bustible gas formed (by increasing the proportion of charcoal formed); (*b*) formation of a fused inactive surface-protective layer upon the combustible surface. Cooling the seat of the fire, the smothering action of liberated, inert gas, and catalytic action may be contributing factors, but their importance seems very limited.

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Literature Cited

(1) Folke, F., Mygind, J., and Adeler, H., pub. in English by Danish Fire Protection Committee, Copenhagen, 1936.
(2) Gay-Lussac, *Ann. chim. phys.*, **18**, 211 (1821).
(3) Metz, L., *Gasschutz u. Luftschutz*, 6, 260 (1936), and other publications.
(4) Palmer, R. C., J. IND. ENG. CHEM., **10**, 264 (1918).
(5) Richardson, N. A., *J. Soc. Chem. Ind.*, **56** 202 (1937).
(6) Serebrennikov, P. P., U. S. Forest Service, Div. of Silvics, *Translation* **9** (151), 1934.
(7) Thomas, C. A., and Hochwalt, C. A., IND. ENG. CHEM., **20**, 575 (1928); *Oil Gas J.*, **27**, 142 (1928).
(8) Truax, T. R., *J. Forestry*, **37**, 674–7 (Sept., 1939); *Quart. Natl. Fire Protec. Assoc.*, **33**, 252–9 (Jan., 1940).

ESTERS OF NITROALCOHOLS

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The propionic, butyric, and isobutyric esters of all of the monohydroxy nitroalcohols which can be formed by the condensation of nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, and 2-nitrobutane with formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and isobutyraldehyde have been made, and certain of their properties determined.

The esters are all colorless mobile liquids boiling with slight decomposition between 210° and 275° C. at atmospheric pressure.

THE recent availability of nitroparaffins (*3*) has stimulated an interest in a large number of possible derivatives. Several esters of nitroalcohols have been described in the literature (*1*, *5*, *6*, *7*), and because of their potential importance in industry the study of these esters has been extended.

This paper describes the propionates, butyrates, and isobutyrates of all of the monohydroxy nitroalcohols which can be made by the condensation of nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, and 2-nitrobutane with formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and isobutyraldehyde, respectively.

All nitroalcohols used, with the exception of 4-nitro-2,4-dimethyl-3-hexanol and 2-nitro-1-ethanol, were prepared by the method described by Vanderbilt and Hass (*7*). 4-Nitro-2,4-dimethyl-3-hexanol was made by the reaction of sodium aci-2-nitrobutane with isobutyraldehyde sodium bisulfite according to the method developed by Kamlet (*4*). 2-Nitro-1-ethanol was prepared in admixture with 2-nitro-1,3-propanediol and tris(hydroxymethyl)nitromethane by the method of Gorski and Makarov (*2*). The mixture was esterified with the appropriate acid, and the ester of 2-nitro-1-ethanol isolated by fractionation.

Esters of primary nitroalcohols were all made by refluxing under a column a mixture of nitroalcohol (1 mole), organic acid (1.08 moles), sulfuric acid (0.01 mole), and benzene (200 cc.). Water of reaction was separated as the reaction proceeded, and approximately the theoretical quantity of water was formed in all cases. The reactions usually required from 6 to 8 hours.

The reaction mixtures were distilled, first at 100 mm. pressure to remove benzene, and then at 1–2 mm. to recover the product. Yields averaged about 90 per cent of the theoretical. The products were redistilled before being analyzed.

In the first few experiments excess organic acid and catalyst were neutralized with sodium hydroxide, sodium carbonate, or sodium bicarbonate solutions, and washed with water. During the distillation there was much decomposition to nitroolefin and organic acid in those esters not having the nitro group joined to a tertiary carbon atom. As a result of this experience, the esters were refined without neutralizing either the excess organic acid or the catalyst. This procedure was satisfactory and resulted in a water-white product without a trace of nitroolefin odor.

An attempt to prepare an ester of a secondary nitroalcohol by direct esterification was not successful. A mixture of 2-nitro-2-methyl-3-hexanol (1.0 mole), propionic acid (1.0 mole), sulfuric acid (0.015 mole), and benzene (300 cc.) was refluxed under a packed column, to the top of which was fitted a decanter arranged so that the lighter oil layer would be returned to the column while water would be trapped out. After 50 hours of refluxing, less than half of the calculated quantity of water had formed. The mixture had become black, and oxides of nitrogen were observed in the column, indicating decomposition.

As a result of this experiment, no further attempts were made to prepare esters of secondary nitroalcohols by direct esterification. They were all made by placing 1 mole of the nitroalcohol and 0.01 mole of concentrated sulfuric acid in a flask and slowly adding 1 mole of acid anhydride; the temperature was kept at about 60° C. The mixture was allowed to stand at least 30 minutes, after which it was distilled from a Claisen flask at 1–2 mm. pressure. The yields averaged 90 per cent. The product was redistilled from a Claisen flask, a fair portion being cut out at the beginning and end of the distillation. This procedure usually gave a fairly pure product as indicated by nitrogen content. In a few cases it was necessary to redistill an ester before its analysis was satisfactory.

TABLE I. PROPERTIES OF NITROESTERS

Ester	Nitrogen, % by Weight Found	Nitrogen, % by Weight Theoretical	Sp. Gr., 20°/20° C.	Refractive Index, n_D^{20}	Boiling Range at 10 Mm., ° C.	Approx. Boiling Range at 760 Mm., ° C.[a]
2-Nitroethyl propionate	9.12	9.54	1.1727	1.43357	106.0-108.2	213[b]
2-Nitroethyl butyrate	8.40	8.72	1.1272	1.43416	114.5-115.8	215[b]
2-Nitroethyl isobutyrate	8.47	8.72	1.1191	1.43117	103.0-107.5	208[b]
2-Nitropropyl propionate	8.88	8.72	1.1201	1.42815	106.8-107.0	225-227
2-Nitropropyl butyrate	7.86	8.02	1.0860	1.43207	115.0-116.0	226-228
2-Nitropropyl isobutyrate	7.67	8.02	1.0771	1.42730	105.0-106.0	229-232
2-Nitro-1-butyl propionate	7.89	8.02	1.0880	1.43117	111.0-112.0	233-235
2-Nitro-1-butyl butyrate	7.30	7.42	1.0611	1.43357	119.0-119.5	244-246
2-Nitro-1-butyl isobutyrate	7.19	7.42	1.0540	1.42941	113.0-114.0	238-240
2-Nitro-2-methylpropyl propionate	8.19	8.02	1.0889	1.43221	105.5-106.3	229-231
2-Nitro-2-methylpropyl butyrate	7.34	7.42	1.0623	1.43351	116.2-117.0	240-244
2-Nitro-2-methylpropyl isobutyrate	7.35	7.42	1.0561	1.43033	106.5-110.0	232-235
2-Nitro-1-pentyl propionate	7.42	7.42	1.0615	1.43386	114.5-115.5	245-246
2-Nitro-1-pentyl butyrate	6.92	6.90	1.0401	1.43583	130.0-133.5	253-257
2-Nitro-1-pentyl isobutyrate	7.00	6.90	1.0329	1.43152	121.0-122.5	248-251
2-Nitro-2-methyl-1-butyl propionate	7.52	7.42	1.0761	1.43768	116.7-118.0	238-243
2-Nitro-2-methyl-1-butyl butyrate	7.09	6.90	1.0531	1.43914	125.2-127.5	247-255
2-Nitro-2-methyl-1-butyl isobutyrate	7.13	6.90	1.0477	1.43582	117.0-121.0	239-248
1-Nitro-2-propyl propionate	8.69	8.72	1.1165	1.42845	104.0-105.0	222-225
1-Nitro-2-propyl butyrate	8.11	8.02	1.0829	1.43087	107.2-107.2	231-237
1-Nitro-2-propyl isobutyrate	8.27	8.02	1.0759	1.42662	104.3-104.8	225-229
3-Nitro-2-butyl propionate	7.92	8.02	1.0879	1.42966	104.0-106.0	227-229
3-Nitro-2-butyl butyrate	7.72	7.42	1.0608	1.43237	116.0-117.3	239-242
3-Nitro-2-butyl isobutyrate	7.34	7.42	1.0537	1.42845	109.4-110.0	232-234
3-Nitro-2-pentyl propionate	7.60	7.42	1.0611	1.43117	109.5-111.8	234-237
3-Nitro-2-pentyl butyrate	7.20	6.90	1.0390	1.43327	119.5-123.0	245-250
3-Nitro-2-pentyl isobutyrate	6.76	6.90	1.0330	1.42996	113.9-116.8	240-244
3-Nitro-3-methyl-2-butyl propionate	7.76	7.42	1.0696	1.43357	109.8-110.5	231-234
3-Nitro-3-methyl-2-butyl butyrate	7.01	6.90	1.0480	1.43563	117.0-118.5	241-247
3-Nitro-3-methyl-2-butyl isobutyrate	7.10	6.90	1.0431	1.43291	106.0-109.0	232-240
3-Nitro-2-hexyl propionate	6.90	6.90	1.0393	1.43457	116.7-119.2	243-247
3-Nitro-2-hexyl butyrate	6.38	6.45	1.0213	1.43315	128.2-129.0	255-260
3-Nitro-2-hexyl isobutyrate	6.36	6.45	1.0158	1.43303	117.5-119.0	249-253
3-Nitro-3-methyl-2-pentyl propionate	6.87	6.90	1.0581	1.43856	117.2-119.0	239-247
3-Nitro-3-methyl-2-pentyl butyrate	6.60	6.45	1.0382	1.44029	125.8-127.5	248-259
3-Nitro-3-methyl-2-pentyl isobutyrate	6.75	6.45	1.0338	1.43710	121.4-123.5	242-252
1-Nitro-2-butyl propionate	8.10	8.02	1.0901	1.43297	111.5-113.0	232-237
1-Nitro-2-butyl butyrate	7.30	7.42	1.0619	1.43475	122.0-122.5	234-245
1-Nitro-2-butyl isobutyrate	7.55	7.42	1.0587	1.43147	109.1-111.2	231-240
2-Nitro-3-pentyl propionate	7.41	7.42	1.0668	1.43386	115.2-115.5	238-240
2-Nitro-3-pentyl butyrate	6.80	6.90	1.0442	1.43615	121.8-123.0	249-253
2-Nitro-3-pentyl isobutyrate	6.77	6.90	1.0407	1.43282	117.0-118.0	242-245
4-Nitro-3-hexyl propionate	7.22	6.90	1.0447	1.43505	116.5-118.2	243-244
4-Nitro-3-hexyl butyrate	6.68	6.45	1.0267	1.43725	124.0-124.6	256-260
4-Nitro-3-hexyl isobutyrate	6.60	6.45	1.0230	1.43460	120.0-122.5	247-252
2-Nitro-2-methyl-3-pentyl propionate	7.15	6.90	1.0552	1.43739	112.0-113.4	237-244
2-Nitro-2-methyl-3-pentyl butyrate	6.57	6.45	1.0364	1.43943	122.0-123.5	246-257
2-Nitro-2-methyl-3-pentyl isobutyrate	6.74	6.45	1.0321	1.43611	120.0-121.8	243-251
4-Nitro-3-heptyl propionate	6.56	6.45	1.0265	1.43681	125.0-127.6	253-257
4-Nitro-3-heptyl butyrate	5.92	6.06	1.0115	1.43856	133.8-136.5	260-268
4-Nitro-3-heptyl isobutyrate	6.07	6.06	1.0071	1.43563	125.2-125.6	258-262
3-Nitro-3-methyl-4-hexyl propionate	6.57	6.45	1.0435	1.44000	122.8-127.5	238-252
3-Nitro-3-methyl-4-hexyl butyrate	6.31	6.06	1.0272	1.44173	132.0-133.0	242-262
3-Nitro-3-methyl-4-hexyl isobutyrate	6.03	6.06	1.0241	1.44173	131.0-132.2	244-261
1-Nitro-2-pentyl propionate	7.31	7.42	1.0638	1.43504	118.3-119.0	237-244
1-Nitro-2-pentyl butyrate	6.88	6.90	1.0425	1.43710	128.0-130.8	250[b]
1-Nitro-2-pentyl isobutyrate	6.92	6.90	1.0367	1.43395	126.0-128.0	235-243
2-Nitro-3-hexyl propionate	7.15	6.90	1.0446	1.43622	119.8-121.1	245-249
2-Nitro-3-hexyl butyrate	6.66	6.45	1.0281	1.43856	133.2-135.0	254-259
2-Nitro-3-hexyl isobutyrate	6.66	6.45	1.0237	1.43534	127.8-129.2	249-254
3-Nitro-4-heptyl propionate	6.58	6.45	1.0253	1.43710	128.5-129.0	252-256
3-Nitro-4-heptyl butyrate	6.19	6.06	1.0127	1.43943	136.0-137.5	259-268
3-Nitro-4-heptyl isobutyrate	6.25	6.06	1.0067	1.43593	131.6-133.5	257-261
2-Nitro-2-methyl-3-hexyl propionate	6.59	6.45	1.0374	1.43929	124.6-125.8	239-252
2-Nitro-2-methyl-3-hexyl butyrate	6.28	6.06	1.0230	1.44158	130.0-132.0	240-264
2-Nitro-2-methyl-3-hexyl isobutyrate	6.14	6.06	1.0179	1.43885	127.7-129.5	246-259
5-Nitro-4-octyl propionate	6.25	6.06	1.0107	1.43797	136.0-138.0	260-265
5-Nitro-4-octyl butyrate	5.80	5.72	0.9978	1.44000	145.0-146.2	266-275
5-Nitro-4-octyl isobutyrate	5.76	5.72	0.9938	1.43815	141.2-143.0	264-271
3-Nitro-3-methyl-4-heptyl propionate	6.00	6.06	1.0266	1.44236	130.8-133.1	242-263
3-Nitro-3-methyl-4-heptyl butyrate	5.96	5.72	1.0134	1.44456	142.0-145.6	236-269
3-Nitro-3-methyl-4-heptyl isobutyrate	5.89	5.72	1.0107	1.44258	135.0-139.8	232-266
1-Nitro-3-methyl-2-butyl propionate	7.72	7.42	1.0655	1.43563	121.0-121.5	238-245
1-Nitro-3-methyl-2-butyl butyrate	6.94	6.90	1.0441	1.43768	131.0-131.7	240-255
1-Nitro-3-methyl-2-butyl isobutyrate	7.11	6.90	1.0387	1.43475	123.0-124.0	235-249
2-Nitro-4-methyl-3-pentyl propionate	6.96	6.90	1.0440	1.43622	116.0-120.2	241-248
2-Nitro-4-methyl-3-pentyl butyrate	6.18	6.45	1.0235	1.43768	128.0-133.0	243-258
2-Nitro-4-methyl-3-pentyl isobutyrate	6.41	6.45	1.0212	1.43510	121.0-126.4	242-253
4-Nitro-2-methyl-3-hexyl propionate	6.45	6.45	1.0305	1.43797	120.5-121.0	252-255
4-Nitro-2-methyl-3-hexyl butyrate	6.39	6.06	1.0159	1.43972	136.8-138.0	261-266
4-Nitro-2-methyl-3-hexyl isobutyrate	6.17	6.06	1.0121	1.43739	130.0-134.0	256-261
2-Nitro-2,4-dimethyl-3-pentyl propionate	6.33	6.45	1.0393	1.44000	121.1-125.1	233[b]
2-Nitro-2,4-dimethyl-3-pentyl butyrate	5.94	6.06	1.0261	1.44109	133.0-134.6	252[b]
2-Nitro-2,4-dimethyl-3-pentyl isobutyrate	6.24	6.06	1.0216	1.43885	124.5-127.8	243[b]
4-Nitro-2-methyl-3-heptyl propionate	6.15	6.06	1.0137	1.43873	133.0-134.5	258-263
4-Nitro-2-methyl-3-heptyl butyrate	5.78	5.72	1.0019	1.44086	143.8-146.4	265-274
4-Nitro-2-methyl-3-heptyl isobutyrate	6.12	5.72	0.9998	1.43885	137.1-138.5	255-269
4-Nitro-2,4-dimethyl-3-hexyl propionate	6.10	6.06	1.0136	1.43885	131.0-132.0	259[b]
4-Nitro-2,4-dimethyl-3-hexyl butyrate	5.72	5.72	1.0008	1.44086	141.5-142.0	270[b]
4-Nitro-2,4-dimethyl-3-hexyl isobutyrate	5.86	5.72	0.9979	1.43914	134.6-137.8	261[b]

[a] Slight decomposition. [b] These boiling points were determined by heating the esters in a test tube and noting the maximum temperature reached by the liquid.

Nitrogen was determined by the method of Dumas. The specific gravity, refractive index, and boiling points at 10 and 760 mm. were determined, and are listed in Table I.

The esters were generally found to be unstable at their boiling points at atmospheric pressure. In order to get an appropriate boiling range, it was necessary to distill a small (10-cc.) sample of the ester quite rapidly. Slow distillation resulted in so much decomposition that it was impossible to determine the true boiling point.

The esters appeared to be fairly stable at temperatures below 150° C. for a reasonable time.

The esters are all colorless, mobile liquids boiling with some decomposition between 210° and 275° C. at atmospheric pressure. They possess pleasant odors, most of them smelling distinctly mustardlike.

Acknowledgment

The author is indebted to C. E. Watts for the determinations of nitrogen, specific gravity, and refractive index.

Literature Cited

(1) Gloor, U. S. Patent 2,128,136 (Aug. 23, 1938).
(2) Gorski and Makarov, *Ber.*, **67B**, 996-1000 (1934).
(3) Hass, Hodge, and Vanderbilt, IND. ENG. CHEM., **28**, 339 (1936).
(4) Kamlet, U. S. Patent 2,151,517 (March 21, 1939).
(5) Pauwels, *Rec. trav. chim.*, **17**, 27 (1898).
(6) Shaw, *Ibid.*, **17**, 50 (1898).
(7) Vanderbilt and Hass, IND. ENG. CHEM., **32**, 34 (1940).

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