Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.28; H, 5.98; N, 19.17. Found: C, 59.64; H, 5.99; N, 19.19.

B. Decarboxylation of XIII in Acid Solution.—A mixture of 90 g. of crude ester XII and 500 ml. of 2.5 *N* sodium hydroxide was boiled under reflux for 24 hours. The hot solution was treated with Darco and filtered. The clear orange filtrate was adjusted to *p*H 1 by the addition of 90 ml. of concentrated hydrochloric acid and then boiled under reflux for 24 hours. The solid which separated from this reaction mixture on cooling was collected and recrystallized from an ethanol-water mixture giving 13.0 g. of amino acid XV, m.p. 264–268°. Concentration of the liquors from this recrystallization to 200 ml. gave 5.3 g. (9%) of acetylamino acid XIV, m.p. 188–190°. A sample of the acetylated compound recrystallized from an ethanol-water mixture, m.p. 190–191°, was submitted for analysis.

Anal. Calcd. for $C_{13}H_{15}N_3O_3$: C, 59.75; H, 5.79; N, 16.08. Found: C, 59.60; H, 5.53; N, 16.19.

When the filtrate from the reaction mixture was adjusted to *p*H 4 by the addition of ammonium hydroxide and concentrated to 300 ml., an additional 8.3 g. of amino acid XV was obtained, m.p. 265–271°. Also, by evaporating all mother liquors to dryness and hydrolyzing the residue again with barium hydroxide, as described above, another 6.3 g. of amino acid was obtained giving a total yield of 27.7 g. (55.5%).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Disproportionation of Tertiary Amines

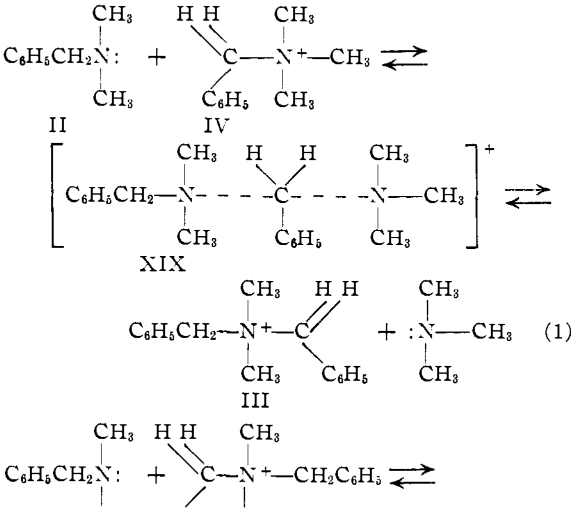
BY H. R. SNYDER, ROBERT E. CARNAHAN[1] AND ELWYN R. LOVEJOY[2]

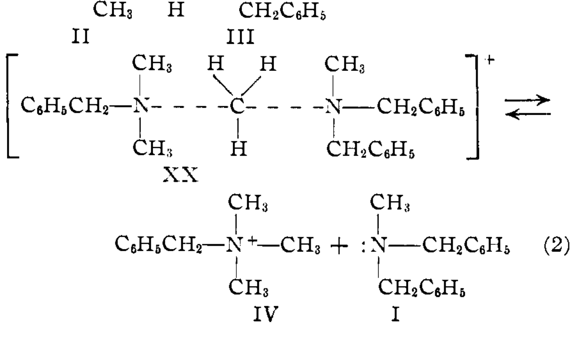
RECEIVED SEPTEMBER 28, 1953

When N,N-dimethylbenzylamine is heated for 17 hours at 200° in the presence of catalytic amounts of its quaternary ammonium salt, it disproportionates to form N-methyldibenzylamine and trimethylamine. An examination of the results of subjecting various tertiary amines to the disproportionation conditions shows that an amine of the benzyl type undergoes the reaction while others do not. This observation agrees with that predicted from the proposed S_N2 displacement reaction sequence.

The formation of N-methyldibenzylamine (I) was observed as a side reaction during the alkylation of methyl cyanoacetate with N,N-dimethylbenzylamine (II).[3] Its formation was explained by the initial quaternization of the amine by the methyl cyanoacetate followed by the reaction of the amine and the salt in a cyclic process in which the dibenzyldimethylammonium cation (III) is an intermediate. When the methyl cyanoacetate was replaced by the salt itself (IV as the chloride) in a 1:1 ratio, a 78% conversion resulted; when the ratio of amine to salt was increased to 10:1, the conversion was 73%. The quaternary ammonium salt thus functioned as the catalyst. Hydrochloric acid and boron trifluoride were also found to catalyze the reaction although not so effectively, the conversions being 8.1 and 15.0%, respectively.[3] Several other tertiary amines have been subjected to the conditions for the disproportionation in an attempt to determine the generality and synthetic value of the reaction.

Those amines containing a benzyl residue were found to undergo the disproportionation to form trimethylamine and a new tertiary amine. The refluxing of N,N-dimethylfurfurylamine (V) in the presence of 0.1 mole of its methiodide for 17 hours produced N-methyldifurfurylamine (VI) in a yield of 50.0%. Similarly, N,N-dimethyl-2-thenylamine (VII) was converted to the previously unknown N-methyl-di-2-thenylamine (VIII) in 56.5% yield. Only a 30.0% conversion was achieved when N,N-dimethyl-α-naphthylmethylamine (IX) was allowed to react. N,N-Dimethyl-*p*-nitrobenzylamine (X) and gramine (XI) appeared to react but no product other than trimethylamine could be isolated although some dimethylamine was evolved by the decomposition of gramine. Tertiary amines containing no group of the benzyl type failed to react. No trimethylamine or disproportionation product was isolated from attempted reactions of N,N-dimethylaniline (XII), N,N-dimethyl-β-naphthylamine (XIII), N,N-dimethylcyclohexylamine (XIV) or N,N-dimethylallylamine (XV). An exception was noted when N-methyl-bis-β-phenethylamine (XVI) was formed to an extent of 2% from N,N-dimethyl-β-phenethylamine (XVII). Styrene





---

[1] Minnesota Mining and Manufacturing Co. Fellow, 1949–1950.

[2] National Science Foundation Fellow, 1952–1953.

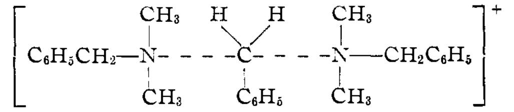
[3] H. R. Snyder, E. L. Eliel and R. E. Carnahan, THIS JOURNAL, **72**, 2958 (1950).

(58%) and XVII (39%) were also recovered from this reaction. Since temperatures considerably higher than that possible with refluxing XV were used in the successful disproportionations, an attempt to disproportionate this amine at elevated temperatures was made in a hydrogenation bomb. Only the original amine was isolated.

The mechanism for the disproportionation would require either the amine or the salt to act as an alkylating agent. Recently, the use of tertiary amines and quaternary ammonium salts as alkylating agents has been summarized.[4] Of the mechanisms so far proposed[4] for such alkylations the S_N2 displacement mechanism will account for the observed results in the disproportionation reaction. The amine acts as the displacing agent in two successive operations on quaternary ions. The transitions states XIX and XX are similar to those proposed in other S_N2 reactions. Only attack by the electron pair of the amine as shown in equations 1 and 2 leads to the products, since attack at a methyl group in step one or at a benzyl group in step two would regenerate the original amine and ion.

It is of interest to examine the factors contributing to the driving force for the disproportionation. For step one, the removal of the volatile product, trimethylamine, undoubtedly is of the greatest importance. It can be seen from a Fisher–Taylor–Hirschfelder model of the ion that there is no obvious steric hindrance to a rearward attack in an S_N2 displacement. The relative basicities of the amines in step one probably tend to inhibit the reaction. The pK_b values for II and trimethylamine in aqueous solution at 25° are 4.98[5] and 4.20,[6] respectively, showing trimethylamine to be the stronger base. However, the difference in basicities is not great, and this factor is insignificant in comparison to the driving force provided by the removal of trimethylamine.

Direct comparison of the relative rates of reactions involving an S_N2 displacement at a methyl carbon attached to nitrogen and a benzyl carbon similarly attached seems not to have been made. An examination of the effect of the structure of the alkyl group on reactivity in other S_N2 reactions[7] indicates that a benzyl carbon would be attacked from 10–20 times more readily than a methyl carbon. Thus, it would be expected that the transition state XXI which does not lead to the products in step two would form more easily than the one XX which does.



XXI

Step two, which occurs *via* a displacement at a methyl carbon, would therefore be expected to be slower than step one.

The forward reaction in step two is not favored by the direct removal of a product as is step one. On the basis of a comparison of the basicities of II and trimethylamine, which indicates a slight decrease in basicity when a methyl group is replaced by a benzyl group, it is predicted that I is a weaker base than II. Although this difference may be a small one, the forward reaction from transition state XX should be slightly more favored than the reverse one. This displacement of a weak base I by a stronger one II may be an important driving force in this step. Again, there is no obvious steric hindrance to the displacement.

The far lower yields in the hydrochloric acid and boron trifluoride catalyzed reactions can be explained on the basis of this proposed displacement mechanism. The initial step in these reactions would be the formation of a substituted ammonium ion and a boron trifluoride–amine complex, respectively. Displacements upon the ion and complex would most likely be at the hydrogen atom or the boron trifluoride group, both of which would reform the same amine and ion or complex. Only the less likely attack at the methyl or benzyl groups would generate an ion capable of catalyzing further reaction. Thus, the catalyst for the actual disproportionation is produced catalytically during the reaction. The better yield of I obtained from the boron trifluoride-catalyzed reaction, in comparison to that of the hydrochloric acid-catalyzed reaction, can be explained by the greater possibility of the attack by the amine upon the methyl or benzyl group of the complex than upon either of these groups in the substituted ammonium ion.

If the proposed reaction mechanism is correct, then it should be possible to synthesize amines containing three different radicals by employing two amines in the same reaction. Both N-methyl-N-benzyl-α-furfurylamine (XXII) and N-methyl-N-benzyl-2-thenylamine (XXIII) were formed in addition to the normal disproportionation products when II was allowed to react in the presence of V and VII, respectively.

Experimental[8]

Disproportionation of N,N-Dimethylfurfurylamine (V).—In a test-tube connected to a solid carbon dioxide–acetone trap by a reflux condenser were mixed V[9] (4.75 g., 0.038 mole) and methyl iodide (0.49 g., 0.0035 mole). The quaternary salt formed immediately with the evolution of heat. The mixture was then refluxed for 17 hours at an oil-bath temperature of 170–180°. The liquid which collected in the trap was proved to be trimethylamine by converting it to a picrate of melting point 221.5–224° (lit.[10] m.p. 220–223°). The mixed melting point with an authentic sample of trimethylamine picrate showed no depression, and the infrared absorption curves were identical.

The reaction mixture was distilled into three fractions.

Fraction	B.p. °C.	Mm.	$n^{20}D$	Wt., g.
1	42–43	12	1.4630	0.28
2	44–100	11	1.4852	0.04
3	119.5–120	11	1.5090	1.63

---

[4] J. H. Brewster and E. L. Eliel in R. Adams, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 99.

[5] M. Bourgeaud and A. Dondelinger, *Compt. rend.*, **179**, 1159 (1924).

[6] L. F. Fieser and M. Fieser, "Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1950, p. 222.

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 154.

[8] Microanalyses by Miss Rachel Kopel, Mrs. Esther Fett, Mrs. Katherine Pih, Mr. M. Dare and Mr. Joseph Nemeth.

[9] M. L. Moore in R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 319.

[10] G. Wittig and M. Wetterling, *Ann.*, **557**, 193 (1947).

Fraction 1 was unreacted V, b.p. 47–47.5° (17 mm.); n^{20}_{D} 1.4620. Fraction 3 corresponded to N-methyldifurfurylamine (50%) (lit.[11] b.p. 100–101° (5 mm.); n^{20}_{D} 1.5086).

N,N-Dimethyl-2-thenylamine (VII).—A three-necked 500-ml. round-bottomed flask was fitted with a mechanical stirrer, gas inlet tube and dropping funnel. The flask was cooled in a solid carbon dioxide–chloroform bath and gaseous dimethylamine was allowed to collect. After a small pool of the amine had formed, 2-chloromethylthiophene (52 g., 0.392 mole) was added dropwise. Stirring was commenced when the mixture became a slush. Absolute ether (100 ml.) was added and the flow of amine stopped. The reaction mixture was stirred five hours at room temperature and an additional 100-ml. portion of absolute ether was added. The flask was allowed to stand seven weeks with the excess dimethylamine escaping through a calcium chloride tube. The white crystalline dimethylamine hydrochloride was filtered off and the ether removed. Distillation gave 42.8 g. (77.4%) of VII which boiled at 77–78° (22 mm.); $n^{17.8}_{D}$ 1.5196 (lit.[12] b.p. 60–61° (10 mm.), n^{20}_{D} 1.5188).

Disproportionation of N,N-Dimethyl-2-thenylamine (VII).—A 50-ml. round-bottomed flask was fitted with a reflux condenser and an exit tube leading to a solid carbon dioxide–acetone trap. N,N-Dimethyl-2-thenylamine (14.1 g., 0.1 mole) and its methiodide (2.8 g., 0.01 mole) were mixed and heated 18 hours at an oil-bath temperature of 190°. The liquid which collected in the trap was proved to be trimethylamine by the formation of a picrate. The reaction mixture was an orange liquid with a little solid present. Anhydrous ether was added and the solid was filtered off leaving 2.2 g. of solid which failed to melt below 355°. It was probably tetramethylammonium iodide. Distillation of the liquid after removal of the ether gave two main fractions, the first corresponding to unchanged VII and the second to the previously unknown N-methyl-di-2-thenylamine (VIII). The latter was redistilled.

Fraction	B.p. °C.	B.p. Mm.	$n^{18.5}_{D}$	Wt., g.
1	82–166	16	1.5277	0.4
2	166–173	16	1.5869	0.8
3	173–176	16	1.5871	5.5

A sample prepared for analysis had a refractive index of n^{21}_{D} 1.5856 and density d^{27}_{4} 1.1542 g./ml. It was a colorless liquid but turned pale yellow on standing a short time. Its picrate, recrystallized from 95% ethanol, melted at 106.5–108.5°.

Anal. Calcd. for $C_{11}H_{13}NS_2$: C, 59.15; H, 5.87; N, 6.27. Found: C, 59.36; H, 5.86; N, 6.13.

The yield of VIII was 56.5%.

N,N-Dimethyl-α-naphthylmethylamine (IX).—To 200 ml. of dry thiophene-free benzene in a three-necked 1-l. round-bottomed flask fitted with stopper, reflux condenser and gas inlet tube, was added α-chloromethylnaphthalene (44 g., 0.25 mole). Dry, gaseous dimethylamine was bubbled into the solution, vigorously at first until the air had been swept out and then slowly. After 15 minutes the solution turned cloudy and the mixture became quite hot. When the mixture cooled to room temperature (about 2.5 hours), the reaction was apparently over. The flow of dimethylamine was stopped after further saturating the reaction mixture at ice-bath temperature. After 45 hours the dimethylamine hydrochloride was filtered off, the solvent removed, and the product distilled. The 36.3 g. of IX was 78.4%. In another run using 112 g. of α-chloromethylnaphthalene and 500 ml. of benzene, the yield was raised to 86.6%.

Disproportionation of N,N-Dimethyl-α-naphthylmethylamine (IX).—A side-arm 100-ml. round-bottomed flask was fitted with a reflux condenser and gas outlet leading to a solid carbon dioxide–acetone trap. An inlet tube for dry, oxygen-free nitrogen was connected to the side arm and a slight pressure differential was maintained by a mercury reservoir on each side of the system. N,N-Dimethyl-α-naphthylmethylamine (27.8 g., 0.15 mole) and its methiodide (4.9 g., 0.015 mole) were mixed and the stream of nitrogen was started to remove the oxygen from the system. Considerable charring occurred unless the oxygen was removed. During the reaction a nitrogen atmosphere was maintained by means of the two mercury reservoirs, but the larger portion of the nitrogen was not allowed to sweep through the system. The reaction mixture was heated 16 hours at an oil-bath temperature of 208°. The liquid which collected in the trap was shown to be trimethylamine by conversion to its picrate. The viscous, brown reaction mixture was dissolved in benzene leaving a white residue which was mostly tetramethylammonium iodide. A stream of gaseous hydrogen chloride was bubbled through the benzene solution, and the hydrochlorides thus precipitated were dissolved in 10% potassium hydroxide solution, and the free amine, taken up with ether, was dried over solid potassium hydroxide. After removal of the solvent, the amines were distilled into four fractions.

Fraction	B.p. °C.	B.p. Mm.	n^{20}_{D}	Wt., g.
1	109–116	1.5–2.0	1.5950	2.4
2	117–125	1.5–2.0	1.5963	2.2
3	125–228	1.5–2.0	1.5926	1.2
4	228–247	1.5–2.0	Solidified	

Fractions 1, 2 and 3 were largely unchanged IX. Fraction 4 was recrystallized from 95% ethanol with difficulty. The 7.0 g. (30.0%) of N-methyl-di-α-naphthylmethylamine had a melting point of 78–80°, while the analytical sample prepared from it melted at 84–85° (lit.[13] m.p. 87–88°). A picrate of melting point 162° (lit.[13] m.p. 166°) and a hydrochloride of melting point 215–216° (lit.[13] m.p. 220°) were formed.

Anal. Calcd. for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50. Found: C, 88.17; H, 6.84; N, 4.59.

Attempted Disproportionation of N,N-Dimethyl-*p*-nitrobenzylamine (X).—In an attempt to disproportionate X in apparatus similar to that used for VII, only trimethylamine could be identified. The evolution of this amine was quite rapid once the temperature of the oil-bath reached 190–193°. The reaction mixture turned dark brown after only 15 minutes. Working up of the brown mass yielded no identifiable amines. Running of the reaction under a nitrogen atmosphere also failed to produce pure products.

Attempted Disproportionation of Gramine (XI).—As in the attempted reaction with X, no disproportionated product could be isolated. In addition to trimethylamine, the volatile gases contained a secondary amine (positive Duke's[14] test) which was probably dimethylamine from the decomposition of XI.

Attempted Disproportionations of N,N-Dimethylaniline (XII), N,N-Dimethyl-β-naphthylamine (XIII) and N,N-Dimethylcyclohexylamine (XIV).—These reactions were carried out by heating each amine in the presence of 0.1 the molar amount of its methiodide at 190–200°. The reaction times for XII, XIII and XIV were 11, 19 and 22.5 hours, respectively. In no reaction was any volatile amine produced. The recovery of XII was 66.4% and of XIV was 84%, but the reaction mixture of XIII was too charred for recovery of any XIII.

Attempted Disproportionation of N,N-Dimethylallylamine (XV).—The temperatures of the previously successful disproportionations could not be reached at atmospheric pressure although the oil-bath temperature was varied. A 78–80% recovery of unchanged XV was achieved in these attempts. When this reaction was tried using a hydrogenation bomb and a temperature of 200° for 16 hours, again only unchanged XV was recovered.

Disproportionation of N,N-Dimethyl-β-phenethylamine (XVII).—In the attempt to disproportionate XVII, a secondary amine was evolved (identified by a positive Duke's[14] test) in addition to trimethylamine. It could not be isolated for positive identification but was probably dimethylamine. After a total period of heating of 85 hours in an experiment employing XVII (14.36 g., 0.096 mole) and its quaternary salt (2.62 g., 0.009 mole), the reaction mixture was cooled and fractionated *in vacuo*. Two fractions were obtained: (1) b.p. 36–39° (11 mm.), n^{20}_{D} 1.5434, weight 0.71 g., and (2) 86–87° (10 mm.), n^{20}_{D} 1.5070, weight 5.58 g. Fraction 1 was shown to be styrene by conversion to the

---

[11] J. Zanetti and J. Bashour, THIS JOURNAL, **62**, 742 (1940).

[12] H. G. Hartough, S. L. Meisel, R. Koft and J. W. Schick, *ibid.*, **70**, 4013 (1948).

[13] J. V. Braun and K. Moldaenke, *Ber.*, **56B**, 2165 (1923).

[14] F. R. Duke, *Ind. Eng. Chem., Anal. Ed.*, **17**, 196 (1945).

dibromide of m.p. 73.7–75.7° (lit.[15] m.p. 73°). In addition, there remained in the distillation flask 5.62 g. of polymeric material which if assumed to be polystyrene brings the total yield of styrene to 58%. Fraction 2 was unchanged XVII (39%). The original amine had a boiling point of 86–87° (9 mm.) and $n^{20}D$ 1.5032. The methiodide melted at 230–232° (lit.[16] m.p. 227°).

A smaller high-boiling fraction was obtained when the bath was heated to 205° (1.9 mm.). It had $n^{20}D$ 1.5118 and weighed 0.23 g. (2.0%). This material was identified as N-methyl-bis-β-phenethylamine as the hydrochloride which melted at 162–164° (lit.[17] m.p. 160°).

Mixed Disproportionation of N,N-Dimethylbenzylamine (II) and N,N-Dimethyl-2-thenylamine (VII).—In the apparatus used for the disproportionation of VII as described above were mixed II (6.76 g., 0.05 mole), benzyltrimethylammonium iodide (1.39 g., 0.005 mole), VII (7.06 g., 0.05 mole) and 2-thenyltrimethylammonium iodide (1.42 g., 0.005 mole), and the mixture was heated 18 hours at an oil-bath temperature of 195–198°. The liquid which collected in the trap was shown to be trimethylamine by its conversion to a picrate which showed no depression in its melting point when mixed with authentic trimethylamine picrate.

The reaction mixture was extracted with dry ether leaving 1.9 g. of a pale yellow solid which was apparently a mixture of tetramethylammonium iodide and those methiodides initially present. After removal of the solvent, the residual liquid was distilled into several fractions. Those which contained mixtures of I, VIII and XXIII were combined and redistilled. The middle fraction was used to prepare an analytical sample of boiling point 180° (18 mm.) and $n^{20}D$ 1.5716 (lit.[18] 148–152° (12 mm.)).

Anal. Calcd. for $C_{13}H_{15}NS$: C, 71.84; H, 6.96; N, 6.45. Found: C, 72.05; H, 6.74; N, 6.26.

The result of the analysis indicates that some N-methyl-N-benzyl-2-thenylamine was formed during the reaction. However, the boiling points of I, VIII and XXIII are too close together for easy separation of the compounds and consequently no per cent. yield was determined.

Mixed Disproportionation of N,N-Dimethylbenzylamine (II) and N,N-Dimethylfurfurylamine (V).—A mixture of II (10.29 g., 0.076 mole), V (9.5 g., 0.076 mole) and methyl iodide (1.96 g., 0.014 mole) were mixed and heated at an oil-bath temperature of 170–190° for twenty and one-third hours. The reaction mixture was distilled *in vacuo* and separated into the following fractions.

Fraction	B.p. °C.	Mm.	$n^{20}D$	Wt., g.
1	52.5–64	15	1.4687	1.03
2	66–71	15	1.4994	1.57
3	66–71	0.3	1.5143	1.72
4	73–78	0.3	1.5274	1.27
5	79–82	0.3	1.5382	3.35
6	97–108	0.75	1.5516	2.22

Fraction 1 was somewhat impure V, fraction 2 impure II, fraction 3 impure VI and fraction 6 impure I.

Fraction 5 was N-methyl-N-benzylfurfurylamine (22%). It was redistilled for analysis and had a boiling point of 82° (0.4 mm.) and a $n^{20}D$ 1.5367.

Anal. Calcd. for $C_{13}H_{15}ON$: C, 77.58; H, 7.51; N, 6.96. Found: C, 78.12; H, 7.92; N, 7.18.

A methiodide was prepared which melted at 135–135.4° (lit.[18] 135°).

URBANA, ILLINOIS

---

[15] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 261.

[16] T. B. Johnson and H. H. Guest, *Am. Chem. J.*, **42**, 348 (1909).

[17] F. Kulz, K. W. Rosenmund, *et al.*, *Ber.*, **72**, 2161 (1939).

[18] J. V. Braun, R. Fussganger and M. Kuhn, *Ann.*, **445**, 201 (1925).

[CONTRIBUTION FROM THE HERCULES POWDER CO., ALLEGANY BALLISTICS LABORATORY]

Organic Acid Esters of Pentaerythritol Trinitrate[1]

BY N. S. MARANS, D. E. ELRICK AND R. F. PRECKEL

RECEIVED SEPTEMBER 17, 1953

A series of organic acid esters of pentaerythritol trinitrate have been prepared by various esterification techniques. These esters are similar to the 2-nitratoethyl esters in their reactivity with dilute base.

Compounds containing the pentaerythritol trinitrate grouping have been mentioned only briefly in the literature. The preparation of several organic acid esters and ethers of pentaerythritol trinitrate was claimed in a patent,[2] but no description of the synthetic methods used or of the physical properties of the compounds obtained were given. A recent paper[3] described the preparation of a number of ethers of pentaerythritol and their nitration products.

Organic acid esters of pentaerythritol trinitrate were desired for comparison of their chemical reactivity with previously synthesized 2-nitratoethyl esters.[4] In both cases, only primary nitrate groups are present. The synthesis of the pentaerythritol trinitrate esters was accomplished by esterification of pentaerythritol trinitrate with acids, acid chlorides or acid anhydrides. Pentaerythritol trinitrate was prepared by nitration of pentaerythrito monoacetate[5] to give the corresponding trinitrate which in turn was subjected to controlled saponification to give the desired trinitratoalcohol.

Controlled saponification of the pentaerythritol acetate trinitrate showed the typical preferential cleavage of the organic ester linkage rather than that of the nitrate ester linkage under alkaline conditions. This was in accordance with previous work on the controlled saponification of 2-nitratoethyl crotonate.[4] In general the prepared series of esters of pentaerythritol trinitrate gave this same cleavage as shown by their neutral equivalents. A few exceptions to this rapid and quantitative hydrolysis of the organic ester linkage were noted, however. The phthalate ester hydrolyzed more slowly than other organic esters and the benzenesulfonate and *p*-toluenesulfonate esters were saponified at a rate equivalent to that of pentaerythritol trinitrate. The esterification of pentaerythritol

---

[1] This work was performed at Allegany Ballistics Laboratory, an establishment owned by the U. S. Navy and operated by Hercules Powder Company under Contract NOrd 10431.

[2] German Patents 638,432 and 638,433 (1936).

[3] R. Evans and J. A. Gallaghan, THIS JOURNAL, **75**, 1248 (1953).

[4] N. S. Marans and R. P. Zelinski, *ibid.*, **72**, 5330 (1950).

[5] R. H. Barth and H. Burrell, U. S. Patent 2,356,745 (Aug. 29, 1944). This patent described the preparation of pentaerythritol diacetate and triacetate only.