*Chemistry of Heterocyclic Compounds, Vol.35, No. 3, 1999*

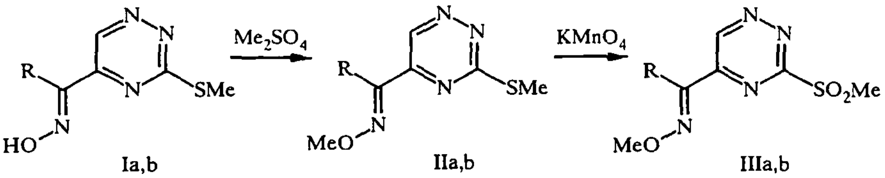
# 1,2,4-TRIAZINES IN ORGANIC SYNTHESIS.
# 8.* INTRAMOLECULAR DIELS-ALDER REACTION OF 5-ACYL-1,2,4-TRIAZINEOXIME ETHERS. NEW ROUTE OF SYNTHESIS OF ALKYLHETARYLKETONES

**T. Lipińska, D. Branowska, and A. Rykowski**

*Intramolecular diene cycloaddition of 5-acyl-1,2,4-triazineoxime ethers involving a dienophile substituent in the 3-position of the triazine ring is studied. New alkylhetarylketones are synthesized by hydrolysis of the condensed N- and O-containing heterocyclic products. The starting materials are prepared by oxidation of 5-acetyl- and 5-butyryl-3-methylthio-1,2,4-triazineoxime ethers with* $KMnO_4$ *to the sulfonyl derviatives with subsequent replacement of the* $CH_3SO_2$ *group by sodium 3-butyn-1-oxide, 4-pentyn-1-oxide and o-cyanophenoxide.*

In a previous article we demonstrated that 5-acyl derivatives of 1,2,4-triazines behave as cyclic dienes in an intermolecular [4+2] cycloaddition reaction with enamines [1]. The present work continues these studies and adresses the use in organic synthesis of an intramolecular cycloaddition in 5-acyl-1,2,4-triazineoxime ethers with a dienophilic substituent in the 3-position of the triazine ring.

The starting materials 5-acetyl- and 5-butyryl-2-methylthio-1,2,4-triazineoxime (Ia,b) were synthesized earlier by us [2, 3]. Introducing a dienophilic substituent into these molecules required protection of the oxime and conversion of the $SCH_3$ group into the easily removed $SO_2CH_3$ substituent. Thus, oximes Ia and Ib were treated with dimethylsulfate in DMF in the presence of sodium hydride to produce the methyl ethers IIa and IIb. These were then oxidized with $KMnO_4$ in a catalytic two-phase system to the corresponding methylsulfonyl derivatives IIIa and IIIb (yield 87 and 95%, respectively).



Ia,b IIa,b IIIa,b

I–III a R = Me, b R = $C_3H_7$

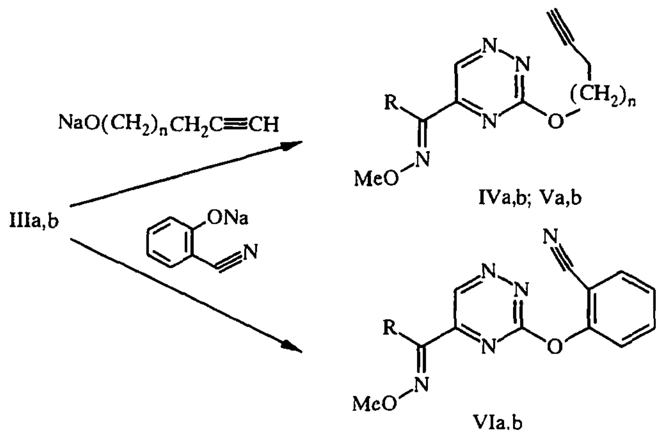
These unpurified products were used for further reactions.

Nucleophilic substitution of the methylsulfonyl substituent in IIIa and IIIb by 3-butynyloxy- and 4-pentynyloxy groups was performed in THF using the corresponding unsaturated alcohols and sodium hydride. The

---

* For Communication 7, see [1].

Institute of Chemistry, Agricultural and Teachers University, Siedlce, 08-110, Poland; e-mail: tlip@wsrp.siedlce.pl. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 381-389, March, 1999. Original article submitted April 17, 1998; Revision submitted January 18, 1999.



IVa,b–VIa.b a R = Me, b R = $C_3H_7$;
IVa,b n = 1, Va,b n = 2

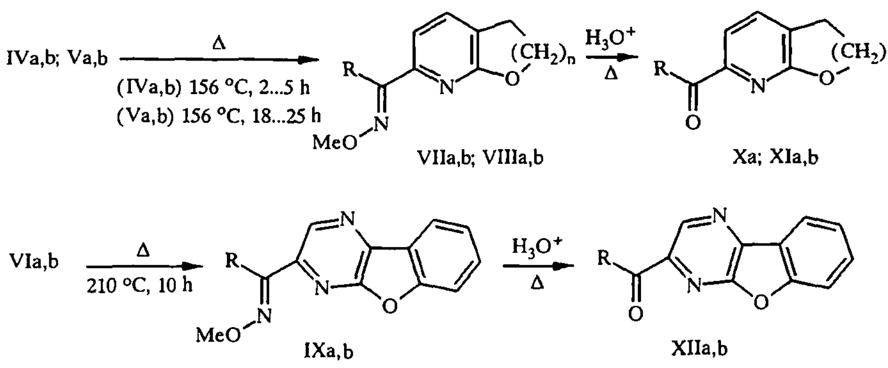
yields of the alkyl-containing products IVa,b and Va,b were 65-68%. Analogous treatment of IIIa and IIIb with sodium *o*-cyanophenoxide gave 3-(*o*-cyanophenoxy)-1,2,4-triazines VIa and IVb in 85-88% yields. The properties of IV-VI are listed in Table 1.

In contrast with the intermolecular cycloaddition of 5-acyl-1,2,4-triazines with enamines [1], the intramolecular Diels-Alder reaction of the 5-methoxyiminoalkyl-1,2,4-triazines IV-VI occurred at higher temperatures and at slower rates.

This difference in reactivity may be explained by the effect of the substituent in the 5-position of the triazine ring.

The previous investigations [1] revealed that an electron-accepting acyl group in this position significantly lowers the energy of the LUMO of the triazine diene, thereby increasing the reactivity for [4+2] cycloaddition reactions. Replacing the acyl substituent by the electron-donating hydroxyiminoalkyl group [4] has the opposite effect. The 5-acyl-1,2,4-triazineoximes Ia and Ib do not react with enamines under the conditions of the intermolecular Diels-Alder reaction [1]. The oxime ethers IIa and IIb behave similarly and do not react with enamines. (They would seem to be appropriate substrates in intermolecular cycloaddition reactions with the usual electronic requirements.) However, this does not mean that 1,2,4-triazine derivatives with the methoxyiminoalkyl group are also unreactive under the conditions of the intramolecular Diels-Alder reaction. Not only the electronic factor but also the entropic factor play an important role in the intramolecular reaction, as demonstrated by Taylor [5] and van der Plas [6]. Therefore, compounds IV-VI with the methoxyiminoalkyl group that decreases the electronegativity of the system underwent the intramolecular [4+2] cycloaddition reaction, although under more forcing conditions.

It is noteworthy that VIIa,b with the five-membered O-containing ring formed more readily than VIIIa,b with a six-membered ring. Cyclization involving the $C\equiv N$ group and formation of IXa,b occurred at a higher temperature than the reaction involving the $C\equiv CH$ group.



VII, X n = 1; VIII, XI n = 2; a R = Me, b R = $C_3H_7$

TABLE 1. Properties of Compounds IVa,b-VIa,b

| Compound | Empirical formula | Found, %<br>Calculated, % | | Mass spectrum, $m/z$ (%) | IR spectrum, $cm^{-1}$ | PMR spectrum, δ, ppm, SSCC, $J$, Hz | mp, °C | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C | H | | | | | |
| IVa | $C_{10}H_{12}N_4O_2$ | 54,54<br>54,67 | 5,49<br>5,39 | $M^+$ 220 (34,9)<br>189 (100) | 3290, 2950<br>1560, 1440<br>1380, 1080 | 2,05 (1H, t, $J = 2,7$, HC≡); 2,49 (3H, s, $CH_3C=$); 2,82 (2H, td, $J_1 = 7,1$, $J_2 = 2,7$, $CH_2C≡$); 4,14 (3H, s, $CH_3O$); 4,70 (2H, t, $J = 7,1$, $CH_2O$); 9,49 (1H, s, 6-CH) | 82...83 | 68 |
| IVb | $C_{12}H_{16}N_4O_2$ | 58,05<br>57,68 | 6,49<br>6,47 | $M^+$ 248 (17,2)<br>217 (30,0)<br>54 (100) | 3310, 2980<br>1570, 1450<br>1370, 1070 | 1,05 (3H, t, $J = 7,4$, $C\underline{H}_3CH_2$); 1,74 (2H, sext, $J = 7,4$, $CH_3C\underline{H}_2$)<br>2,03 (1H, t, $J = 2,7$, HC≡); 2,68 (2H, t, $J = 7,4$, $CH_2C=$)<br>2,81 (2H, td $J_1 = 7,1$, $J_2 = 2,7$, $CH_2C≡$); 4,15 (3H, s, $CH_3O$)<br>4,70 (2H, t, $J = 7,1$, $CH_2O$); 9,45 (1H, s, 6-CH) | 34...35 | 65 |
| Va | $C_{11}H_{14}N_4O_2$ | 56,39<br>56,20 | 6,02<br>5,81 | $M^+$ 234 (48)<br>219 (40)<br>206 (100) | 3290, 3000<br>2975, 2950<br>1560, 1440<br>1350, 1070 | 1,98 (1H, t, $J = 2,6$ HC≡); 2,12 (2H, quint, $J = 6,4$, $C\underline{H}_2CH_2O$)<br>2,25 (3H, s, $CH_3C=$); 2,46 (1H, td, $J_1 = 6,4$, $J_2 = 2,6$, $CH_2C≡$); 4,14 (3H, s, $CH_3O$)<br>4,69 (2H, t, $J = 6,4$, $CH_2O$); 9,48 (1H, s, 6-CH) | 55...56 | 66 |
| Vb | $C_{13}H_{18}N_4O_2$ | 59,52<br>59,49 | 6,88<br>6,86 | $M^+$ 262 (3,6)<br>224 (100)<br>221 (22,5)<br>204 (35,5)<br>197 (76,3) | 3300<br>2980...2950<br>1570, 1450<br>1380, 1070 | 1,05 (3H, t, $J = 7,4$, $C\underline{H}_3CH_2$); 1,74 (2H, sext, $J = 7,4$, $CH_3C\underline{H}_2$)<br>1,95 (1H, t, $J = 2,6$, HC≡); 2,10 (2H, quint, $J = 6,4$, $C\underline{H}_2CH_2O$)<br>2,45 (2H, td, $J_1 = 6,4$, $J_2 = 2,6$, $CH_2C≡$); 2,85 (2H, t, $J = 7,4$, $CH_2C=$)<br>4,25 (3H, s, $CH_3O$); 4, 76 (2H, t, $J = 7,4$, $CH_2O$); 9,52 (1H, s, 6-CH) | 39...40 | 68 |
| VIa | $C_{13}H_{11}N_5O_2$ | 57,99<br>57,85 | 4,12<br>4,04 | $M^+$ 269 (14,2)<br>236 (100) | 2970, 2250<br>1560, 1420<br>1360, 1080 | 2,23 (3H, s, $CH_3C=N$); 4,16 (3H, s, $CH_3O$); 7,25...7,45 (2H, m, $o$-$H_{arom}$)<br>7,66...7,84 (2H, m, $m$-$H_{arom}$); 9,62 (1H, s, 6-CH) | 82...83 | 82 |
| VIb | $C_{15}H_{15}N_5O_2$ | 60,59<br>60,56 | 5,09<br>5,25 | $M^+$ 297 (30,5)<br>264 (100) | 2980, 2260<br>1570, 1485<br>1370 | 0,98 (3H, t, $J = 7,4$, $C\underline{H}_3CH_2$); 1,55 (2H, sext, $J = 7,4$, $CH_3C\underline{H}_2$)<br>2,60 (2H, t, $J = 7,4$, $CH_2C=$); 4,20 (3H, s, $CH_3O$); 7,30...7,70 (4H, m, $H_{arom}$)<br>9,55 (1H, s, 6-CH) | — | 88 |

TABLE 2. Properties of Compounds VIIa,b-IXa,b

| Compound | Empirical formula | Found, % / Calculated, % |  |  | Mass spectrum, *m/z* (%) | IR spectrum, $cm^{-1}$ | PMR spectrum, δ, ppm, SSCC, *J*, Hz | mp, °C | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
|  |  | C | H | N |  |  |  |  |  |
| VIIa | $C_{10}H_{12}N_2O_2$ | 62,49<br>62,30 | 6,29<br>6,32 | 14,57<br>14,56 | $M^+$ 192 (79,8)<br>147 (56,2)<br>121 (100) | 2990, 2950<br>1605, 1460<br>1430, 1260<br>1080 | 2,26 (3H, s, $CH_3C$=); 3,26 (2H, t, *J* = 8,8, 3-$CH_2$); 4,00 (3H, s, $CH_3O$)<br>4,64 (2H, t, *J* = 8,8, 2-$CH_2$); 7,44 (1H, d, *J* = 7,6, 5-CH)<br>7,46 (1H, dt, $J_1$ = 7,6, $J_2$ = 0,9, 4-CH) | 56 | 95 |
| VIIb | $C_{12}H_{16}N_2O_2$ | 65,43<br>65,60 | 7,32<br>7,29 |  | $M^+$ 220 (82,5)<br>175 (28,5)<br>121 (100) | 2980, 2890<br>1560, 1460<br>1260, 1080 | 0,94 (3H, t, *J* = 7,7, $C\underline{H}_3CH_2$); 1,55 (2H, m, $CH_3C\underline{H}_2$)<br>2,83 (2H, t, *J* = 7,7, $CH_2C$=); 3,25 (2H, td, $J_1$ = 8,8, $J_2$ = 1,1, 3-$CH_2$)<br>3,97 (3H, s, $CH_3O$); 4,64 (2H, t, *J* = 8,8, 2-$CH_2$)<br>7,38 (1H, d, *J* = 8,6, 5-CH); 7,46 (1H, dt, $J_1$ = 8,6, $J_2$ = 1,1, 4-CH) | 42...43 | 88 |
| VIIIa | $C_{11}H_{14}N_2O_2$ | 64,06<br>64,12 | 6,84<br>6,90 |  | $M^+$ 206 (88,7)<br>161 (69,2)<br>135 (100) | 2990, 2965<br>1600, 1460<br>1430, 1260<br>1080 | 1,97...2,08 (2H, m, 3-$CH_2$); 2,27 (3H, s, $CH_3C$=)<br>2,82 (2H, t, *J* = 6,2, 4-$CH_2$); 4,00 (3H, s, $CH_3O$);<br>4,37 (2H, t, *J* = 6,2, 2-$CH_2$); 7,36 (1H, dt, $J_1$ = 7,7, $J_2$ = 0,9, 5-CH)<br>7,48 (1H, d, *J* = 7,7, 6-CH) | 47 | 74 |
| VIIIb | $C_{13}H_{18}N_2O_2$ | 66,64<br>66,64 | 7,74<br>7,98 | 11,96<br>11,79 | $M^+$ 234 (16,6)<br>203 (100)<br>175 (61,6)<br>161 (63,3) | 2990, 2890<br>1570, 1480<br>1420, 1260<br>1080 | 0,92 (3H, t, *J* = 7,1, $C\underline{H}_3CH_2$); 1,58 (2H, m, $CH_3C\underline{H}_2$)<br>2,05...2,17 (2H, m, 3-$CH_2$); 2,79...2,89 (4H, m, 4-$CH_2$, $CH_2C$=)<br>3,95 (3H, s, $CH_3O$); 4,38 (2H, t, *J* = 6,1, 2-$CH_2$)<br>7,25 (1H, dt, $J_1$ = 7,7, $J_2$ = 0,9, 5-CH); 7,40 (1H, d, *J* = 7,7, 6-CH) | Oil | 61 |
| IXa | $C_{13}H_{11}N_3O_2$ | 64,72<br>64,50 | 4,59<br>4,60 | 17,42<br>17,42 | $M^+$ 241 (93,5)<br>169 (100) | 2960, 1630<br>1465, 1380<br>1190, 1070 | 2,39 (3H, s, $CH_3C$=); 4,11 (3H, s, $CH_3O$)<br>7,45...7,67 (3H, m, 5-, 6-, 7-CH); 8,20...8,35 (1H, m, 8-CH)<br>9,28 (1H, s, 3-CH) | 174...175 | 70 |
| IXb | $C_{15}H_{15}N_3O_2$ | 66,90<br>67,00 | 5,61<br>5,67 | 15,60<br>15,81 | $M^+$ 269 (75,5)<br>169 (100) | 2980, 1630<br>1460, 1390<br>1200, 1080 | 0,98 (3H, t, *J* = 7,0, $C\underline{H}_3CH_2$); 1,33...1,68 (2H, m, $CH_3C\underline{H}_2$)<br>2,95 (2H, t, *J* = 7,2, $CH_2C$=); 4,05 (3H, s, $CH_3O$)<br>7,35...7,75 (3H, m, 5-, 6-, 7-CH); 8,25 (1H, d, *J* = 8,5, 8-CH)<br>9,25 (1H, s, 3-CH) | 135...136 | 65 |

TABLE 3. Properties of Compounds X-XII

| Compound | Empirical formula | Found, % / Calculated, % | | | Mass spectrum, $m/z$ (%) | IR spectrum, $cm^{-1}$ | PMR spectrum, δ, ppm, SSCC, $J$, Hz | mp, °C | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | | | | | |
| Xa | $C_9H_9NO_2$ | 66,26<br>66,20 | 5,56<br>5,61 | 8,58<br>8,62 | $M^+$ 163 (94,1)<br>135 (56,8)<br>120 (100) | 2980, 1695<br>1660, 1650<br>1435, 1285 | 2,54 (3H, s, $CH_3C$=O); 3,04 (2H, td, $J_1$ = 6,4, $J_2$ = 0,9, 3-$CH_2$)<br>3,85 (2H, t, $J$ = 6,4, 2-$CH_2$); 6,88 (1H, d, $J$ = 6,8, 5-CH)<br>7,43 (1H, dt, $J_1$ = 6,8, $J_2$ = 0,9, 4-CH) | 74...75 | 22 |
| XIa | $C_{10}H_{11}NO_2$ | 67,78<br>67,88 | 6,26<br>6,38 | | $M^+$ 177 (100)<br>149 (52,7)<br>135 (82,5)<br>134 (57,4) | 2980, 2960<br>1700, 1585<br>1470, 1420<br>1370, 1270<br>1070 | 2,00...2,12 (2H, m, 3-$CH_2$); 2,67 (3H, s, $CH_3C$=O)<br>2,89 (2H, t, $J_1$ = 6,2, $J_2$ = 1,0, 4-$CH_2$); 4,42 (2H, t, $J$ = 5,2, 2-$CH_2$)<br>7,52 (1H, dt, $J_1$ = 5,6, $J_2$ = 1,0, 5-CH); 7,63 (1H, d, $J$ = 5,6, 6-CH) | 102...103 | 80 |
| XIb | $C_{12}H_{15}NO_2$ | 70,22<br>70,37 | 7,36<br>7,52 | | $M^+$ 205 (100)<br>177 (60,5)<br>163 (50,5)<br>132 (30,5) | 2990, 1700<br>1580, 1480<br>1430, 1295<br>1090 | 1,02 (3H, t, $J$ = 7,2, $C\underline{H}_3CH_2$); 1,77...1,95 (2H, m, $CH_3C\underline{H}_2$)<br>2,10...2,17 (2H, m, 3$CH_2$); 2,95 (2H, t, $J$ = 6,4, 4-$CH_2$)<br>3,85 (2H, t, $J$ = 7,3, $CH_2C$=O), 4,45 (2H, t, $J$ = 6,3, 2-$CH_3$)<br>7,48...7,52 (2H, m, 5-CH, 6-CH) | 39...40 | 93 |
| XIIa | $C_{12}H_8N_2O_2$ | | 3,80<br>3,70 | 13,20<br>13,06 | $M^+$ 212 (65,1)<br>197 (34,3)<br>184 (24,3)<br>170 (40,8)<br>169 (100) | 2980, 1700<br>1640, 1465<br>1390, 1195<br>1130 | 2,73 (3H, s, $CH_3C$=O); 7,51...7,59 (1H, m, $H_{arom}$)<br>7,73...7,78 (2H, m, $H_{arom}$); 8,28...8,32 (1H, m, $H_{arom}$)<br>9,36 (1H, s, 3-CH) | 145...146 | 95 |
| XIIb | $C_{14}H_{12}N_2O_2$ | | 5,03<br>5,02 | | $M^+$ 240 (20,1)<br>212 (73,9)<br>169 (100) | 2980, 1700<br>1480, 1390<br>1250, 1200<br>1130 | 1,25 (3H, t, $J$ = 7,2, $C\underline{H}_3CH_2$); 1,75...2,02 (2H, m, $CH_3C\underline{H}_2$)<br>3,40 (2H, t, $J$ = 7,4, $CH_2C$=O); 7,55...7,90 (3H, m, $H_{arom}$)<br>8,08 (1H, d, $J$ = 8,2, $H_{arom}$); 9,33 (1H, s, 3-CH) | 107...108 | 90 |

TABLE 4. Properties of Compounds XIII-XIV

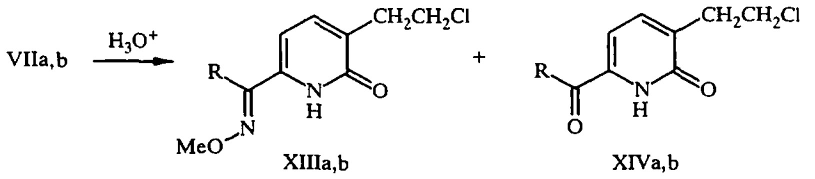
| Compound | Empirical formula | Found, % / Calculated, % | | | Mass spectrum, $m/z$ (%) | IR spectrum, $cm^{-1}$ | PMR spectrum, δ, ppm, SSCC, $J$, Hz | mp, °C | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | | | | | |
| XIIIa | $C_{10}H_{13}N_2O_2Cl$ | 52,63<br>52,31 | 5,70<br>5,75 | 12,28<br>12,02 | $M^+$ 228 (17,75)<br>193 (100<br>179 (24,5) | 3300, 3150<br>2980, 1660<br>1630, 1470<br>1070 | 2,089 (3H, s, $CH_3C=$); 2,99 (2H, t, $J$ = 6,5, $C\underline{H}_2CH_2Cl$)<br>3,83 (2H, t, $J$ = 6,5, $CH_2Cl$); 4,01 (3H, s, $CH_3O$)<br>6,33 (1H, d, $J$ = 6,9, CH); 7,32 (1H, d, $J$ = 6,9, CH)<br>9,70 (1H, s, NH) | 122...123 | 16 |
| XIIIb | $C_{12}H_{17}N_2O_2Cl$ | 56,14<br>56,29 | 6,67<br>6,37 | 10,09<br>9,95 | $M^+$ 256 (15,5)<br>221 (100)<br>207 (30,5) | 3300, 3150<br>2980, 1650<br>1620, 1475<br>1080 | 0,97 (3H, t, $J$ = 7,4, $C\underline{H}_3CH_2$); 1,57 (2H, m, $CH_3C\underline{H}_2$)<br>2,54 (2H, t, $J$ = 7,0, $CH_2C=$); 2,99 (2H, t, $J$ = 6,5, $C\underline{H}_2CH_2Cl$)<br>3,83 (2H, t, $J$ = 6,5, $CH_2Cl$); 3,99 (3H, s, $CH_3O$)<br>6,33 (1H, d, $J$ = 7,0, CH); 7,40 (1H, d, $J$ = 7,0, CH)<br>9,70 (1H, s, NH) | 115...116 | 58 |
| XIVa | $C_9H_{10}NO_2Cl$ | 54,35<br>53,59 | 6,03<br>4,95 | 7,04<br>6,81 | $M^+$ 199 (8,9)<br>164 (100) | 3600, 3400<br>3250, 3000<br>1700, 1670<br>1485, 1445<br>1380, 1290<br>1170 | 2,54 (3H, s, $CH_3C=O$); 3,05 (2H, t, $J$ = 6,3, $C\underline{H}_2CH_2Cl$)<br>3,86 (2H, t, $J$ = 6,3, $CH_2Cl$); 6,88 (1H, d, $J$ = 6,8, CH)<br>7,43 (1H, dt, $J_1$ = 6,8, $J_2$ = 0,8, CH); 9,49 (1H, s, NH) | 103 | 31 |
| XIVb | $C_{11}H_{14}NO_2Cl$ | 63,30<br>62,35 | 6,25<br>6,26 | 6,15<br>6,17 | $M^+$ 227 (5,3)<br>192 (100) | 3300, 3000<br>2970, 1700<br>1660, 1480<br>1390, 1310<br>1275, 1220<br>1200, 1115 | 1,05 (3H, t, $J$ = 7,4, $C\underline{H}_3CH_2$); 1,62...1,80 (2H, m, $CH_3C\underline{H}_2$)<br>2,78...3,08 (4H, m, $C\underline{H}_2CH_2Cl$, $CH_2C=O$)<br>3,80 (2H, t, $J$ = 6,6, $CH_2Cl$); 6,85 (1H, d, $J$ = 7,0, CH)<br>7,40 (1H, d, $J$ = 7,0, CH); 9,88 (1H, s, NH) | 92...93 | 12 |

The difference noted by us and previous investigators [7] between the rate of formation of the five-membered furan and six-membered pyrane rings is due to the specific geometry of the transition state. A difference in the reactivity of dienophiles containing $-C\equiv CH$ and $-C\equiv N$ groups was noted earlier [8].

Quantitative relationships among the type of carbonyl group, the size of the alkyl substituent R, and the nature of the substituent on the $C_{(3)}$ atom will be the subject of a separate report.

We performed a cycloaddition reaction on IV(a,b)-VI(a,b) to prepare VII(a,b)-IX(a,b) (Table 2). The latter group was then subjected to acid hydrolysis. Thus, maintaining VIII and IX at 80-90°C in 25% HCl broke the MeON=C bond to form the corresponding ketones XI and XII (Table 3).

Opening of the furan ring and formation of the polyfunctional pyridine derivatives XIII(a,b) and XIV(a,b) is observed during hydrolysis of VII(a,b) (refluxling in 20% HCl for ~15 min) (Table 4).



Thus, derivatives of furo[2,3-*b*]pyridines VIIa and VIIb behave differently. The acyl derivative Xa is formed in small yield (22%) along with XIIIa and XIVa from VIIa (Table 3). Hydrolysis of VIIb does not stop at the ketone Xb but opens the THF ring to give XIIIb and XIVb.

Thus, heterocyclic compounds containing an acyl group can be synthesized by the described methods. Compounds of this type can be used in the synthesis of indole alkaloids [2].

## EXPERIMENTAL

Melting points were measured on a Buchi apparatus and are uncorrected. IR spectra were obtained on a UR-20 instrument. NMR spectra were taken on Varian EM-60 or Varian Gemini (200 MHz) instruments with TMS internal standard in $CDCl_3$. Mass spectra were measured on an ATD-604 instrument. Kieselgel 40 (0.063-0.200 mm) activated by heating under 1.3-2.0 kPa vacuum at 150°C for 2 h was used for column chromatography. The course of the reactions was followed and column chromatography was performed on Kieselgel 60 F-254 plates with visualization by UV light.

**5-(1-Methoxyiminoethyl)-3-methylthio-1,2,4-triazine (IIa).** Sodium hydride (0.132 g, 5.5 mmol), prepared by treating 0.220 g of its 60% suspension in oil with ether, and dimethylsulfate (0.63 g, 5.0 mmol) was added successively to solution of 5-acetyl-3-methylthio-1,2,4-triazineoxime (0.92 g, 5.0 mmol, 1 ml) in anhydrous DMF (10 ml) cooled to 10°C. The reaction mixture was stirred for 3 h. Water with ice (100 ml) was added. The product was extracted with diethyl ether. The extract was dried over anhydrous $MgSO_4$. The ether was evaporated. Yield 0.881 g (89%) of IIa.; mp 87-88°C (aqueous ethanol). IR spectrum: 1060 $cm^{-1}$. PMR spectrum ($CDCl_3$): 2.20 (3H, s, $CH_3C=N$), 2.70 (3H, s, $CH_3S$), 4.10 (3H, s, $CH_3O$), 9.45 ppm (1H, s, CH). Found, %: C 42.30; H 5.50. $C_7H_{10}N_4OS$. Calculated, %: C 42.42; H 5.05.

**5-(1-Methoxyiminobutyl)-3-methylthio-1,2,4-triazine (IIb)** was prepared analogously from 5-acetyl-3-propylthio-1,2,4-triazineoxime. Yield 83%; mp 129-130°C (aqueous ethanol). IR spectrum: 1070 $cm^{-1}$ (C–O–N). PMR spectrum ($CDCl_3$): 0.90 (3H, t, $C\underline{H}_3CH_2$), 1.20-1.80 (2H, m, $CH_3C\underline{H}_2$), 2.90-2.60 (5H, m, $CH_3S$, $CH_2C=N$), 4.10 (3H, s, $CH_3O$), 9.40 ppm (1H, s, CH). Found, %: C 47.31; H 6.43. $C_9H_{14}N_4OS$. Calculated, %: C 47.79; H 6.19.

**5-(1-Methoxyiminoethyl)-3-methylsulfonyl-1,2,4-triazine (IIIa).** Solution of IIa (0.198 g, 1.0 mmol) in benzene (10 ml), acetic acid (2.2 ml), and tetrabutylammonium bromide (0.032 g, 1.0 mmol) was added successively to solution of $KMnO_4$ (0.395 g, 2.5 mmol) in water (15 ml). The reaction mixture was vigorously stirred for 2 h at room temperature. The course of the reaction was followed using TLC ($CHCl_3$–acetone, 50:1). The mixture was treated with sodium pyrosulfite solution and washed with saturated $K_2CO_3$ solution. The organic layer and benzene extract of the aqueous layer were dried over anhydrous $MgSO_4$. The benzene was distilled in argon atmosphere. Yield 0.14 g (86.9%) of yellow crystalline IIIa. IR spectrum: 1390, 1340, 1080 $cm^{-1}$. PMR spectrum ($CDCl_3$): 2.40 (3H, s, $CH_3C{=}N$), 3.45 (3H, s, $SO_2CH_3$), 4.20 ppm (3H, s, $CH_3O$), 9.85 ppm (1H, s, CH).

**5-(1-Methoxyimnobutyl)-3-methylsulfonyl-1,2,4-triazine (IIIb)** was prepared analogously from triazine IIb. Yield 96%. IR spectrum: 1335 ($SO_2$), 1150, 1070 $cm^{-1}$ (C–O–N). PMR spectrum ($CDCl_3$): 1.05 (3H, t, $\underline{CH_3}CH_2$), 1.60 (2H, m, $CH_3\underline{CH_2}$), 2.95 (2H, t, $CH_2C{\equiv}N$), 3.45 (3H, s, $SO_2CH_3$), 4.20 ppm (3H, s, $CH_3O$).

**3-(3-Alkynyloxy)-5-(1-methoxyiminoethyl)-1,2,4-triazines (IVa,b and Va,b) (General Synthesis Method).** Suspension of sodium hydride (0.027 g, 1.1 mmol) in anhydrous THF (2 ml) was treated in argon atmosphere with 3-butyn-1-ol (0.07 g, 1.0 mmol) or 4-pentyn-1-ol (0.084 g, 1.0 mmol) dissolved in THF (3 ml). The reaction mixture was stirred for 10 min at room temperature and then cooled to 0°C. Solution of IIIa or IIIb in THF (0.5 ml) was added with stirring. The mixture was stirred for 24 h at room temperature in argon atmosphere. The reaction mixture is treated with diethyl ether (50 ml) and saturated $NaHCO_3$ (5 ml). The ether extract is dried over anhydrous $MgSO_4$. The solvent is evaporated. The crude product is purified by column chromatography (300×11 mm, eluent $CHCl_3$).

**3-(3-Butynyloxy)-5-(1-methoxyiminoethyl)-1,2,4-triazine (IVa), 3-(3-Butynyloxy)-5-(1-methoxyiminobutyl)-1,2,4-triazine (IVb), 5-(1-Methoxyiminoethyl)-3-(4-pentynyloxy)-1,2,4-triazine (Va), and 5-(1-Methoxyiminobutyl)-3-(4-pentynyloxy)-1,2,4-triazine (Vb)** are prepared by this method. The properties of the compounds synthesized are listed in Table 1.

**3-(*o*-Cyanophenoxy)-5-(1-methoxyiminoethyl)-1,2,4-triazine (VIa).** Suspension of sodium *o*-cyanophenoxide (0.043 g, 0.3 mmol) in anhydrous THF (5 ml) at 0°C is treated in argon atmosphere with solution of IIIa (0.069 g, 0.3 mmol) in anhydrous THF (2 ml). The reaction mixture is held for 24 h at room temperature in argon atmosphere. The solvent is distilled *in vacuo*. The solid is treated with $CHCl_3$ (50 ml) and water (2 ml). The $CHCl_3$ extract is washed with saturated $NaHCO_3$ and dried over anhydrous $MgSO_4$. The solvents are distilled. Product VIa is isolated by column chromatography (300×19 mm, eluent $CHCl_3$) from the residue.

**3-(*o*-Cyanophenoxy)-5-(1-methoxyiminobutyl)-1,2,4-triazine (VIb)** is prepared analogously from IIIb (see Table 1).

**Intramolecular Diels-Alder Reaction of IV-VI (General Method).** Solution of IVa,b or Va,b (1 mmol) in bromobenzene (10 ml) or VIa,b in nitrobenzene (10 ml) is refluxed in argon atmosphere for 2, 5, 18, 25, 10 and 10 h, respectively. The course of the reaction is monitored using TLC ($CHCl_3$–acetone, 20:1). The solvents are distilled *in vacuo* after the reaction is finished. The crude product is purified by column chromatography (300×19 mm, eluent $CHCl_3$). The products are 6-(1-methoxyiminoethyl)-(2,3-dihydrofuro)[2,3-*b*]pyridine (VIIa), 6,1-(methoxyiminobutyl)-(2,3-dihydrofuro)[2,3-*b*]pyridine (VIIb), 7-(1-methoxyiminoethyl)-(3,4-dihydro-2H-pyrano)-[2,3-*b*]pyridine (VIIIa), 7-(1-methoxyiminobutyl)-(3,4-dihydro-2H-pyrano)[2,3-*b*]pyridine (VIIIb), 2-(1-methoxyiminoethyl)benzo[*b*]furo[2,3-*b*]pyrazine (IXa), and 2-(1-methoxyiminobutyl)benzo[*b*]furo[2,3-*b*]pyrazine (IXb). Their properties are given in Table 2.

**Hydrolysis of VII-IX (General Method).** Compounds VIIIa,b and IXa,b (0.3 mmol) in HCl (3 ml, 25%) are mixed in a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. The mixture is held at 80-90°C for 2 h until a transparent solution forms. The reaction mixture is neutralized with saturated $NaHCO_3$. The product is extracted with $CHCl_3$ (5×20 ml). The extract is dried over anhydrous $MgSO_4$. The solvent is evaporated. The solid is crystallized from hexane. The products are 7-acetyl(3,4-dihydro-2H-pyrano)[2,3-*b*]-pyridine (XIa), 7-butyryl(3,4-dihydro-2H-pyrano)[2,3-*b*]pyridine (XIb), 2-acetyl(benzo[*b*]furo[2,3-*b*])pyrazine (XIIa), and 2-butyryl(benzo[*b*]furo[2,3-*b*])pyrazine (XIIb). The properties of these are given in Table 3.

**Hydrolysis of VIIa and VIIb.** Compound VIIa (0.5 mol) in HCl (4 ml, 20%) is boiled until a transparent solution forms (~15 min). The cooled reaction mixture is neutralized with saturated $NaHCO_3$ and extracted with $CHCl_3$ (6×20 ml). The $CHCl_3$ extract is dried over anhydrous $MgSO_4$. The solvent is distilled. The products 6-acetyl-2,3-dihydrofuro[2,3-*b*]pyridine (Xa), 6-(1-methoxyiminoethyl)-3-(2-chlroethyl)-1,2-dihydropyridin-2-one (XIIIa) and 6-acetyl-3-(2-chloroethyl)-1,2-dihydropyridin-2-one (XIVa) are isolated by TLC ($CHCl_3$–acetone, 50:1) from the residue.

**3-(2-Chloroethyl)-6-(1-methoxyiminobutyl)-1,2-dihydropyridin-2-one (XIIIb) and 6-Butyryl-3-(2-chloroethyl)-1,2-dihydropyridin-2-one (XIVb)** are the principal products obtained under analogous conditions from VIIb (see Tables 3 and 4).

The authors thank Professor N. P. Erchak of the Agricultural Pedagogical University in Siedlce (Poland) and Brest State University (Belarus) for help with preparing the manuscript.

## REFERENCES

1. A. Rykowski and T. Lipińska, *Pol. J. Chem.*, **71**, 83 (1997).
2. A. Rykowski and T. Lipińska, *Synth. Commun.*, **26**, 4409 (1996).
3. A. Rykowski, E. Guzik, M. Makosza, and W. Hozler, *J. Heterocycl. Chem.*, **30**, 413 (1993).
4. H. Goda, M. Satj, H. Ihara, and C. Hirayama, *Synthesis*, No. 9, 849 (1992).
5. E. C. Taylor, J. L. Pont, and J. C. Warner, *Tetrahedron*, **43**, 5159 (1987).
6. B. Geurtsen, A. Dick, and H. van der Plas, *Tetrahedron*, **45**, 6519 (1989).
7. E. C. Taylor and J. E. Macor, *Tetrahedron Lett.*, **26**, 2419 (1985).
8. E. C. Taylor, *Bull. Soc. Chim. Belg.*, **97**, 599 (1988).
9. D. L. Boger and S. N. Weinreb, *Hetero Diels-Alder Methodology in Organic Synthesis*, H. H. Wasserman (ed.), Academic Press, New York (1987), p. 323.