Synthesis of 1,4,6,7-Tetrahydroimidazo[2,1-*c*][1,2,4]triazines

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From 2-methylthioimidazoline and phenacylbromides in DMF there were obtained the 2-(2-methylthio-2-imidazolin-1-yl)acetophenones **3a-3f**. From these the substituted 3-phenyl-1,4,6,7-tetrahydroimidazo[2,1-*c*][1,2,4]triazines **4a-4n** were prepared upon reaction with hydrazine and methylhydrazine respectively. Compound **4a** was degraded to the triazine **6**. From the (2-methylthio-2-imidazolin-1-yl)-acetic acid ester **10**, the imidazo[2,1-*c*][1,2,4]triazines **11a-11c** were prepared. Selective ethylation on the oxygen was achieved with **11b** in the presence of Meerwein's salt.

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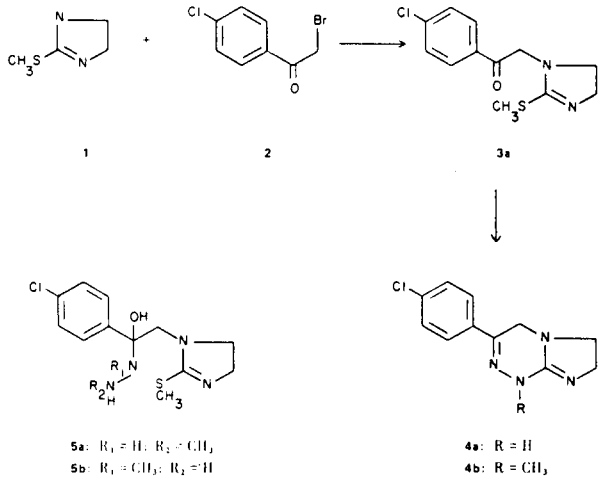
The literature contains only a few references (1-3) pertaining to the imidazo[2,1-*c*][1,2,4]triazine ring system. In the first published report (1), 2-amino-3-phenacyl-5-phenyloxazolium bromide was allowed to react with hydrazine to give a 1,4-dihydro-3,7-diphenylimidazo[2,1-*c*][1,2,4]triazine. In another case (2), 2-acetylimino-3-phenacyl-4-thiazole was rearranged in the presence of hydrazine to give 1,4-dihydro-7-phenylimidazo[2,1-*c*]-[1,2,4]triazine.

Our own experiments (4) started from the readily available 2-methylthioimidazoline (**1**) (5). When this compound was heated to reflux with *p*-chlorophenacylbromide (**2**) in acetone a new product **3a** could be isolated albeit in low yield. A marked acceleration was observed when the reaction was carried out in dimethylformamide as solvent: A few minutes after mixing the reactants an exothermic reaction took place which required some cooling to control the temperature. From the cold solution the product **3a** precipitated as the hydrobromide in good yield and was characterized with the aid of analytical and spectral data to verify the structural assignment.

Scheme I



When the compound **3a** was allowed to react with hydrazine in DMF as solvent, an exothermic reaction with evolution of methylmercaptan was observed. A new product, isolated as the free base, was assigned structure **4a** based on spectral and analytical data.

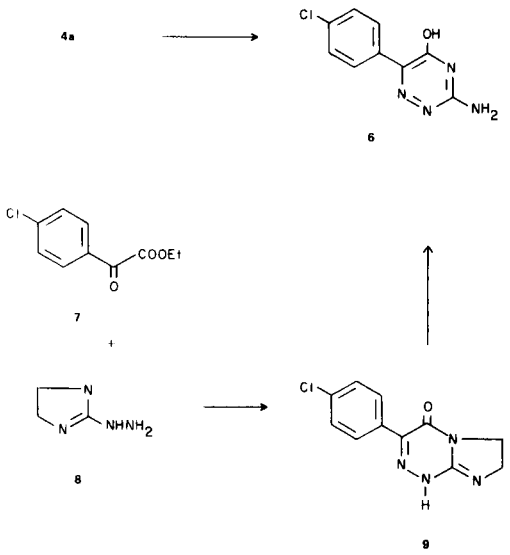
When methylhydrazine was allowed to react with **3a** under similar conditions as described above the product precipitated as the hydrobromic acid addition salt **4b**. Analytical and spectral data was in agreement with structure **4b** for both the salt and the free base liberated from the salt.

Since only *one* product was isolated from the reaction between **3a** and methylhydrazine it may be concluded that the formation of the hydrazone represents the first step of the sequence followed by the loss of methylmercaptan *via* an intramolecular cyclization reaction. If the loss of methylmercaptan were to occur at the stage of the hydrazinoalcohol **5a,b** or *via* an intermolecular condensation as the first step of the sequence, the formation of two different products might be anticipated. We have reason to believe that the loss of methylmercaptan as the first step is improbable based on experiments to be described below.

The reaction of 2-methylthioimidazoline (**1**) with a variety of substituted phenacylbromides allowed the introduction of substituents on the phenyl ring as exemplified in Tables I and II. We were not able however to extend the condensation to other ψ-ureas such as 2-methylthiotetrahydropyrimidine (6), 2-methylthiotetrahydro-1*H*-diazepine (7) and 2-methylthiobenzimidazole (8).

When the compound **4a** was treated with chromium trioxide in glacial acetic acid, degradation of the imidazoline ring and oxidation of the triazine occurred to form compound **6**.

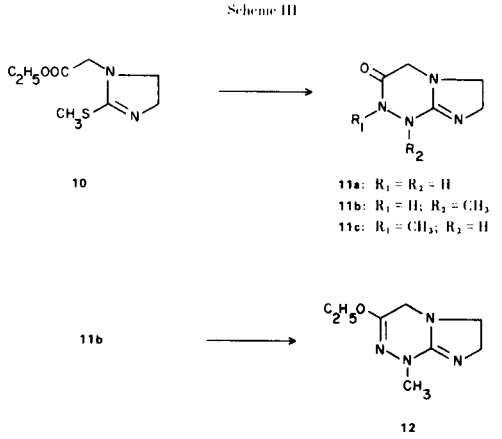
Scheme II



The structure of **6** was established by allowing ethyl *p*-chlorobenzoylformate (9) (**7**) to react with 2-hydrazinoimidazoline (10) (**8**) to form 3-(*p*-chlorophenyl)-6,7-dihydroimidazo[2,1-*c*][1,2,4]triazin-4(1*H*)one (**9**). This was treated with chromium trioxide under conditions similar to those described above to give a substance identical with the compound obtained from **4a**. This conclusion was reached after comparison of the mass spectra of the two compounds. Comparison of other analytical and spectral data was all but impossible due to the unfavorable physical properties of this compound.

As the last example we investigated the reaction between 2-methylthioimidazoline (**1**) and ethyl bromoacetate. An exothermic reaction was observed in DMF as was in the previous examples and the product **10** was isolated as the hydrobromide in 72% yield. Attempts to react **10** in the presence of hydrazine were not successful until the hydrobromic acid was removed from the reaction mixture by employing the starting material **10** as the free base, which was heated in the presence of hydrazine in ethanol. The high melting 1,2,3,4,6,7-hexahydroimidazo[2,1-*c*][1,2,4]triazin-3-one (**11a**) was isolated in 90% yield. Starting with methylhydrazine, compound **10** (also as the free base) gave rise to approximately equal amounts of 1-methyl- and 2-methyl-1,2,3,4,6,7-hexahydroimidazo-[2,1-*c*][1,2,4]triazine-3-ones (**11a** and **11b**), respectively.

Scheme III



Structures were assigned based on the following transformation. The higher melting isomer was allowed to react with triethyloxonium fluoroboride (11) and then neutralized with carbonate solution. A non polar liquid was isolated which we formulated as structure **12**. In the nmr spectrum of **12** a quartet at δ 4.12 ppm was assigned to the methylene group of the ethyl ether, indication that *O*-alkylation had occurred on a secondary amide.

Carbon-13 Nmr Spectra of Compounds **11b**, **11c** and **12**.

For additional support of the assigned structures we have studied the cmr spectra of the forementioned compounds. The results are listed in Tables IV, V and VI (see Experimental). The lactam carbon in **11b** (12) gave rise to a peak at 161.1 ppm. In agreement with observations recorded for *N*-methylated amides (13), the corresponding peak for **11c** is shifted to higher field and observed at 157.2 ppm. Similar differences were observed for the guanidine carbon. In the case of **11c** the peak at 153.4 ppm was assigned to the guanidine carbon. Attachment of a methyl group on the guanidine nitrogen resulted in a higher chemical shift for the corresponding carbon with an observed value of 149.5 ppm for **11b**. The peak at 62.7 ppm observed for **12** was assigned to the methylene carbon of the ethoxy group which is in good agreement with observations published (14) for the corresponding carbon of ethyl esters. All the methylene and methyl carbons on the nitrogen atom of **12** are shifted to lower field. This might well be due to the change in solvent, required by the insolubility of compounds **11b** and **11c**.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary

Table I

Compound (a)	X	Yield	M.p. °C	*Anal.*	C	H	N	S	Br	Cl	Formula
3b	4-OCH_3	72	211-213	Calcd.	45.2	4.9	8.1	9.3	23.1		$C_{13}H_{16}N_2O_2S$·HBr
				Found	45.6	5.1	8.1	9.3	22.9		
3c	H	66	177-179	Calcd.	45.7	4.8	8.9	10.2	25.3		$C_{12}H_{14}N_2OS$·HBr
				Found	45.2	4.9	9.0	10.2	25.3		
3d	2,4-Cl_2	45	187-188	Calcd.	37.5	3.4	7.3	8.3	20.8	18.5	$C_{12}H_{12}Cl_2N_2OS$·HBr
				Found	37.3	3.5	7.1	8.5	20.7	18.6	
3e	4-F	44	204-206	Calcd.	43.3	4.2		9.6	24.0		$C_{12}H_{13}FN_2OS$·HBr
				Found	43.2	4.3		9.7	23.8		
3f	4-CH_3 not isolated										

(a) Analogues **3b-3f** were prepared following the procedure described for **3a.**

Table II

Compound	R	X	Yield %	M.p. °C	*Anal.*	C	H	N	Hal	Formula
4c	H	4-OCH_3	60	258-260	Calcd.	62.6	6.1	24.3		$C_{12}H_{14}N_4O$
					Found	62.5	6.7	24.5		
4d	CH_3	4-OCH_3	74	235-237	Calcd.	48.0	5.3	17.2	24.6	$C_{13}H_{16}N_4O$·HBr
					Found	45.4	6.8	16.6	24.4	
4e	CH_3	4-OCH_3		111-112	Calcd.	63.9	6.6	22.9		$C_{13}H_{16}N_4O$
					Found	63.6	6.9	23.1		
4f	H	H	70	228-230	Calcd.	66.0	6.0	28.0		$C_{11}H_{12}N_4$
					Found	65.8	6.4	28.3		
4g	CH_3	H	39	255-257	Calcd.	46.0	5.5		25.5	$C_{12}H_{14}N_4$·HBr·H_2O
					Found	45.8	5.6		25.3	
4h	CH_3	H		82-83	Calcd.	67.3	6.6	26.2		$C_{12}H_{14}N_4$
					Found	67.5	7.1	25.8		
4i	H	2,4-Cl_2	80	194-197	Calcd.	49.1	3.7	20.8	26.3	$C_{11}H_{10}Cl_2N_4$
					Found	49.3	3.9	20.7	26.0	
4j	CH_3	2,4-Cl_2	63	105-106	Calcd.	50.9	4.3	19.8	25.0	$C_{12}H_{12}Cl_2N_4$ (a)
					Found	51.0	4.3	20.0	24.7	
4k	H	4-F	52	254-257	Calcd.	60.5	5.1	25.7		$C_{11}H_{11}FN_4$
					Found	60.4	5.2	25.4		
4l	CH_3	4-F	55	274-275	Calcd.	46.0	4.5	17.9		$C_{12}H_{13}FN_4$·HBr
					Found	46.4	4.6	17.5		
4m	H	4-CH_3	41	266-268	Calcd.	67.3	6.6	26.2		$C_{12}H_{14}N_4$
					Found	67.1	7.1	26.3		
4n	CH_3	4-CH_3		97-98	Calcd.	68.4	7.1	24.5		$C_{13}H_{16}N_4$ (a)
					Found	68.0	7.6	24.6		

(a) Base obtained from hydrobromide salt.

melting point apparatus and are not corrected. Nmr spectra were measured on either a Varian A-60 or T-60 spectrometer and are recorded in δ values (ppm) from TMS as internal standard. The ^{13}C-nmr spectra were measured on a Varian XL-100 spectrometer and are recorded in ppm values from TMS as internal standard. Ir spectra were taken on a Perkin-Elmer Model 247 or 457. Mass spectra were taken on a LKB 9000 Mass spectrometer.

4'-Chloro-2-(2-methylthio-2-imidazolin-1-yl)acetophenone Hydrobromide (**3a**).

A solution of 23.0 g. (0.20 mole) of 2-methylthio-2-imidazoline (5) in 75 ml. of anhydrous DMF was treated with 45 g. (0.20 mole) of commercial *p*-chlorophenacyl bromide. After a few minutes an exothermic reaction was observed (60°). From the cold solution the product precipitated, m.p. 210-213°, yield 49.0 g. (73%). A sample was recrystallized from hot ethanol, m.p. 220-222°; m/e: 268 [M^+]; nmr (trifluoroacetic acid): δ 2.42 (s, 3, SCH_3), 3.83 (s, 4, 2 NCH_2), 4.77 (s, 2, $COCH_2$), 7.0-7.8 (m, 5, C_6H_4+N*H*); ir (nujol): 1698 (C=O) cm^{-1}; uv: 256 nm (ε, 24,000).

Anal. Calcd. for $C_{12}H_{13}ClN_2OS \cdot HBr$ (349.7): C, 41.2; H, 4.0; O, 4.6; Br, 22.9; Cl, 10.1; S, 9.2. Found: C, 41.3; H, 4.1; O, 4.7; Br, 22.8; Cl, 10.3; S, 9.2.

3-(4-Chlorophenyl)-1,4,6,7-tetrahydroimidazo[2,1-c][1,2,4]triazine (**4a**).

A solution of 12 g. (0.1 mole) of 2-methylthioimidazoline in 50 ml. of DMF was treated with 24.0 g. (0.1 mole) of *p*-chlorophenacyl bromide. After the onset of the exothermic reaction, the mixture was stirred at room temperature for 20 minutes. To the mixture, 10 g. (0.3 mole) of hydrazine was added. Another exothermic reaction was observed with evolution of methylmercaptan (hood). Stirring was continued for 30 minutes. A solid precipitated, was filtered off and washed with a small amount of DMF and water to yield 16.7 g. (70%) of **4a**, m.p. 263-265°; m/e 234 [M^+]; nmr (trifluoroacetic acid): δ 3.58 (s, 4, 2 CH_2), 4.13 (s, 2, CH_2), 6.9-7.3 (m, 4, C_6H_4); ir (nujol): 1660 (weak) cm^{-1}; uv: 233 nm (ε, 8,000), 239 (8,000), 316 (12,450).

Anal. Calcd. for $C_{11}H_{11}ClN_4$ (234.7): C, 56.9; H, 4.7; Cl, 15.1. Found: C, 56.9; H, 4.8; Cl, 15.0.

The hydrochloride of **4a** was prepared following the usual procedures, m.p. 222-223°.

Anal. Calcd. for $C_{11}H_{11}ClN_4 \cdot HCl$ (270.1): C, 48.7; H, 4.5; N, 20.7; Cl, 26.2. Found: C, 48.7; H, 5.1; N, 20.4; Cl, 25.9.

3-(4-Chlorophenyl)-1-methyl-1,4,6,7-tetrahydroimidazo[2,1-c]-[1,2,4]triazine (**4b**).

To 14.7 g. (0.042 mole) of **3a** in 20 ml. of DMF there was added 8.0 g. (0.175 mole) of methylhydrazine. An exothermic reaction was observed. After 1 hour at room temperature, the solid was filtered off to yield 9.1 g. (90%) of **4b**·HBr, m.p. 279-281°. A sample was recrystallized from ethanol, m.p. 282-283°; nmr (trifluoroacetic acid): δ 3.24 (s, 3, CH_3), 3.58 (s, 4, 2 CH_2), 4.09 (s, 2, CH_2), 6.8-7.4 (m, 4, C_6H_4); ir (nujol): 1637, 1615 cm^{-1}; uv: 219 nm (ε, 9,460), 258 (9,800), 302 (15,400).

Anal. Calcd. for $C_{12}H_{13}ClN_4 \cdot HBr$ (329.6): C, 43.7; H, 4.3; Cl, 10.7; N, 17.0; Br, 24.2. Found: C, 43.7; H, 4.3; N, 17.0; Br, 24.2; Cl, 10.7.

The free base was prepared in the usual manner to give **4b**, m.p. 138-140°; m/e: 248 [M^+]; nmr (deuteriochloroform): δ 3.50 (s, 3, CH_3), 3.3-3.9 (m, 4, NCH_2CH_2N), 3.98 (s, 2, $N{=}CCH_2$), 7.43 (q, J = 9 cps, Δν = 12 cps, 4, C_6H_4); ir (dichloromethane): 1620 (C=N) cm^{-1}; uv: 229 nm (ε, 9,100), 316 (20,400).

Anal. Calcd. for $C_{12}H_{13}ClN_4$ (248.7): C, 58.0; H, 5.3; N, 22.4. Found: C, 58.0; H, 5.3; N, 22.4.

3-Amino-6-(4-chlorophenyl)-[1,2,4]triazin-5-ol (**6**).

A. From **4a**.

To a solution of 15.0 g. (0.06 mole) of **4a** in 150 ml. of glacial acetic acid there was added a solution of 30 g. (0.3 mole) of chromium trioxide in 30 ml. of water. The mixture was heated to reflux for 30 minutes. The solid precipitated from the cold solution, was filtered and washed with water and ethanol to yield 9.4 g. (66%) of **6**, m.p. > 330°; m/e: 222 [M^+]; nmr (deuteriosulfuric acid): δ 7.65 (q, J = 8.5 cps, Δν = 22.4 cps, C_6H_4); ir (potassium bromide): 3360, 1666, 1636 cm^{-1}.

Anal. Calcd. for $C_9H_7ClN_4O$ (222.6): C, 48.6; H, 3.2; Cl, 15.9. Found: C, 48.5; H, 3.3; Cl, 15.9.

B. From **9**.

A solution of 3.0 g. (0.03 mole) of chromium trioxide in 3 ml. of water was added to a solution of 1.5 g. (0.006 mole) of **9** in 25 ml. of glacial acetic acid. The product was isolated following the same procedures as described for the oxidation of **4a**, m.p. >330°; m/e: 222 [M^+].

3-(4-Chlorophenyl)-4-oxo-1,4,6,7-tetrahydroimidazo[2,1-c][1,2,4]-triazine (**9**).

To a solution of 5.6 g. (0.1 mole) of potassium hydroxide in 100 ml. of ethanol, 22.8 g. (0.1 mole) of 2-hydrazinoimidazoline·HI (**10**) (**8**) was added followed by 21.2 g. (0.1 mole) of ethyl *p*-chlorobenzoylformate (9). After 2 hours at room temperature, 100 ml. of water was added to precipitate 21.0 g. (85%) of **9**, m.p. 262-264°. A sample was recrystallized from acetic acid/water, m.p. 298-300°; m/e: 248 [M^+].

Anal. Calcd. for $C_{11}H_9ClN_4O$ (248.7): C, 53.1; H, 3.6; Cl, 14.3; N, 22.5. Found: C, 52.8; H, 3.7; Cl, 14.5; N, 22.5.

(2-Methylthio-2-imidazolin-1-yl)acetic Acid Ethyl Ester (**10**).

When a solution of 8.35 g. (0.05 mole) of ethyl bromoacetate in 15 ml. of DMF was treated with 5.8 g. (0.05 mole) of **1** at room temperature an exothermic reaction was observed. After an additional hour at room temperature, the solid was filtered off to yield 10.0 g. (72%) of **10**, m.p. 148-150°; m/e: 202 [M^+]; nmr (deuteriochloroform): δ 1.33 (t, 3, J = 7 cps, CH_2CH_3), 3.03 (s, 3, SCH_3), 4.0-4.6 (m, 8, 4 CH_2); ir (dichloromethane): 1750 (C=O) cm^{-1}; uv: 223 nm (ε, 10,500).

Anal. Calcd. for $C_8H_{14}N_2O_2S \cdot HBr$ (283.20): C, 33.9; H, 5.3; N, 9.9; S, 11.3; Br, 28.2. Found: C, 33.9; H, 5.3; N, 10.3; S, 11.4; Br, 28.7.

3-Oxo-1,2,3,4,6,7-hexahydroimidazo[2,1-c][1,2,4]triazine (**11a**).

A mixture of 14.5 g. (0.07 mole) of **10** and 5 g. (0.16 mole) of hydrazine in 50 ml. of ethanol was heated to reflux during 1 hour. A solid precipitated and was removed by filtration to yield 9.0 g. (90%) of **11a**, m.p. 282-284°; m/e: 140 [M^+]; ^{13}C nmr, see Table III; nmr (deuteriochloroform + trifluoroacetic acid): δ 3.5-4.2 (m); ir (potassium bromide): 1680 cm^{-1}; uv: 268 nm (ε, 5,800).

Anal. Calcd. for $C_5H_8N_4O$ (140.2): C, 42.9; H, 5.8; N, 40.0. Found: C, 42.7; H, 6.3; N, 39.8.

Table III

^{13}C Nmr Spectrum of **11a** in Deuterium Oxide (Pyridine as Internal Standard)

Absorptions observed	Relative Intensities	Assignment
46.9	132	$N\text{-}CH_2$
45.4	64	$N\text{-}CH_2$
39.6	125	$N\text{-}CH_2\text{-}C{=}O$
147.6, 135.8, 122.9		Pyridine

1-Methyl and 2-Methyl-3-oxo-1,2,3,4,6,7-hexahydroimidazo[2,1-c]-[1,2,4]triazine (**11b** and **11c**).

A mixture of 22.0 g. (0.11 mole) of **10** and 15 g. (0.33 mole) of methylhydrazine in 80 ml. of ethanol was heated to reflux over night. The solid was filtered off to yield 5.5 g. (38%) of **11b**, m.p. 312-315°. When recrystallized from ethanol/ether, it had m.p. 317-318°; m/e: 154 [M^+]; ^{13}C nmr, see Table IV; nmr (deuterium oxide): δ 3.18 (s, 3, CH_3), 3.70 (s, 4, NCH_2CH_2N), 3.73 (s, 2, $O{=}CCH_2N$); ir (nujol): 1665 (C=O) cm^{-1}; uv: 265 nm (ε, 6,400).

Anal. Calcd. for $C_6H_{10}N_4O$ (154.2): C, 46.7; H, 6.5; N, 36.3. Found: C, 46.9; H, 6.9; N, 36.4.

Table IV

^{13}C Nmr Spectrum of **11b** in Deuterium Oxide (Pyridine as Internal Standard)

Absorptions observed	Relative Intensities	Assignment
161.1	29	C=O
149.5	14	N-C=N
46.2	168	$N\text{-}CH_2$
43.3	216	$N\text{-}CH_2$
39.4	154	$N\text{-}CH_2\text{-}C{=}O$
35.6	60	$N\text{-}CH_3$
146.8, 135.7, 122.6		Pyridine

The mother liquors were concentrated to give 5.8 g. (36%) of **11c**; m.p. 180-182°; recrystallized from acetone/hexane it had m.p. 185-186°; m/e: 154 [M^+]; ^{13}C nmr, see Table V; nmr (deuterium oxide): δ 3.17 (s, 3, CH_3), 3.4-3.6 (m, 4, NCH_2CH_2N), 3.83 (s, 2, $O{=}CCH_2N$); nmr (deuteriochloroform): δ 3.20 (s, 3, CH_3), 3.3-3.7 (m, 4, NCH_2CH_2N), 3.75 (s, 2, $O{=}CCH_2N$), 5.5-5.9 (broad, 1, NH); ir (nujol): 1680 and 1625 (C=O, C=N) cm^{-1}; uv: 265 nm (ε, 5,900).

Anal. Calcd. for $C_6H_{10}N_4O$ (154.2): C, 46.7; H, 6.5; N, 36.3. Found: C, 46.8; H, 6.7; N, 36.1.

Table V

^{13}C Nmr Spectrum of **11c** in Deuterium Oxide (Pyridine as Internal Standard)

Absorptions observed	Relative Intensities	Assignment
157.2	16	C=O
153.4	8	N-C=N
46.4	206	$N\text{-}CH_2$
45.0	216	$N\text{-}CH_2$
38.9	144	$N\text{-}CH_2\text{-}C{=}O$
33.5	67	$N\text{-}CH_3$
146.8, 135.7, 122.6		Pyridine

3-Ethoxy-1-methyl-1,4,6,7-tetrahydroimidazo[2,1-*c*][1,2,4]triazine (**12**).

The higher melting isomer **11b** was treated with triethyl oxonium fluoroboride (11) (Meerwein salt) in dichloromethane. When all the starting material was dissolved, the mixture was poured on 2*N* sodium carbonate solution and extracted to give **12** as a liquid, yield 15.0 g. (90%); m/e: 182 [M^+]; nmr (deuteriochloroform): δ 1.30 (t, 3, J = 7.0 cps, $CH_2\text{-}CH_3$), 3.27 (s, 3, NCH_3), 3.63 (s, 2, NCH_2COEt), 3.2-3.9 (m, 4, $NCH_2\text{-}CH_2\text{-}N$), 4.12 (q, 2, J = 7.0 cps, OCH_2).

Table VI

^{13}C Nmr Spectrum of **12** in Deuteriochloroform (TMS as Internal Standard)

Absorptions observed	Relative Intensities	SFORD	Assignment
156.9	15	s	N=C-OEt
149.9	23	s	N-C=N
62.7	65	t	$O\text{-}CH_2$
53.5	61	t	$N\text{-}CH_2$
50.4	74	t	$N\text{-}CH_2$
46.0	84	t	$N\text{-}CH_2$
38.9	34	q	$N\text{-}CH_3$
14.2	40	q	$C\text{-}CH_3$

Acknowledgment.

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