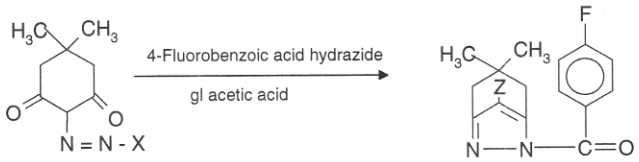
N^1-(4-Fluorobenzoyl)-5,5-dimethylcyclohexane-4-sulpha/substitutedphenylazo)-1,2-diazoles

A mixture of sulpha/substituted phenylazo 5,5′-dimethyl cyclohexane-1,3-dione (0.05 mol) and 4-Fluorobenzoic acid hydrazide (0.05 mol) was refluxed in gl acetic acid for 6 hr and contents were left over night. The coloured solid mass was filtered, washed with water and dried. It was recrystallized from gl acetic acid to furnish shining crystals. By analogous procedure, several substituted-1,2-diazoles have been synthesized. Their characteristics are recorded in Table-1.

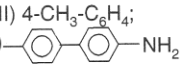
The structures of the synthesized compounds were supported by IR spectra. The parent compound showed a peak at 780 cm^{-1} (aromatic ring) and a sharp peak at 1360 as the [-C-$(CH_3)_2$] group is present. A number of peaks were obtained at 1110, 1550, 1600, 1610 which indicate the presence of C-F, N=N, C=C and C=N respectively. A characteristic peak at 1710 due to bicyclic ring and a peak at 1740 (C=O) of tert. amide having N in diazole ring were recorded, which helped in establishing the structure. The above structures were confirmed by PMR spectra.

N^1-(4-Fluorobenzoyl)-5,5′-dimethyl cyclohexane -4-(2-chlorophenylazo)-1,2-diazole (I)

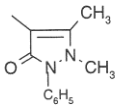
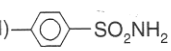
δ 1.62 (s, 6H, C $(CH_3)_2$); 2.12 (s, 4H, 2xCH_2); 7.20-

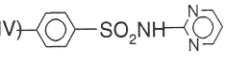
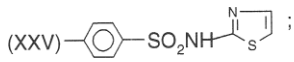


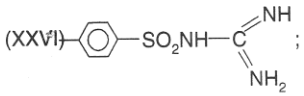
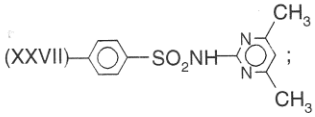
Where Z => N=N-X

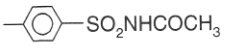
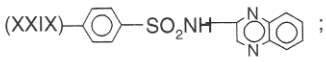
X = (I) C_6H_5; (II) 2-Cl-C_6H_4; (III) 3-Cl-C_6H_4 (IV) 4-Cl-C_6H_4;
(V) 2,4,6-$(Br)_3$-C_6H_2; (VI) 3-F-C_6H_4; (VII) 2-Cl-4-NO_2-C_6H_3;
(VIII) 2-NO_2-C_6H_4; (IX) 3-NO_2-C_6H_4; (X) 4-NO_2-C_6H_4;
(XI) 3-NO_2-4-CH_3-C_6H_3; (XII) 2-CH_3-C_6H_4; (XIII) 4-CH_3-C_6H_4;
(XIV) 2-OCH_3-C_6H_4; (XV) 4-OCH_3-C_6H_4; (XVI)  ;

(XVII)  ; (XVIII)  ; (XIX) 4-COOH-C_6H_4; (XX) 4-OH-C_6H_4;

(XXI)  ; (XXII)  (XXIII)  ;

(XXIV)  ; (XXV)  ;

(XXVI)  ; (XXVII)  ;

(XXVIII)  ; (XXIX)  ;

SCHEME-1

Table-1
Characteristics of N^1-(4-fluorobenzoyl)-5,5′-dimethyl cyclohexane-4- (X) azo-1,2-diazoles

Compd	Yield (%)	M.P. (°C)
I	70	189
II	73	158
III	70	175
IV	78	183
V	71	201
VI	65	189
VII	82	201
VIII	87	190
IX	69	197
X	73	205
XI	82	255
XII	68	158
XIII	83	183
XIV	72	192
XV	68	192
XVI	65	179
XVII	76	135
XVIII	79	144
XIX	65	198
XX	72	187
XXI	81	201
XXII	84	176
XXIII	78	205
XXIV	73	162
XXV	68	198
XXVI	69	178
XXVII	79	176
XXVIII	72	179
XXIX	70	203

All the compounds gave correct elemental analyses.

7.76 (d, ArH, C_6H_4Cl, J=8Hz); 6.90 (dd, 2, ArH-F ortho to C=O, J=20 and 2Hz); 7.10 (dd, 2, ArH-F meta to C=O, J=20 and 2Hz).

N^1-(4-Fluorobenzoyl)-5,5-dimethyl cyclohexane-4-(2-nitrophenylazo)-1,2-diazole (VIII)

1.64 (s, 6H,C $(CH_3)_2$); 2.14 (s, 4H, 2x CH_2); 7.72-8.20 (m, ArH, $C_6H_4NO_2$); 6.90 (dd, 2ArH-F ortho to C=O, J=20 and 2Hz); 7.10 (dd, 2H, ArH-F meta to C=O, J=20 and 2Hz).

N^1-(4-Fluorobenzoyl)-5,5′-dimethyl cyclohexane -4- (4-nitrophenylazo)- 1,2-diazole (X)

1.55 (s, 6H, C $(CH_3)_2$); 2.13 (s, 4H, 2x CH_2); 7.35 (d, 2m meta to NO_2, J=6 Hz); 7.93 (dd, 2, ortho to NO_2, J=9 and 3 Hz); 6.90 (dd, 2, ArH-F ortho to C=O, J=20 and 2H); 7.10 (dd, 2, ArH-F meta to C=O, J=20 and 2Hz).

N^1-(4-Fluorobenzoyl)-5,5′-dimethyl cyclohexane-4-(2-methoxyphenylazo)-1,2-diazole (XIV)

1.63 (s, 6H, C $(CH_3)_2$); 2.14 (s, 4H, 2xCH_2); 3.65 (s, 3H, OCH_3); 6.60-6.80 (m, 4H, ArH); 6.90 (dd, 2, ArH-F ortho to C=O, J=20 and 2Hz); 7.10 (dd, 2, ArH-F meta to C=O, J=20 and 2Hz).

N^1-(4-Fluorobenzoyl)-5,5-dimethyl cyclohexane-4-(2-acetyl sulphanilamidobenzene azo)-1,2-diazole (XXVIII)

1.64 (s, 6H, C $(CH_3)_2$); 2.15 (s, 4H, 2x CH_2); 7.22-7.35 (m, 4H, ArH); 8.02 (br, s, 1H, -NH); 2.38 (s, 3H, -$COCH_3$); 6.90 (dd, 2, ArH-F ortho to C=O, J=20 and 2Hz); 7.10 (dd, 2, ArH-F meta to C=O, J=20 and 2Hz).

Biological assay

All the synthesized compounds were screened for their termiticidal activities against *Microcerotermes beesoni* at different concentrations. It was compared with standard pesticide Endosulfan at various concentrations.

A graphical study reveals that the standard compound Endosulfan showed 100% mortality against termites in 10 hr, 7.5 hr and 6 hr at 0.25%, and 1.0% concentrations while **III, VII, IX, XII, XVII, XXIII** and **XXVIII** showed 100% mortality in 9 to 10 hr, 6 to 7.5 hr and 5 to 6 hr at 1%, 2% and 2.5% concentrations respectively.

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