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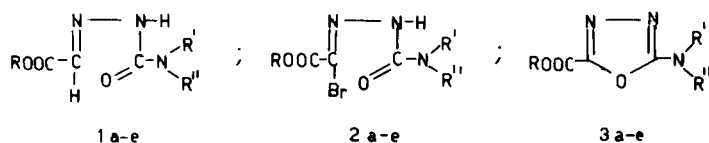
A number of 5-alkyl(or aryl)-amino-1,3,4-oxadiazole-2-carboxyalkylesters have been prepared.

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Sir:

As a part of our continuing program involving the reactivity of A-CH=N-NR-CX-B system, and their related cyclization products (1), we became interested to investigate the properties of some 5-alkyl(or aryl)-amino-1,3,4-oxadiazole-2-carboxyalkylesters as ligands. These compounds possess more sites activated *versus* a possible coordination and could be usefully tested in the synthesis of transition metal ion (e.g., V^{5+} , Mo^{6+} , VO^{2+}) complexes. These latter are increasingly used as homogeneous phase-catalyst for the selective transfer of oxygen from peroxide compounds to organic substrates (2) and efficiency of catalytic action is well-known to be linked to the nature of ligands (3).

This preliminary note reports the preparative method and the physical characterization of 1,3,4-oxadiazoles **3a-e**, through 1,5-dipolar cycloaddition reaction of the semicarbazone bromides **2a-e** (4), according to the following scheme:



- a: R = n-C₄H₉; R' = H; R'' = CH₃
 b: R = n-C₄H₉; R' = R'' = CH₃
 c: R = n-C₄H₉; R' = H; R'' = C₆H₅
 d: R = n-C₄H₉; R' = R'' = C₆H₅
 e: R = CH₃; R' = H; R'' = C₆H₅

The first step of this synthesis is an extension of the condensation reaction of *n*-butyl glyoxylate with variously substituted semicarbazides (5). Treatment at room temperature of substrates **1a-e** (6) with bromine-sodium acetate reagent (7) gave the intermediate semicarbazone bromides **2a-e** (yields 80-90%), which by the action of triethylamine furnished the esters **3a-e** (yields 75-90%). These by reaction with sodium hydroxide furnished the acids, and the corresponding methyl esters when reacted with ethereal solution of diazomethane (8). The physical, and spectral data (9,10) for each of the compounds **2a-e** and **3a-e** are as follows: **2a**, m.p. 101° (methanol); nmr: 0.80-2.06 (m, 7H, OCH₂CH₂CH₂CH₃), 2.94 (d, 3H, NHCH₃, J = 4.2 Hz), 4.33 (m, 2H, OCH₂CH₂CH₂CH₃), 6.23 (br. signal, 1H, NHCH₃), 8.62 (br. s, 1H, NH); **2b** oil; nmr: 0.74-1.96 (m, 7H, OCH₂CH₂CH₂CH₃), 3.12 (s, 6H, N(CH₃)₂), 4.25 (m, 2H, OCH₂CH₂CH₂CH₃),

8.56 (br. s, 1H, NH); **2c**, m.p. 134-136° (methanol); nmr: 0.76-2.19 (m, 7H, OCH₂CH₂CH₂CH₃), 4.35 (m, 2H, OCH₂CH₂CH₂CH₃), 6.98-7.75 (m, 5H, ArH), 8.25 (br. s, 1H, NH), 8.68 (br. s, 1H, NH); **2d**, m.p. 126-127° (ethanol); nmr: 0.75-1.98 (m, 7H, OCH₂CH₂CH₂CH₃), 4.27 (m, 2H, OCH₂CH₂CH₂CH₃), 7.22-7.60 (m, 10H, 2 ArH); 8.59 (br. s, 1H, NH); **2e**, m.p. 136-138° (methanol); nmr: 3.94 (s, 3H, OCH₃), 6.85-7.65 (m, 5H, ArH), 8.27 (br. s, 1H, NH), 8.66 (br. s, 1H, NH); **3a**, m.p. 88-90° (benzene-ligroin); nmr: 0.77-2.10 (m, 7H, OCH₂CH₂CH₂CH₃), 3.10 (d, 3H, NHCH₃, J = 2.5 Hz), 4.40 (m, 2H, OCH₂CH₂CH₂CH₃), 7.16 (br. signal, 1H, NH); **3b**, m.p. 52-54° (ether); nmr: 0.80-2.00 (m, 7H, OCH₂CH₂CH₂CH₃), 3.20 (s, 6H, N(CH₃)₂), 4.41 (m, 2H, OCH₂CH₂CH₂CH₃); **3c**, m.p. 117-119° (ligroin); nmr: 0.75-2.12 (m, 7H, OCH₂CH₂CH₂CH₃), 4.44 (m, 2H, OCH₂CH₂CH₂CH₃), 6.92-7.75 (m, 5H, ArH), 9.85 (br. s, 1H, NH); **3d**, m.p. 81-82° (cyclohexane); 0.72-2.00 (m, 7H, OCH₂CH₂CH₂CH₃), 4.34 (m, 2H, OCH₂CH₂CH₂CH₃), 7.08-7.70 (m, 10H, 2ArH); **3e** (8).

Work is now in progress to determine the properties as ligands of these compounds.

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- The structure of the products **1a-e** which have not been previously reported, are based on elemental analytical data and spectral data; yields: 75-90%, m.p., **1a**, 149° (water); **1b**, 88-90° (water); **1c**, 165-166° (benzene); **1d**, 181-183° (ethanol); **1e**, 184-186° (ethanol).
- We are currently pursuing an investigation with interhalogen.
- G. Werber, F. Buccheri, R. Noto and M. Gentile, *J. Heterocyclic Chem.*, **14**, 1385 (1977).
- All the nmr spectra were recorded by a Jeol C-60 H nuclear magnetic resonance spectrometer in deuteriochloroform and chemical shifts are reported in parts per million (δ) downfield from TMS.
- All the products **2a-e** and **3a-e** gave satisfactory elemental analysis (C, H, N, Br).