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The Mass Spectra of 1,2,4-Triazine and some of its Derivatives

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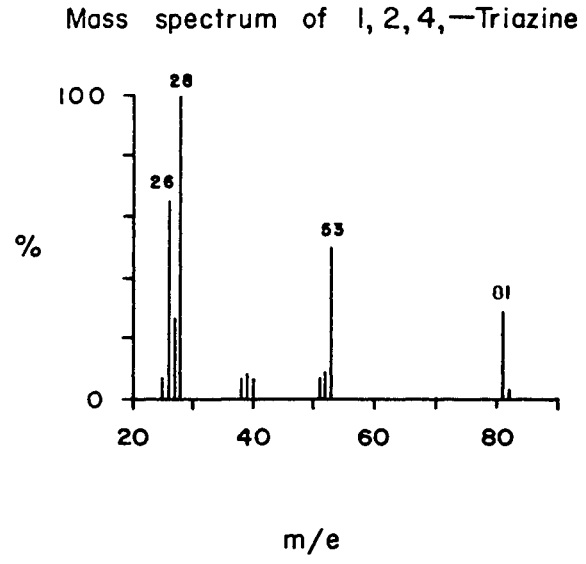
The mass spectra of some esters of 1,2,4-triazine-3-carboxylic acid and of 1,2,4-triazine itself are reported, and their fragmentation patterns are analyzed.

The syntheses of the methyl and of the *t*-butyl esters of 1,2,4-triazine-3-carboxylate are described.

In connection with studies of the mass spectra of heteroaromatic systems (1) and the recently accomplished synthesis of 1,2,4-triazine (2) it became of interest to study the behavior of this compound and some of its 3-carboxylic acid esters upon electron bombardment.

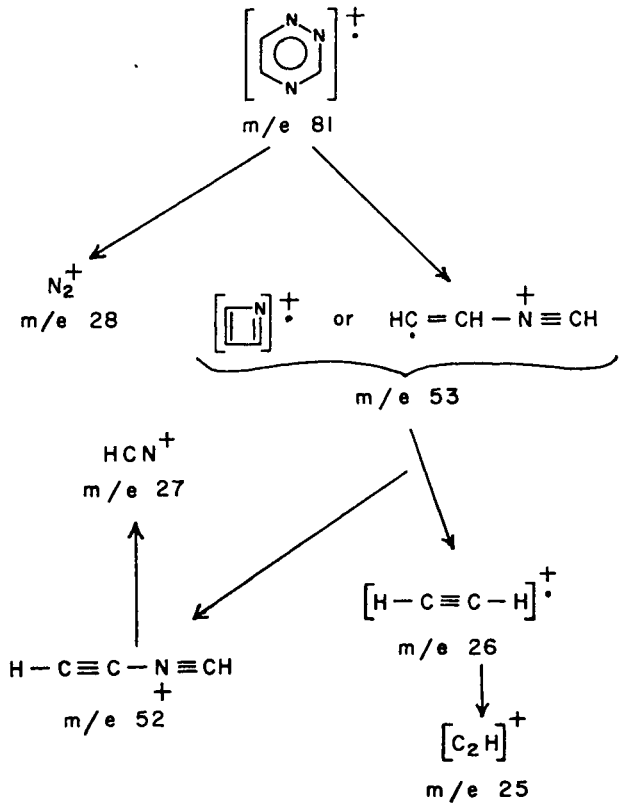
Electron impact on 1,2,4-triazine results in the formation of only eleven (5% of the base peak or larger) fragment ions (Figure 1), one of the most

FIGURE 1.



abundant of which is due to the loss of N_2. The resulting species, $[C_3H_3N]^+$ (m/e 53), decomposes further to species at m/e 52, 27, and 26. In the 3-deutero-1,2,4-triazine corresponding fragments appear at 54, 53, 28, and 26 m/e units. Thus, it is clear that the m/e 53, 52, and 27 fragments in the 3-protio-compound contain the proton at position 3 in the 1,2,4-triazine. The following scheme is consistent with these results:

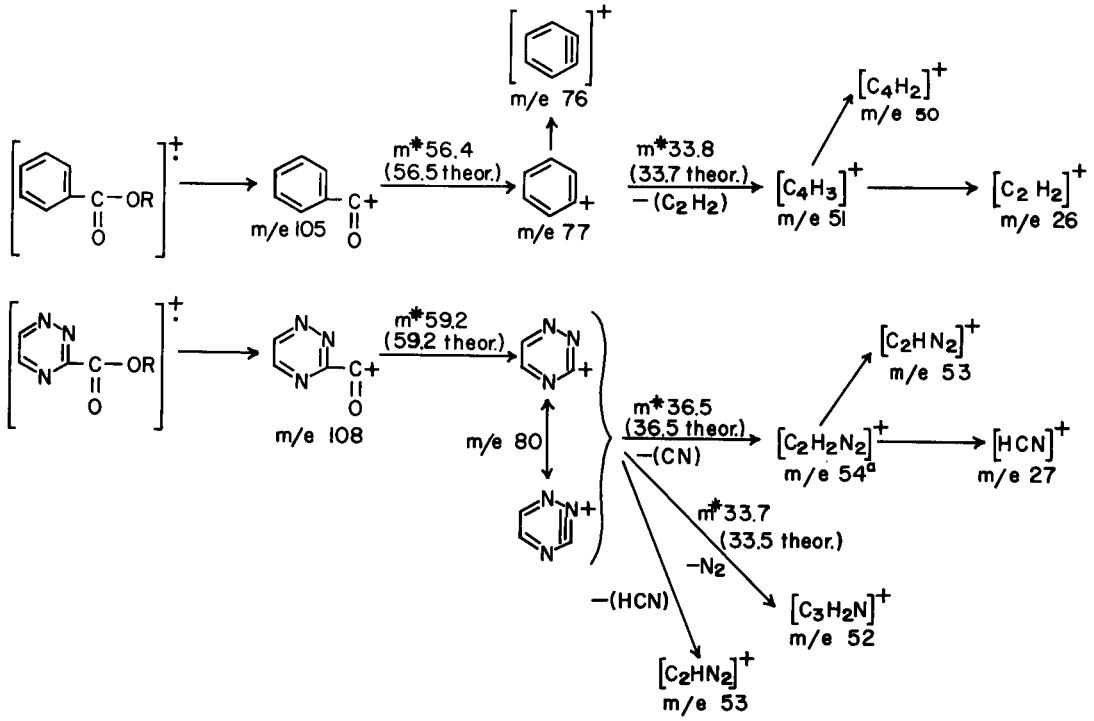
SCHEME I.



The mass spectra of aromatic and aliphatic esters have been studied in great detail (3,4,5,6,7,8), and certain patterns to be expected from electron impact reactions upon esters have now emerged. Benzoate esters ($Ar\text{-}CO_2\text{-}R$) afford major fragments due to R^+, $[Ar\text{-}CO]^+$, and Ar^+; and peaks due to the single and double McLafferty rearrangements ($[R\text{-}1H]^+$ and $[ArCO_2+2H]^+$). In those instances where R is C_3 and larger both of these rearrangements occur, while the double rearrangement does not take place to an appreciable extent in the cases where R is an ethyl group.

Fischer and Djerassi (7) have recently commented upon the formation of a tropylium ion in the mass spectrum of *t*-butyl benzoate. This had been ob-

SCHEME 2.



[a] an alternative, but unlikely, species is $[C_2NO]^+$

SCHEME 3.

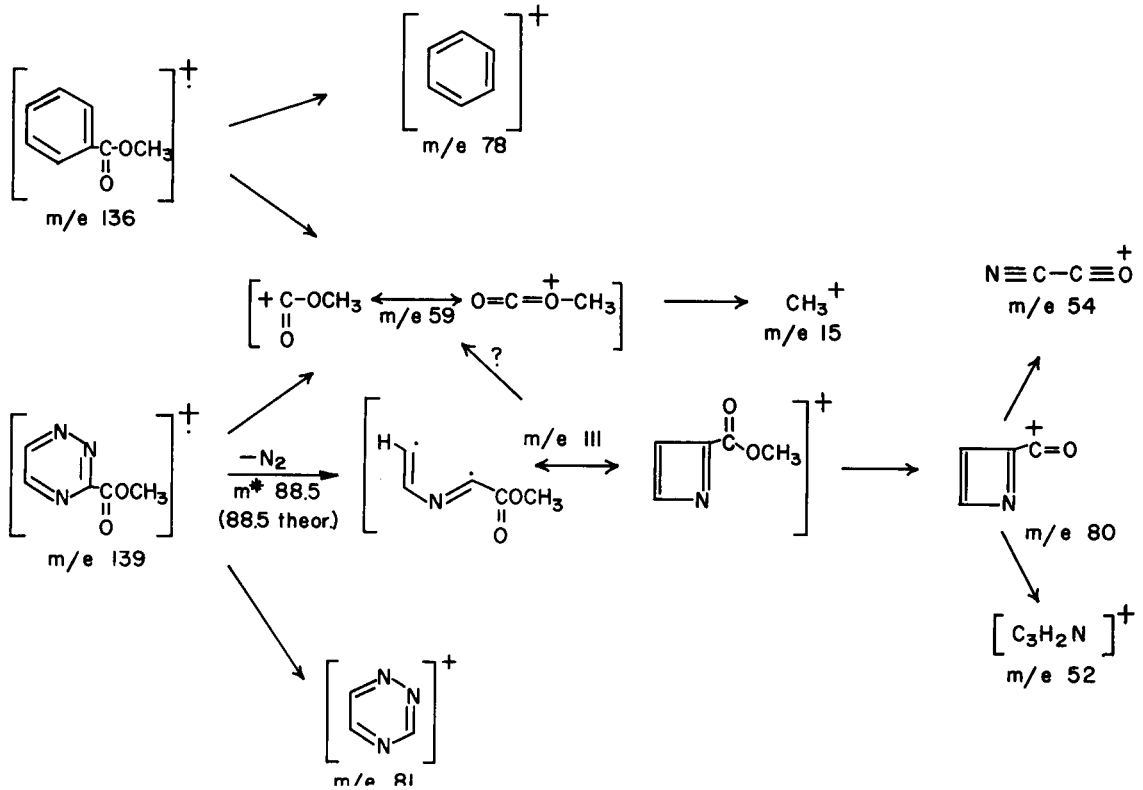
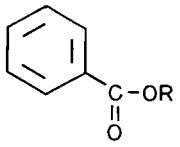
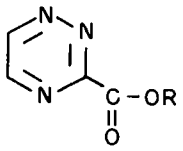


TABLE I

Mass Spectral Data (% Σ_{35})



($ArCO_2R$)



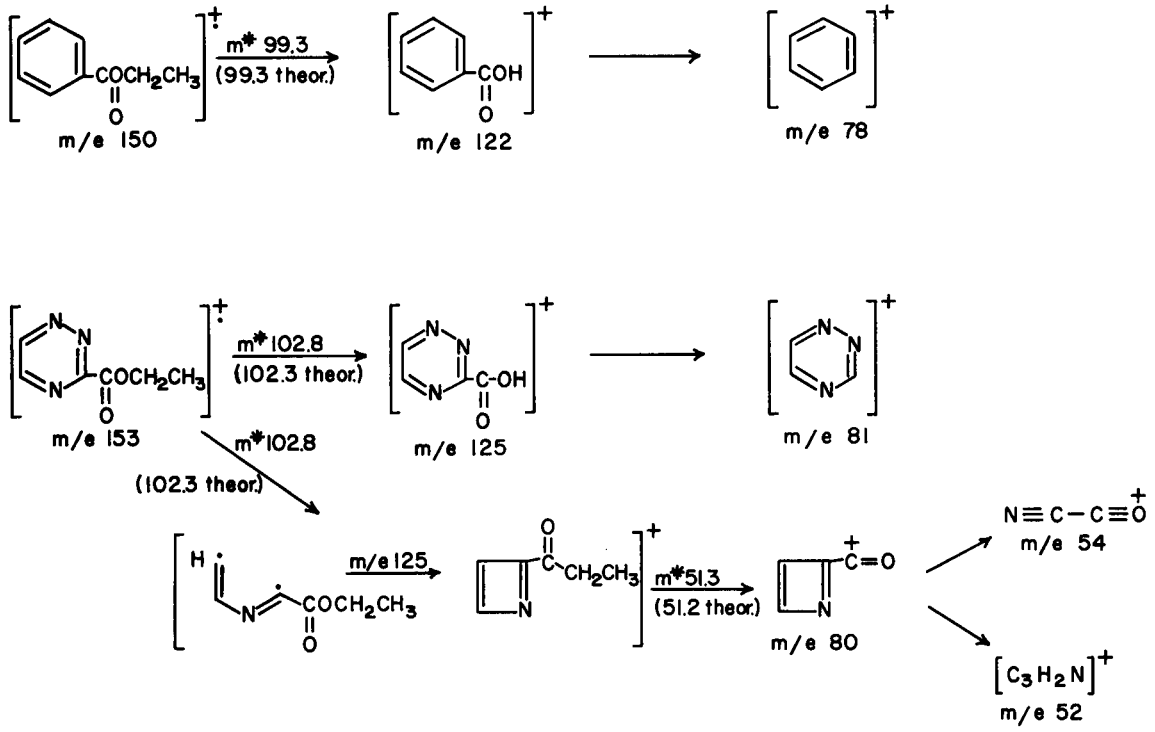
(1,2,4-$TrCO_2R$)

	Methyl		Ethyl		*t*-Butyl	
m/e	Ar	1,2,4-Tr	Ar	1,2,4-Tr	Ar	1,2,4-Tr
37	0.51	0.20	-----	-----	-----	-----
38	0.89	1.18	-----	0.60	0.38	0.88
39	1.20	2.55	0.93	2.04	3.28	5.53
40	0.38	7.86	-----	2.44	0.69	2.97
41	-----	7.66	-----	2.39	8.38	14.17
42	-----	14.54	-----	1.44	0.47	0.94
43	-----	0.69	-----	1.54	1.90	2.90
44	-----	1.18	-----	1.00	-----	0.74
45	-----	0.45	0.74	0.95	-----	-----
49	0.51	-----	-----	-----	-----	-----
50	5.64	0.51	3.71	-----	1.99	1.21
51	11.44	3.83	10.52	3.04	5.62	2.90
52	0.82	11.00	0.74	12.95	0.38	4.12
53	0.68	4.72	-----	32.87	0.31	1.89
54	-----	5.11	-----	7.72	-----	1.28
55	-----	0.45	-----	1.79	0.67	1.62
56	-----	-----	-----	5.73	9.25	6.07
57	-----	-----	-----	-----	18.32	26.32
58	-----	-----	-----	-----	0.85	1.35
59	0.44	12.38	-----	0.75	-----	-----
60	-----	0.43	-----	-----	-----	-----
66	-----	2.16	-----	0.55	-----	-----
67	-----	0.20	-----	-----	-----	-----
73	0.34	-----	-----	-----	-----	-----
74	1.54	-----	1.05	-----	0.36	-----
75	1.06	-----	0.80	-----	0.35	-----
76	1.30	-----	1.24	-----	0.66	-----
77	21.86	-----	19.18	-----	8.90	3.04
78	1.57	0.20	1.67	-----	1.19	0.67
79	-----	-----	-----	-----	0.90	-----
80	-----	1.08	-----	3.54	-----	1.08
81	-----	0.24	-----	0.80	-----	0.67
91	0.65	-----	-----	-----	-----	-----
92	0.68	-----	-----	-----	-----	-----
105	32.96	-----	37.13	-----	16.42	5.40
106	2.46	-----	3.28	-----	1.19	-----
108	-----	3.24	-----	6.23	-----	5.33
109	-----	0.26	-----	0.85	-----	-----
111	-----	10.61	-----	0.60	-----	-----
112	-----	0.71	-----	-----	-----	-----
122	-----	-----	0.99	-----	1.19	0.67

TABLE I (Continued)

m/e	Methyl Ar	Methyl 1,2,4-Tr	Ethyl Ar	Ethyl 1,2,4-Tr	*t*-Butyl Ar	*t*-Butyl 1,2,4-Tr
123	-----	-----	0.74	-----	15.21	4.79
124	-----	-----	-----	-----	1.12	-----
125	-----	-----	-----	5.23	-----	0.67
126	-----	-----	-----	-----	-----	1.48
135	0.51	-----	-----	-----	-----	-----
136	11.61(P)$^+$	-----	0.93	-----	-----	-----
137	0.96	-----	-----	-----	-----	-----
139		6.09(P)$^+$	-----	-----	-----	-----
140		0.49	-----	-----	-----	-----
150			6.81(P)$^+$	-----	-----	-----
151			0.62	-----	-----	-----
153				4.98(P)$^+$	-----	-----
163					0.17	-----
166					-----	1.55
178					0.20(P)$^+$	-----
181						1.08(P)$^+$

SCHEME 4.



served at an inlet system temperature of 200° and at an ionization voltage of 70 ev with an ionizing current of 50 μa. The mass spectrum of *t*-butyl benzoate obtained by us at 80°, 80 ev, and 70 μa no longer affords the m/e 91 (tropylium ion) fragment. At 200° we did observe this peak, but found that its presence is dependent upon the length of time that the *t*-butyl benzoate has been in the heated reservoir as well as upon the temperature of the inlet system. These observations prompted us to study the mass spectra of the 1,2,4-triazine-3-carboxylate esters at an inlet system temperature of 80°. This temperature is high enough to vaporize sufficient amounts of the esters, yet hopefully low enough to preclude excessive thermal decomposition prior to electron impact.

In order to permit a direct comparison of the mass spectra of the methyl, ethyl, and *t*-butyl 1,2,4-triazine-3-carboxylates and the analogous benzoates, the spectra of these six compounds were obtained (Table I) under identical conditions of temperature, ionization current, ionization voltage (*vide supra*), as well as at the same reservoir pressures.

The discussion of the results can be divided into two portions: (a) fragmentations involving the aroyl portions of the esters and (b) fragmentations involving the carboalkoxy portions of the esters.

Aroyl Portions Fragmentations.

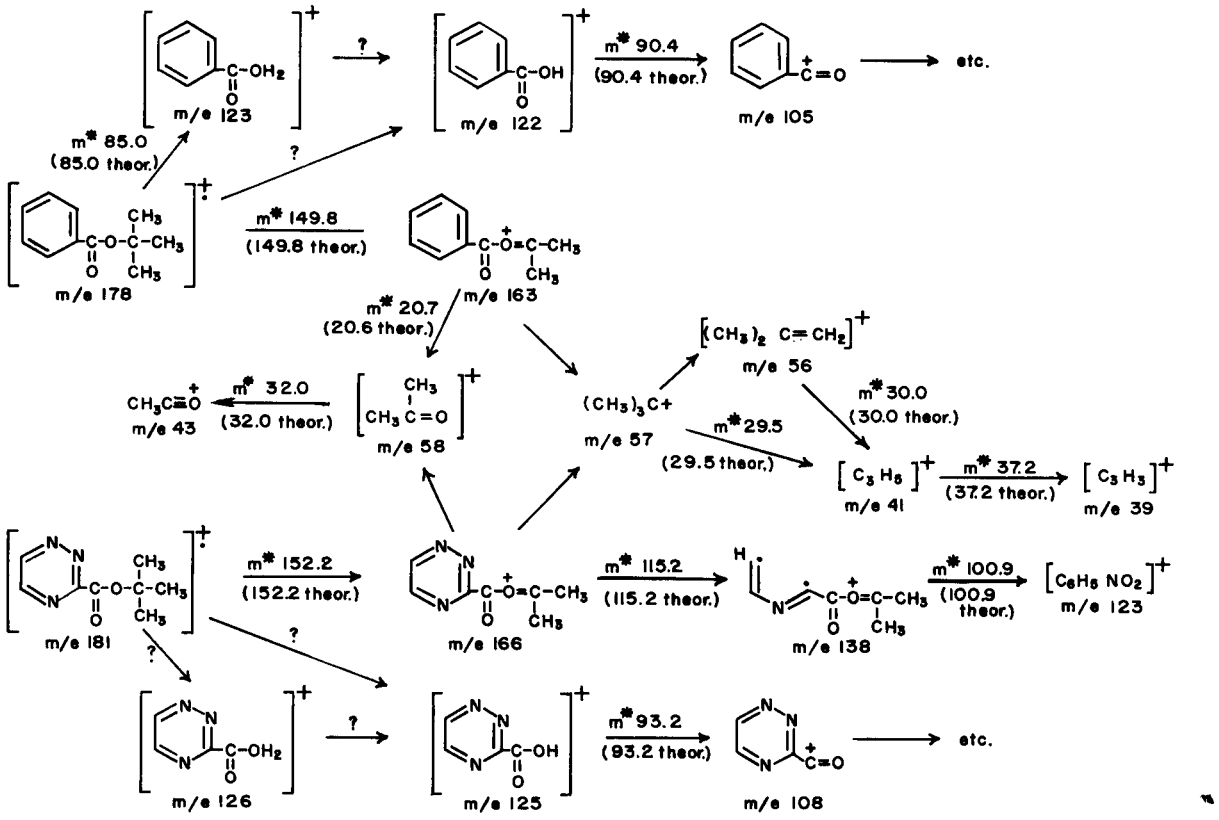
The following sequence (Scheme 2) clearly demonstrates and identifies the various fragment ions obtained from the six esters as far as they fit this category. Most of the transformations are substantiated by the metastable peaks indicated. The parallel nature of these fragmentations in the benzoates and in the 1,2,4-triazine-3-carboxylates is evident.

Carboalkoxy Portion Fragmentation.

The methyl esters of the two series (Scheme 3) behave similarly with the exception being the lower stability of the 1,2,4-triazine ion-radical itself. The loss of N_2 from the methyl ester (m/e 139) to afford a fragment at m/e 111 is a fairly predominant process which is substantiated by a metastable.

The ethyl esters of the two series again fragment in a similar fashion including the formation of the carboxylic acid via the rearrangement as described by McLafferty and Gohlke (5) (*cf* Scheme 4). The triazine ester differs again by the loss of N_2 to afford the fragment m/e 125. This peak appears as a doublet in the mass spectrum and thus is in agreement with the scheme drawn which involves two different m/e 125 fragments. The decay of the P-N_2 ion follows the same process as that observed in the methyl ester.

SCHEME 5.



The *t*-butyl esters (*cf* Scheme 5), as expected (3) afford the fragment due to a double McLafferty rearrangement corresponding to ions m/e 123 and m/e 126 of the benzoate and 1,2,4-triazine-3-carboxylate respectively. These ions fragment further as shown in the scheme. The loss of a methyl group from the parent ions is verified by the presence of a metastable in each of the series. The resulting fragment ions (m/e 163 and m/e 166 respectively) affords the acetone ion-radical which fragments further as expected. The *t*-butyl ion is also observed in both of the esters, and its further fragmentation is clearly shown.

As in the other esters, N_2 is also lost in *t*-butyl 1,2,4-triazine-3-carboxylate. However, it is not as abundant and only occurs after the loss of a methyl fragment from the *t*-butyl grouping. This fragmentation is substantiated by a metastable as is the loss of a methyl group from the resulting fragment (m/e 138 ⟶ m/e 123).

EXPERIMENTAL (9)

Benzoate Esters.

The methyl and ethyl benzoates used were commercially obtained and their purities checked by infrared spectroscopy and by vapor phase chromatography. *t*-Butyl benzoate was prepared by the reported (10) method.

1,2,4-Triazine-3-carboxylate Esters.

Ethyl 1,2,4-triazine-3-carboxylate was prepared as previously reported (2) except that the final purification was accomplished by sublimation at 70-85°/1 mm. instead of by recrystallization. The methyl ester was prepared similarly to the ether ester except that methanol and methyl acetate were substituted for ethanol and ethyl acetate in the appropriate steps. Methyl 1,2,4-triazine-3-carboxylate is a pale yellow crystalline material (m.p. 91.5-92.5°); yield: 0.282 g. (4.8%).

Anal. Calcd. for $C_5H_5N_3O_2$: C, 43.18; H, 3.62; N, 30.21; mol. wt., 139. Found: C, 43.34; H, 3.69; N, 29.96; mol. wt., 139 (mass spectrometric).

t-Butyl 1,2,4-Triazine-3-carboxylate.

(a) *t*-Butyl Monothioöxamate.

t-Butyl monothioöxamate was prepared by direct application of the method reported (11) for the preparation of the corresponding ethyl compound. From 12.7 g. (0.1 mole) of *t*-butyl cyanoformate (12) and excess hydrogen sulfide were obtained 10.0 g. (62.0%) of bright yellow crystals (m.p. 115-115.5°). The material was subjected to the following reaction without further purification.

(b) *t*-Butyl Oxalamidrazonate.

The preparation recorded by Schmidt and Druey (13) for the preparation of the analogous ethyl ester was adapted as follows: 3.22 g. (0.02 mole) of *t*-butyl monothioöxamate was dissolved in 60 ml. of absolute ethanol. A solution of 1.2 g. (0.02 mole) of 85% hydrazine hydrate in 20 ml. of absolute ethanol was then added at room temperature, under nitrogen, with magnetic stirring over a period of one hour. After an additional 19 hours stirring under the same conditions TLC (silica gel; 1:1 methanol:ethyl acetate) indicated total utilization of the thioöxamate. After evaporation to dryness, under vacuum and below 40°, the residue was dissolved in 50 ml. of a 1:1 mixture of chloroform-petroleum ether (20-40°) and the resulting dark orange solution was rapidly passed through 100 g. of neutral alumina (grade I, Brockman) followed by an additional 125 ml. of eluant. This light yellow solution is diluted with 600 ml. of low boiling petroleum ether, placed in an icebath and stirred vigorously. The product, which gradually separated, upon recrystallization gave 0.75 g. (23.6%) of pale yellow *t*-butyl oxalamidrazonate (m.p. 123-125°).

(c) *t*-Butyl 1,2,4-Triazine-3-carboxylate.

t-Butyl oxalamidrazonate (750 mg., 4.8 mmoles) dissolved in 25 ml. of *t*-butyl alcohol was added dropwise over a period of 12 hours to a stirred solution of 1.4 g. (10 mmoles) of 40% glyoxal in 120 ml. of *t*-butyl alcohol at room temperature. After 36 hours of additional stirring at room temperature, the bright yellow solution was filtered, evaporated to a sticky amber-colored oil. This oil was finally kept at a vacuum of 1 mm. for several hours. The oil was extracted with anhydrous ether and evaporated under vacuum to afford a yellow oily residue. This oil was "sublimed" directly from the flask to a cold finger (70-90°/1 mm.) to form 75 mg. (9.0%) of light yellow crystals (m.p. 52.5-53.5°).

Anal. Calcd. for $C_8H_{11}O_2N_3$: C, 53.13; H, 6.12; N, 23.19; mol. wt., 181. Found: C, 53.03; H, 5.98; N, 23.20; mol. wt., 181 (mass spectrometric).

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REFERENCES

(1) W. W. Paudler and T. J. Kress, *J. Org. Chem.*, 32, in press (1967).
(2) W. W. Paudler and J. M. Barton, *ibid.*, 31, 1720 (1966).
(3) F. W. McLafferty, *Anal. Chem.*, 31, 82 (1959).
(4) A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel, *ibid.*, 31, 87 (1959).
(5) F. W. McLafferty and R. S. Gohlke, *ibid.*, 31, 2076 (1959).
(6) E. M. Emery, *ibid.*, 32, 1495 (1960).
(7) M. Fischer and C. Djerassi, *Chem. Ber.*, 99, 750 (1966).
(8) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, 87, 5756 (1966).
(9) Melting points are uncorrected. Mass spectra were obtained with a Hitachi-Perkin Elmer RMU-6E Instrument. The microanalyses were performed by Mrs. S. DeBoer of this department.
(10) J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, 54, 2098 (1932).
(11) W. R. Boon, *J. Chem. Soc.*, 601 (1945).
(12) L. Carpino, *J. Am. Chem. Soc.*, 82, 2725 (1960).
(13) P. Schmidt and J. Druey, *Helv. Chim. Acta*, 38, 1560 (1955).

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