Reactions with Hydrazonoyl Halides. Part 15. A Synthetic Approach to 2,3-Dihydrothiadiazoles

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Hydrazonoyl halides 1 and 6a-f reacted with methyl hydrazincarbodithioate (2) and methyl 3-[1-(aryl)alkylmethylidene]hydrazinocarbodithioates (9a-d or 10a,b), in ethanolic triethylamine solution, to afford the corresponding 2-hydrazono-3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazole (3), 5-methyl-2-methylsulfanyl-6-phenylhydrazono-1,3,4-thiadiazole (8) and 2,3-dihydro-1,3,4-thiadiazoles 17-20a-f, respectively.

It has been reported that dithiocarbazic acid reacts with haloacetophenones\(^2\) and 2-halo compounds\(^3\) to give 1,3,4-thiadiazines and 2-halomethyl-1,3,4-thiadiazoles, which have been reported to exhibit antiprotosolal,\(^4\) antiviral,\(^5\) bactericidal\(^6\) and fungicidal\(^7\) properties. However, the reaction of hydrazonoyl halides with dithiocarbazate has not yet been reported.\(^8\) In this paper, we report a study of this reaction.

Treatment of N-phenylbenzohydrazonoyl chloride (1) with methyl hydrazincarbodithioate (2) in ethanolic triethylamine afforded a product which gave analytical and spectral data in accord with its formula as 2-hydrazono-3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazole (3). Compound 3 was authentically obtained by other routes: \((a)\) via reaction of 1 with thiosemicarbazide; \((b)\) by reduction of 2-nitrosoimino-3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazole\(^9\) (4). Also, 3 reacted with benzaldehyde to give the corresponding hydrazine 5 (see Scheme 1). In contrast to the above results, treatment of N-phenylbenzohydrazonoyl chloride (1) with methyl 3-[1-(2-thienyl)ethylidene]hydrazincarbodithioate (9a) in ethanolic triethylamine at room temperature gave the 2,3-dihydro-1,3,4-thiadiazole 13a (see Scheme 3). In contrast, treatment of 1 with ethyl 3-[1-(2-thienyl)ethylidene]hydrazincarbodithioate 10a, at room temperature, produced the same product (13a). These results indicate the following facts: \((a)\) structure 12 is not the final product; \((b)\) 13a is formed via loss of methane-(or ethane)-thiol; \((c)\) structure 11 is ruled out (see Scheme 3).

Similarly, compounds 9b-d reacted with 1 to give 2,3-dihydro-1,3,4-thiadiazole derivatives 13b-d, respectively. The products 13a-d are assumed to be formed via elimination of alkanethiol from the corresponding cycloadduct 12, resulting from 1,3-dipolar cycloaddition of nitrile imide to the C=S of the methyl or ethyl dithiocarbazate [similar to the reaction of hydrazonoyl halides with substituted thiourea\(^8\)] (see Scheme 4). The formation of 13a-d can also be explained by the reaction of a dithiocarbazate of general formula 9 (or 10) with the hydrazonoyl chloride 1, in the presence of a base such as triethylamine or potassium hydroxide. The corresponding 2,3-dihydro-1,3,4-thiadiazole can be easily obtained through the nucleophilic attack of the thiolate group followed by ring closure and methanal-(or ethanenol)-thiol elimination.

The elimination of the thiole moiety was confirmed by isolation of the same product (13a) when using 10a and 1, respectively. All attempts to isolate the hydrazone 14 were
unsuccessful. Unequivocal support for structure 13 was provided by the preparation of 13a via two routes. The first involves the reaction of 5-hydrazino-2,4-diphenyl-1,3,4-thiadiazole 3 with 2-acetyltiophene (15), in propan-2-ol, the second by the reaction of N-phenylbenzohydrazonoyl chloride (1) with 1-[1-(2-thienyl)ethylidene]thiosemicarbazide (16), in boiling ethanol. All the products were identical with 13a [see eqn. (1)].

In order to study the effect of a carbonyl group on the reactivity of the hydrazonoyl halides, the reaction of \( \alpha \)-oxo-hydrazonoyl halides 6a-f with 9a-d, in ethanolic triethylamine at room temperature, was investigated and found to give the corresponding 2,3-thiadiazoles 17-20a-f. The structures of the products were confirmed by their spectra and alternative synthesis. Thus, the reaction of 10a,b with 6a,b in ethanol containing equimolar amounts of triethylamine gave products identical with 17a,b and 18a,b respectively (see Scheme 5).

**Scheme 5**

Techniques used: 'H NMR, IR, mass spectrometry

Tables: 2

References: 23

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References cited in this synopsis

Reactions with Hydrazonoyl Halides XV : A Synthetic Approach to 2,3-Dihydrothiadiazoles

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Abstract: Hydrazonoyl halides 1 and 6a-f reacted with methyl hydrazine-carbodithioate (2) and methyl 3-[1-(aryl)alkylidene]hydrazinecarbodithioates (9a-d or 10a,b) in ethanolic triethylamine solution, to afford the corresponding 2-hydrazono-3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazoles (3), 5-methyl-2-methylsulfanyl-6-phenylhydrazono-1,3,4-thiadiazine (8) and 2,3-dihydro-1,3,4-thiadiazoles 17-20a-f, respectively. The thiadiazole and thiadiazine structures were established on the basis of elemental analyses, spectral data studies and alternative synthetic routes.

Introduction

It has been reported that dithiocarbazooic acid reacts with haloacetophenones and α-halo compounds to give 1,3,4-thiadiazines and 2-halomethyl-1,3,4-thiadiazoles, which have been reported to exhibit antiprotozoal, antiviral, bactericidal and fungicidal properties. However, the reaction of hydrazonoyl halides with dithiocarbazooate has not yet been reported. In this paper, we wish to report the study of this reaction.

Results and Discussion

Treatment of N-phenylbenzohydrazonoyl chloride (1) with methyl hydrazinecarbodithioate (2) in ethanolic triethylamine afforded a product which gave analytical and spectral data in accord with its formulation as 2-hydrazono-3,5-diphenyl-2,3-dihydro-1,3,4-thiadazole (3). Thus its 1H NMR (δ ppm) spectrum showed signals at 4.66 (s, br., 2H, NH₂) which disappeared upon shaking with D₂O and 7.41-7.87 (m, 10H, ArH's). Its IR (cm⁻¹) spectrum revealed bands at 3218, 3160 (NH₂). Compound 3 was authentically obtained by another routes; a) via reaction of 1 with thiosemicarbazide in ethanolic triethylamine. b) by reduction of 2-nitrosoimino-3,5-diphenyl-2,3-dihydro-1,3,4-thiadazole with zinc dust in presence of acetic

References: see frames 0178 and 0179
acid. Also, 3 reacted with benzaldehyde to give the corresponding hydrazone 5 (cf. Scheme 1)

\[
\text{PhCl} + \text{H}_2\text{NNHC(S)SCH}_3 \rightarrow \text{PhS-SCH}_3
\]

\[
\text{2} \quad \text{H}_2\text{NNHC(S)NH}_2 \quad \text{PhCHO} \quad \text{Zn/AcOH}
\]

\[
\text{Ph} \quad \text{N} \quad \text{NN=CHPh} \quad \text{Ph}\]

Scheme 1

In contrast to the above results, 1-chloro-2-phenylhydrazonopropan-2-one (6c) reacted with 2 to give a product formulated as 5-methyl-2-methylsulfanyl-6-phenylhydrazono-1,3,4-thiadiazine (8) according to elemental analysis and spectral data. The IR (cm\(^{-1}\)) spectrum revealed a band at 3269 (NH) and the absence of any absorption band due to a CO group. The \(^1\)H NMR (8 ppm) spectrum showed signals at 2.20(s, 3H, CH\(_3\)), 2.41(s, 3H, SCH\(_3\)), 7.03-7.26(m, 5H, ArH's) and 8.71(s, br., 1H, NH). These results indicate that intermediate 7 undergoes cyclization by loss of one molecule of water to give the thiadiazine 8 (cf. Scheme 2).

\[
\text{6c} + 2 \rightarrow \text{7} \quad \text{8}
\]

Scheme 2
Treatment of N-phenylbenzohydrazonoyl chloride (1) with methyl 3-[1-(2-thienyl)ethylidene]hydrazinecarbodithioate (9a) in ethanolic triethylamine at room temperature gave the 2,3-dihydro-1,3,4-thiadiazole 13a (cf. Scheme 3). The \(^1\)H NMR (8 ppm) spectrum of the product showed two signals at 2.44(s, 3H, CH₃) and 7.02-8.10(m, 13H, ArH's and thiophene H's). Its mass spectrum showed peaks at m/z 376 (45%), 239 (29%) and 110 (100%) which confirms its structure. On the other hand, treatment of 1 with ethyl 3-[1-(2-thienyl)ethylidene]hydrazinecarbodithioate (10a), at room temperature, produced the same product (13a). These results indicate the following facts: a) structure 12 is not the final product. b) 13a is formed via loss of methanethiol (or ethanethiol) from 12. c) structure 11 may be ruled out (cf. Scheme 3).

![Scheme 3](image)

Similarly, compounds 9b-d reacted with 1 to give 2,3-dihydro-1,3,4-thiadiazole derivatives 13b-d, respectively. The products 13a-d are assumed to be formed via elimination of alkanethiol from the corresponding cycloadduct 12, resulting from 1,3-
dipolar cycloaddition of the nitrile imide to the C=S of the methyl or ethyl dithiocarbazoate [similar to the reaction of hydrazonoyl halides with substituted thiourea\(^9\)] (cf. Scheme 4). The formation of 13a-d can also be explained by the reaction of a dithiocarbazoate of the general formula 9 (or 10) with the hydrazonoyl chloride 1, in presence of a base such as triethylamine or potassium hydroxide. The corresponding 2,3-dihydro-1,3,4-thiadiazole can be easily obtained through nucleophilic attack of the thiolate group followed by ring closure and methane- (or ethane-) thiol elimination. The elimination of the thiole moiety was confirmed by isolation of the same product 13a when using 10a and 1. All attempts to isolate the hydrazone 14 were unsuccessful. Unequivocal support for structure 13 was provided by the preparation of 13a via two routes (cf. Scheme 4).

Scheme 4

The first involves the reaction of 5-hydrazino-2,4-diphenyl-1,3,4-thiadiazole 3 with 2-acetyltiophene (15), in 2-propanol, the second by the reaction of N-phenylbenzohydrazonoyl chloride (1) with 1-[1-(2-thienyl)ethyldene]thiosemi-
carbazide (16), in boiling ethanol. All the products were identical with 13a. (cf. Equation 1).

![Chemical reaction diagram]

In order to study the effect of a carbonyl group on the reactivity of the hydrazonoyl halides, the reaction of α-oxo-hydrazonoyl halides 6a-f with 9a-d, in ethanolic triethylamine at room temperature, was investigated and found to give the corresponding 2,3-thiadiazoles 17-20a-f. The structures of the products were confirmed by their spectra and alternative synthesis. Thus, the reaction of 10a,b with 6a,b in ethanol containing equimolar amounts of triethylamine, gave products identical with 17a,b and 18a,b respectively (cf. scheme 5).

![Scheme 5]

Scheme 5
Experimental

All melting points are uncorrected. IR spectra were recorded (KBr) on a FT-IR 8201 PC Shimadzu spectrophotometer. \(^1\)H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer and chemical shifts are expressed in \(\delta\) (ppm) units from TMS as internal reference. Mass spectra were recorded on a GC-MS QP1000 EX (Shimadzu, Japan). Elemental analyses were carried out at the Microanalytical Center at Cairo University. Compounds 1\textsuperscript{11}, 9a-d\textsuperscript{12,13}, 3\textsuperscript{14}, 16\textsuperscript{15} and 6a-f\textsuperscript{16-22} were prepared according to literature procedures.

Synthesis of 10a,b: General procedure.

Ethyl hydrazinecarbodithioate\(^9\) (0.7 g, 5 mmol) and each of 2-acetylthiophene or 2-acetylthiophene (5 mmol) were dissolved in 2-propanol (20 ml). The solutions were heated under reflux for 3 hr. After cooling, the solid was collected, washed with cold 2-propanol and crystallized from ethanol to give compounds 10a,b in good yields. The analytical and spectral data for compounds 10a,b are listed in Tables 1 and 2.

Synthesis of 1,3,4-thiadiazine, 2,3-dihydro-1,3,4-thiadiazoles 3, 13a-d and 17-20a-f: General procedure.

To a solution of the appropriate 2 or 9a-d or 10a,b (5 mmol) and the appropriate hydrazonoyl halides 1 or 6a-f (5 mmol) in ethanol (20 ml) was added triethylamine (0.7 ml, 5 mmol), while stirring at room temperature. Stirring was continued for 2 hr. The formed precipitate was collected, washed with ethanol and crystallized from an appropriate solvent. The compounds 3, 8, 13a-d and 17-20a-f prepared together with their physical constants are listed in Tables 1 and 2.

Synthesis of 13a: Alternative methods.

\(\text{A})\) A mixture of 2-hydrazino-1,3-diphenyl-2,3-dihydro-1,3,4-thiadiazole (3) (1.34 g, 5 mmol) and 2-acetylthiophene (0.630 g, 5 mmol) in 2-propanol (20 ml) was heated

References: see frame 0179
under reflux for 2 hr. After cooling, the formed precipitate, was collected, washed with cold 2-propanol and crystallized from ethanol.

B) To a solution of 2-acetylthiophene thiosemicarbazone (1 g, 5 mmol) and the hydrazonoyl chloride 1 (1.15 g, 5 mmol) in ethanol (20 ml) was heated under reflux for 6 hr. After cooling, the solid, so formed, was collected, and crystallized from ethanol. The samples of 13a prepared by methods (A & B) were the same as those obtained from the general procedure.

Synthesis of 2,3-dihydro-1,3,4-thiadiazole 5.

Method (A). Equimolar amounts of each of 2-hydrazone-3,5-diphenyl-2,3-dihydro-thiadiazole (3) and benzaldehyde (5 mmol) in 2-propanol (20 ml) were stirred at room temperature for 15 min. The solid was collected, washed with ethanol and recrystallized from acetic acid to give thiadiazole 5.

Method (B). To equimolar amounts of each of the hydrazonoyl chloride 1 and methyl 3-(phenylmethylene)hydrazinecarbodithioate (5 mmol) in ethanol (20 ml), triethylamine (0.7 ml, 5 mmol) was added while stirring at room temperature. The solid was collected after 15 min., washed with ethanol and recrystallized from ethanol to give a product identical (m.p., mixed m.p. and spectra) with the sample obtained via method (A) (cf. Tables 1 and 2).

Table 1: Characterization of the newly synthesized compounds.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>M.p. °C</th>
<th>Yield %</th>
<th>Mol. Formula</th>
<th>% Analyses C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Calcd. / Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>173-5°</td>
<td>87</td>
<td>C_{14}H_{12}N_{4}S</td>
<td>62.66</td>
<td>4.50</td>
<td>20.88</td>
<td>11.93</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>153-5°</td>
<td>91</td>
<td>C_{21}H_{16}N_{4}S</td>
<td>70.76</td>
<td>4.52</td>
<td>15.71</td>
<td>8.99</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>204-6°</td>
<td>84</td>
<td>C_{11}H_{12}N_{4}S_{2}</td>
<td>49.98</td>
<td>4.57</td>
<td>21.19</td>
<td>24.24</td>
<td></td>
</tr>
<tr>
<td>10a</td>
<td>122-3°</td>
<td>75</td>
<td>C_{9}H_{12}N_{2}S_{3}</td>
<td>44.23</td>
<td>4.95</td>
<td>11.46</td>
<td>39.36</td>
<td></td>
</tr>
</tbody>
</table>

Reference: see frame 0179
<p>| 10b  | 103-5*   | 72 | C₉H₁₂N₂OS₂  | 47.34 | 5.30 | 12.27 | 28.09 |
| 13a  | 138-40*  | 88 | C₂₀H₁₆N₄S₂  | 63.80 | 4.28 | 14.88 | 17.03 |
| 13b  | 115-6*   | 85 | C₂₀H₁₆N₄OS  | 66.65 | 4.47 | 15.54 | 8.90 |
| 13c  | 165-6b   | 83 | C₂₁H₁₇N₅S   | 67.90 | 4.61 | 18.85 | 8.63 |
| 13d  | 158-60c  | 87 | C₂₁H₁₇N₅S   | 67.90 | 4.61 | 18.85 | 8.63 |
| 17a  | 102-3d   | 83 | C₁₇H₁₆N₄O₃S₂| 54.82 | 4.33 | 15.04 | 17.22 |
| 17b  | 190-2d   | 87 | C₂₁H₁₇N₅OS₂  | 60.12 | 4.08 | 16.69 | 15.29 |
| 17c  | 150-2d   | 85 | C₁₆H₁₅N₄OS₂  | 56.12 | 4.12 | 16.36 | 18.73 |
| 17d  | 124-5d   | 86 | C₂₁H₁₆N₄OS₂  | 62.22 | 3.99 | 13.85 | 15.85 |
| 17e  | 170-2d   | 81 | C₁₉H₁₄N₄O₃S₂| 57.85 | 3.58 | 14.20 | 16.26 |
| 17f  | 158-9d   | 79 | C₁₉H₁₄N₅O₃   | 55.59 | 3.44 | 13.65 | 23.43 |
| 18a  | 102-4a   | 81 | C₁₇H₁₆N₄O₃S  | 57.29 | 4.53 | 15.72 | 9.00 |
| 18b  | 178-80d  | 76 | C₂₁H₁₇N₅O₃S  | 62.52 | 4.25 | 17.36 | 7.95 |
| 18c  | 152-4d   | 77 | C₁₆H₁₄N₄O₂S  | 58.88 | 4.32 | 17.17 | 9.82 |
| 18d  | 169-71d  | 85 | C₂₁H₁₆N₄O₂S  | 64.93 | 4.15 | 14.42 | 8.25 |
| 18e  | 205-7d   | 87 | C₁₉H₁₄N₅O₃S  | 60.31 | 3.73 | 14.81 | 8.47 |
| 18f  | 194-6d   | 88 | C₁₉H₁₄N₄O₃S₂| 57.85 | 3.58 | 14.20 | 16.26 |
| 19a  | 163-5b   | 82 | C₁₈H₁₇N₅O₃S  | 58.84 | 4.66 | 19.06 | 8.73 |
| 19b  | 183-5b   | 85 | C₂₂H₁₈N₆OS  | 63.75 | 4.38 | 20.28 | 7.74 |
| 19c  | 170-2d   | 87 | C₁₇H₁₅N₄OS  | 60.52 | 4.48 | 20.76 | 9.50 |
| 19d  | 168-70d  | 82 | C₂₂H₁₇N₅OS  | 66.15 | 4.29 | 17.53 | 8.03 |
| 19f  | 216-8d   | 83 | C₂₀H₁₅N₅OS₂  | 59.24 | 3.73 | 17.27 | 15.81 |
| 20a  | 145-7b   | 81 | C₁₈H₁₇N₅O₂S  | 58.84 | 4.66 | 19.06 | 8.73 |
| 20b  | 238-40b  | 89 | C₂₂H₁₈N₆OS  | 63.75 | 4.38 | 20.28 | 7.74 |
| 20c  | 148-50a  | 90 | C₁₇H₁₅N₅OS  | 60.52 | 4.48 | 20.76 | 9.50 |</p>
<table>
<thead>
<tr>
<th>Comp.</th>
<th>IR (cm⁻¹)</th>
<th>^1H NMR (δ ppm)</th>
<th>m/z</th>
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<tr>
<td>10a</td>
<td>3165</td>
<td>1.41(t, 3H, CH₂CH₃), 2.32(s, 3H, CH₃), 3.31(q, 2H, CH₂-CH₃), 7.03-7.41(m, 3H, thiophene H's) and 9.72(s, br, 1H, NH).</td>
<td></td>
</tr>
<tr>
<td>10b</td>
<td>3189</td>
<td>1.43(t, 3H, CH₂CH₃), 2.39(s, 3H, CH₃), 3.29(q, 2H, CH₂-CH₃), 6.32-7.50(m, 3H, furan H's) and 9.79(s, br, 1H, NH).</td>
<td></td>
</tr>
<tr>
<td>13a</td>
<td>1587 (C=N)</td>
<td>2.44(s, 3H, CH₃) and 7.08-8.10(m, 13H, ArH's and thiophene H's).</td>
<td>376, 239, 110</td>
</tr>
<tr>
<td>13b</td>
<td>1597(C=N)</td>
<td>2.49(s, 3H, CH₃) and 6.35-7.85(m, 13H, ArH's and furan H's).</td>
<td>360, 239, 94</td>
</tr>
<tr>
<td>13c</td>
<td>1598 (C=N)</td>
<td>2.63(s, 3H, CH₃) and 7.32-8.57(m, 14H, ArH's and pyridine H's).</td>
<td>371, 239, 105</td>
</tr>
<tr>
<td>13d</td>
<td>1606 (C=N)</td>
<td>2.68(s, 3H, CH₃) and 7.29-8.45(m, 14H, ArH's and pyridine H's).</td>
<td></td>
</tr>
<tr>
<td>17a</td>
<td>1734 (CO)</td>
<td>1.47(t, 3H, CH₂CH₃), 2.45(s, 3H, CH₃), 4.72(q, 2H, CH₂-CH₃) and 7.12-7.81(m, 8H, ArH's and thiophene H's).</td>
<td>372, 235, 110</td>
</tr>
<tr>
<td>17b</td>
<td>3386 (NH), 1679 (CO)</td>
<td>2.43(s, 3H, CH₃), 7.10-7.67(m, 13H, ArH's and thiophene H's) and 8.73(s, br, 1H, NH).</td>
<td></td>
</tr>
<tr>
<td>17c</td>
<td>1678 (CO)</td>
<td>2.44(s, 3H, CH₃), 2.61(s, 3H, CH₃CO) and 7.02-8.11(m, 8H, ArH's and thiophene H's).</td>
<td>342, 205, 110</td>
</tr>
<tr>
<td>17d</td>
<td>1637 (CO)</td>
<td>2.39(s, 3H, CH₃) and 7.25-7.83(m, 13H, ArH's and thiophene H's).</td>
<td>404, 266, 110</td>
</tr>
<tr>
<td>17e</td>
<td>1633 (CO)</td>
<td>2.42(s, 3H, CH₃) and 6.32-7.89(m, 11H, ArH's thiophene H's and furan H's).</td>
<td></td>
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<tr>
<td>17f</td>
<td>1618 (CO)</td>
<td>2.41(s, 3H, CH₃) and 7.06-7.67(m, 11H, ArH's and thiophene H's).</td>
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<tr>
<td>18a</td>
<td>1745 (CO)</td>
<td>1.42(t, 3H, CH₂CH₃), 2.37(s, 3H, CH₃), 4.55(q, 2H, CH₂-CH₃) and 6.47-8.09(m, 8H, ArH's and furan H's).</td>
<td>356, 205, 94</td>
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<tr>
<td>18b</td>
<td>3392 (NH), 1672 (CO)</td>
<td>2.36(s, 3H, CH₃), 6.34-7.81(m, 13H, ArH's and furan H's) and 8.81(s, br, 1H, NH).</td>
<td>403, 281, 94</td>
</tr>
<tr>
<td>18c</td>
<td>1681 (CO)</td>
<td>2.32(s, 3H, CH₃), 2.65(s, 3H, CH₃CO) and 6.31-7.94(m, 8H, ArH's and furan H's).</td>
<td></td>
</tr>
</tbody>
</table>

Crystallization Solvents: *EtOH, **EtOH/Dioxane, † Dioxane, ‡ HOAc

Table 2: Spectroscopic data for selected compounds.
18d 1627 (CO) 2.38(s, 3H, CH₃) and 6.41-7.88(m, 13H, ArH's and furan H's) 388, 266, 94
18e 1641 (CO) 2.37(s, 3H, CH₃) and 6.33-7.76(m, 11H, ArH's and furan H's).
18f 1626 (CO) 2.35(s, 3H, CH₃) and 6.33-7.76(m, 11H, ArH's and thiophene II's and furan H's).
19a 1743 (CO) 1.39(t, 3H, CH₂CH₃), 2.58(s, 3H, CH₃), 4.61(q, 2H, CH₂-CH₃) and 7.10-8.45(m, 9H, ArH's and pyridine H's).
19c 1683 (CO) 2.55(s, 3H, CH₃), 2.61(s, 3H, CH₃CO) and 7.23-8.42(m, 9H, ArH's and pyridine H's).
19d 1627 (CO) 2.59(s, 3H, CH₃) and 7.26-8.65(m, 14H, ArH's and pyridine H's).
20a 1735 (CO) 1.45(t, 3H, CH₂CH₃), 2.56(s, 3H, CH₃), 4.55(q, 2H, CH₂-CH₃) and 7.11-8.59(m, 9H, ArH's and pyridine H's).
20b 1660 (CO) 2.57(s, 3H, CH₃), 7.24-8.25(m, 14H, ArH's and pyridine H's) and 9.28(s, br, 1H, NH).
20c 1685 (CO) 2.58(s, 3H, CH₃), 2.60(s, 3H, CH₃CO) and 7.19-8.49(m, 9H, ArH's and pyridine H's).
20d 1637 (CO) 2.60(s, 3H, CH₃) and 7.16-8.60(m, 14H, ArH's and pyridine H's).

REFERENCES.


