[CONTRIBUTION NO. 313 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

The Trimerization of Nitriles at High Pressures

BY T. L. CAIRNS, A. W. LARCHAR AND B. C. MCKUSICK

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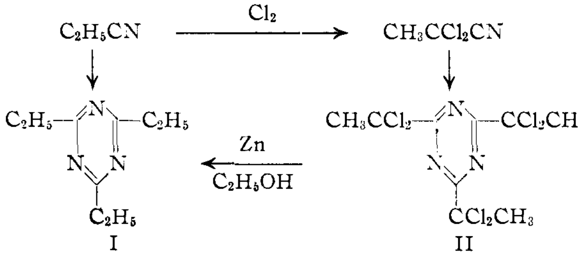
Nitriles are readily trimerized to *s*-triazines under the influence of methanol or weak bases at pressures of 7000–8500 atmospheres. This has been demonstrated with acetonitrile, propionitrile, *n*-valeronitrile, α,α-dichloropropionitrile and benzonitrile. Trimerization to 4-amino-2,6-dimethylpyrimidine is an important competing reaction in the case of acetonitrile.

Nitriles having no α-hydrogens can be trimerized to *s*-triazines rather easily by strong acids[1,2] less easily by alkali-metals[3,4,17] or strong bases.[4,5] Dibromoacetonitrile has been trimerized to an *s*-triazine,[6] and *s*-triazines have been prepared by combining two molecules of trichloroacetonitrile with one molecule of acetonitrile or oleonitrile,[7] but in general it has not been possible to trimerize nitriles with α-hydrogens to *s*-triazines. It has now been found that nitriles with or without α-hydrogens can be so trimerized under the influence of high pressures, preferably pressures of 7000–8500 atmospheres.

Acetonitrile dissolved in an equal weight of methanol gave 2,4,6-trimethyl-*s*-triazine in 39% yield when heated at 60° under a pressure of 7200–6400 atmospheres. The trimerization did not occur when the experiment was repeated in the absence of methanol and occurred less well or not at all with other solvents. Ammonia and several other weak bases were able to catalyze the reaction. No triazine was detected at pressures below 1000 atmospheres under conditions otherwise suitable for trimerization.

Propionitrile and *n*-valeronitrile behaved much like acetonitrile except that higher temperatures were necessary in order to obtain *s*-triazines. α,α-Dichloropropionitrile and benzonitrile were converted to *s*-triazines in 74–82% yield when methanol solutions were heated at 100–125° at a pressure of 7500–6300 atmospheres; yields were much lower when methanol was replaced by other alcohols or when the pressure was lowered.

That the product obtained from propionitrile was 2,4,6-triethyl-*s*-triazine (I) was proved by direct comparison of its physical properties, including infrared absorption spectrum (Fig. 1), with those of an authentic sample prepared by the reduction of 2,4,6-tris-(1,1-dichloroethyl)-*s*-triazine (II).[8]



The properties of the *s*-triazines from acetonitrile, α,α-dichloropropionitrile and benzonitrile agreed with those reported elsewhere. Evidence that the trimer from *n*-valeronitrile was 2,4,6-tri-*n*-butyl-*s*-triazine was supplied by its ultraviolet absorption spectrum, which was very similar to the spectra of 2,4,6-trimethyl-*s*-triazine and 2,4,6-triethyl-*s*-triazine.

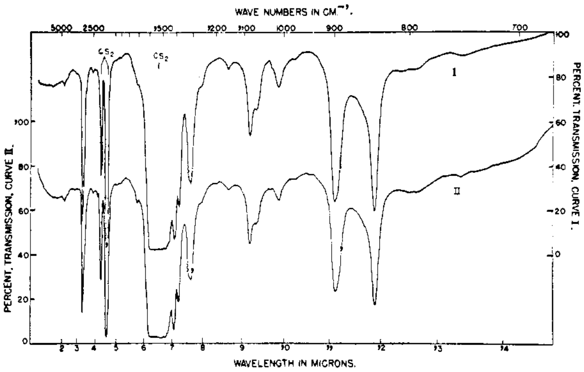


Fig. 1.—Infrared absorption spectra of 2,4,6-triethyl-*s*-triazine prepared (curve I) by trimerization of propionitrile and (curve II) by reduction of 2,4,6-tris-(1,1-dichloroethyl)-*s*-triazine. Spectra were determined in a cell 0.005 in. thick with carbon disulfide solutions containing 0.100 g. of triazine per ml.

The trimerization of acetonitrile to 4-amino-2,6-dimethylpyrimidine (III) competed with its trimerization to 2,4,6-trimethyl-*s*-triazine. At 150°, especially in the presence of a base such as ammonia, pyrimidine formation became the predominant reaction. Yields were as high as 67%. In some cases the pyrimidine was accompanied by a tetramer of acetonitrile, N-(2,6-dimethyl-4-pyrimidyl)-acetamidine (V). The structure Vb, in which the double bond of the side-chain is conjugated with the pyrimidine ring, is preferred to structure Va because maximum absorption of ultraviolet light by the acetamidine is greater and at a longer wave length than in the case of the parent 4-amino-2,6-dimethylpyrimidine (III) or the latter's N-acetyl derivative (IV). The best proof for the structure of the amidine is its smooth hy-

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(1) E. V. Zappi and J. O. Defarrari, *Anales asoc. quim. argentina* **34**, 146 (1946); C. V. Wilson, THIS JOURNAL, **70**, 1901 (1948); N. Tscherven-Iwanoff, *J. prakt. Chem.*, **46**, 142 (1892); C. Broche, *ibid.*, **50**, 97 (1894); E. Ott, *Ber.*, **52**, 656 (1919); K. Dachlauer (to I. G. Farbenindustrie), German Patent 699,493 (1940).

(2) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

(3) A. Lottermoser, *J. prakt. Chem.*, **54**, 113 (1896).

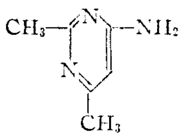
(4) R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 323 (1941).

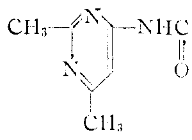
(5) F. W. Swamer, G. A. Reynolds and C. R. Hauser, *J. Org. Chem.*, **16**, 43, 165 (1951); E. Frankland and J. C. Evans, *J. Chem. Soc.*, **37**, 560 (1880); O. Neunhoeffer and F. Nerdel, *Ann.*, **526**, 47 (1936); J. E. Mahan and S. D. Turk (to Phillips Petroleum Co.) U. S. Patent 2,598,811 (1952).

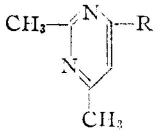
(6) E. Ghigi, *Gazz. chim. ital.*, **71**, 641 (1941).

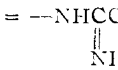
(7) K. Dachlauer (to I. G. Farbenindustrie), German Patent 682,391 (1939).

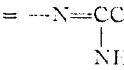
(8) J. Troeger, *J. prakt. Chem.*, **50**, 446 (1894).

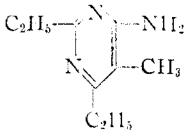

III


IV



Va, R =

$-\mathrm{NH}\underset{\underset{\mathrm{NH}}{\|}}{\mathrm{C}}\mathrm{CH_3}$

Vb, R =

$-\mathrm{N{=}}\underset{\underset{\mathrm{NH_2}}{|}}{\mathrm{C}}\mathrm{CH_3}$


VI

drolysis to 4-acetamido-2,6-dimethylpyrimidine (IV), identical in properties with the N-acetyl derivative of an authentic sample of 4-amino-2,6-dimethylpyrimidine. The latter was made from acetonitrile by the procedure of Ronzio and Cook[9] with the convenient modification that a small amount of sodium methoxide replaced a large amount of potassium methoxide as catalyst in the trimerization.

2,4,6-Triethyl-*s*-triazine (I) in ammoniacal methanol at 150° and a pressure of 8500 atmospheres partially (32%) rearranged to the isomeric 4-amino-2,6-diethyl-5-methylpyrimidine (VI). Under similar conditions, 2,4,6-trimethyl-*s*-triazine rearranged partially to 4-amino-2,6-dimethylpyrimidine (III). There are insufficient data to say to what extent 2,4,6-trimethyl-*s*-triazine may have been an intermediate in the trimerization of acetonitrile to 4-amino-2,6-dimethylpyrimidine at high pressures.

Bridgman's review of the effect of pressure on chemical reactions[10] shows that there are not many reactions known that have been observed only at pressures above 1000 atmospheres. It is of interest, then, that the trimerization of aliphatic nitriles with two α-hydrogens to *s*-triazines seems to be of this class. Thus, good yields of 2,4,6-trimethyl-*s*-triazine can be obtained from acetonitrile at 7500 atmospheres under conditions that give no *s*-triazine at pressures below 1000 atmospheres, and conditions that can effect the trimerization at low pressures have not yet been found. There is also a pressure effect in the trimerization of nitriles to pyrimidines, for acetonitrile is converted to 4-amino-2,6-dimethylpyrimidine in good yield at 7000–8000 atmospheres and 150° under weakly basic conditions that give no appreciable amount of pyrimidine at pressures much below 3000 atmospheres. However, the pressure effect is less noteworthy in this case, for the adverse effect of lowering the pressure can be completely overcome by using a stronger catalyst such as sodium methoxide.

Acknowledgment.—We were given help and advice by many people in these laboratories, among whom H. S. Young deserves special mention.

TABLE I

TRIMERIZATION OF NITRILES, RCN, TO *s*-TRIAZINES UNDER AN INITIAL PRESSURE OF 7500 ATM.

R	Medium[a]	Temp., °C.[b]	Yield of *s*-triazine, %
CH_3[c]	....	...	..[c]
C_2H_5	Methanol	70[b]	36
n-C_4H_9	Methanol	150	35
n-C_4H_9	Methanol	100	7
CH_3CCl_2	Methanol	100	74
CH_3CCl_2	1-Butanol	125	8
C_6H_5	Methanol	100	76
C_6H_5	Methanol	125	82
C_6H_5	Methanol	150[d]	0
C_6H_5	Ethanol	100	24
C_6H_5	2-Propanol	150	46
C_6H_5	2-Ethylhexanol	125	22
C_6H_5	None	125	6

[a] The nitrile was dissolved in an equal weight (about 4 g.) of the medium. [b] The reaction time was 18 hours except with R = C_2H_5 (65 hours). [c] Results of experiments with acetonitrile are given elsewhere. [d] The initial pressure was only 950 atm.

Experimental

Apparatus.—The experiments at high pressure were generally done in collapsible lead tubes with a Bridgman-type apparatus according to a procedure described elsewhere.[11] Similar silver tubes were occasionally used, but were less convenient except for very corrosive mixtures. In the experiments described below it seemed to make no difference whether lead or silver was used, so it is unlikely that either metal was acting as a catalyst.

Trimerization of Acetonitrile. A. In Methanol.—A mixture of 3.57 g. of acetonitrile and 3.57 g. of methanol was held at 60° and 7200–6400 atm. for 65 hours. Distillation gave A, 4.1 g. of a methanol–acetonitrile mixture, b.p. 58–66°; B, 1.50 g. of a solid that distilled when the distillation pot was heated at 100–150° under a pressure of 11 mm.; and C, 0.10 g. (3% yield) of 4-amino-2,6-dimethylpyrimidine, isolated by sublimation of the pot residue. Ether was added to B and 0.06 g. (1% yield) of ether-insoluble material, identified as acetamide by its m.p. and mixed m.p. (79–80°), was separated by filtration. Evaporation of the ether left 1.40 g. (39% yield) of crude 2,4,6-trimethyl-*s*-triazine, m.p. 54–56°.

The experiment was repeated at 100° and various pressures, the reaction time being 18 hours. The yields of 2,4,6-trimethyl-*s*-triazine were: 8500–7500 atm., 40%; 7500–6900 atm., 25%; 980–950 atm., 0%.

B. In **Other Alcohols.**—When experiment A was repeated at 130° for 18 hours, 1.79 g. (25% yield) of 2,4,6-trimethyl-*s*-triazine and 0.42 g. (6% yield) of 4-amino-2,6-dimethylpyrimidine were obtained. Replacement of methanol by the following alcohols gave the yields indicated: absolute ethanol, 5% triazine, 4% pyrimidine; 2-propanol, 1% pyrimidine.

C. **In the Presence of Ammonia.**—A 6.84-g. sample of acetonitrile saturated with gaseous ammonia at 25° was held at 150° and 7300–6000 atm. for 17 hours. The material not volatile at 10 mm. (pot temp. 25°) was a yellow solid weighing 6.7 g. It was co-distilled with 80 ml. of kerosene. 4-Amino-2,6-dimethylpyrimidine crystallized from the distillate. After being filtered, washed with hexane, and dried, it weighed 4.6 g. (67% yield). A similar experiment showed that small amounts of 2,4,6-trimethyl-*s*-triazine and N-(2,6-dimethyl-4-pyrimidyl)-acetamidine are also formed under these conditions.

The experiment was repeated at various temperatures and pressures. The weight of material (principally 4-amino-2,6-dimethylpyrimidine) not volatile at 10 mm. (pot temp. 25°) was as follows: 150°, 4200–3800 atm., 2.06 g.; 150°, 2100–1600 atm., 0.21 g.; 150°, 1070–750 atm., 0.12 g.; 200°, 2100–1100 atm., 2.12 g.; 200°, 1100–500 atm., 1.12 g.

Acetonitrile (6.67 g.) and 0.39 g. of 28% aqueous ammonia were held at 150° and 7300–7000 atm. for 17 hours. Working up the reaction mixture as described in experiment D

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[9] A. R. Ronzio and W. B. Cook, *Org. Syntheses*, **24**, 6 (1944).

[10] P. W. Bridgman, *Rev. Modern Phys.*, **18**, 79 (1946).

[11] T. L. Cairns, A. W. Larchar and B. C. McKusick, *J. Org. Chem.*, in press.

TABLE II

PROPERTIES OF PRODUCTS OBTAINED FROM NITRILES AT HIGH PRESSURES, WITH DERIVATIVES

Compound	M.p., °C.	λ_{max}^{Alc}, mμ (log ε)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Molecular weight Calcd.	Molecular weight Found[a]	Molecular weight Found[b]
2,4,6-Trimethyl-*s*-triazine	59–60[c]	256 (2.90)	$C_6H_9N_3$	58.5	58.7	7.4	7.7	34.1	33.5	123	132	127
2,4,6-Triethyl-*s*-triazine (I)	24–25[d,e,f]	259 (2.83)	$C_9H_{15}N_3$							165	164	
2,4,6-Tri-*n*-butyl-*s*-triazine	.....[m]	259 (2.84)	$C_{15}H_{27}N_3$	72.3	71.7	10.8	10.9	16.9	17.0	249		278
2,4,6-Tris-(1,1-dichloroethyl)-*s*-triazine (II)	72–74[d,g]		$C_9H_7Cl_6N_3$	29.1	29.2	2.4	2.6					
2,4,6-Triphenyl-*s*-triazine	231–232[d,h]											
4-Amino-2,6-dimethylpyrimidine (III)	182–183[d,i]	235, 267 (4.02, 3.62)										
4-Acetamino-2,6-dimethylpyrimidine (IV)	188–189[d,j]	233, 263 (3.98, 3.97)	$C_8H_{11}N_3O$					25.4	25.1			
N-(2,6-Dimethyl-4-pyrimidyl)-acetamidine (V)	147–148	340 (4.49)	$C_8H_{12}N_4$	58.5	58.7	7.4	7.5	34.1	33.0	164	162	163
Dihydrate of V	.....[k]		$C_8H_{16}N_4O_2$	48.0	48.8	8.1	8.0					
N-Acetyl derivative of V[l]	121–122	319 (4.32)	$C_{10}H_{14}N_4O$	58.2	58.5	6.8	7.1					
Hydrochloride monohydrate of V	220–225		$C_8H_{15}ClN_4O$	43.9	43.2	6.9	6.4	25.6	25.3			

[a] Ebullioscopic in ethanol. [b] Neutral equivalent by titration in acetic acid with perchloric acid. [c] B.p. 156° (760 mm.). Ref. 13 reports b.p. 154–156° (750 mm.), m.p. 55–56°. [d] Alone or mixed with authentic sample. [e] B.p. 75–80° (10 mm.), 199° (760 mm.); n^{25}_D 1.4672, d^{25}_4 0.947. R. Otto and K. Voigt, *J. prakt. Chem.*, **36**, 78 (1887); E. von Meyer and F. Näbe, *ibid.*, **82**, 537 (1910), and ref. 8 report b.p. 193–195° (760 mm.), m.p. 29–30°. [f] Infrared absorption spectrum identical with that of authentic (ref. 8) sample (Fig. 1). [g] J. Troeger, *J. prakt. Chem.*, **46**, 353 (1892), reports m.p. 73–74°. [h] Ref. 2 reports m.p. 232°. [i] Ref. 9 reports m.p. 182–183°. [j] Ref. 15 reports m.p. 185°. [k] Water lost at 50–65° to give V. [l] Ultraviolet absorption data favors $—N=C(NHCOCH_3)CH_3$ as the structure of the side-chain. [m] B.p. 85–91° (0.5 mm.), 284–287° (760 mm.), n^{25}_D 1.4660.

gave 1.40 g. (21% yield) of 2,4,6-trimethyl-*s*-triazine, 2.65 g. (40% yield) of 4-amino-2,6-dimethylpyrimidine, and 1.54 g. (23% yield) of N-(2,6-dimethyl-4-pyrimidyl)-acetamidine. Replacing half the acetonitrile by methanol and operating at 100° gave 2.87 g. of solid material of which the principal constituent (1.63 g., 49% yield) was the triazine.

D. In the Presence of Piperidine.—A mixture of 6.60 g. of acetonitrile and 0.36 g. of piperidine was held at 150° and 7500–6600 atm. for 16 hours. Removal of material volatile at 10 mm. (pot temp. 25°) left 6.63 g. of residue from which 0.49 g. (7% yield) of 2,4,6-trimethyl-*s*-triazine was separated by sublimation at 25° (0.5 mm.). The material that did not sublime was co-distilled with 80 ml. of kerosene. The distillate was held at 0° for several hours and filtered to remove a crystalline solid. The solid was extracted with petroleum ether (b.p. 35–60°) in a Soxhlet extractor. Evaporating the extract to dryness left 2.23 g. (34% yield) of crude N-(2,6-dimethyl-4-pyrimidyl)-acetamidine. The material insoluble in petroleum ether was 4-amino-2,6-dimethylpyrimidine (1.45 g., 22% yield).

Purification and Properties of Products Obtained from Acetonitrile.—**2,4,6-Trimethyl-*s*-triazine**[12,13] was most conveniently prepared by the method of experiment C above, where equal parts of acetonitrile and methanol were heated under pressure at 100° in the presence of 28% aqueous ammonia. The crude sublimed triazine was purified by dissolving it in ether, filtering to remove ether-insoluble material, evaporating the ether and resubliming the residue one or more times. It could be recrystallized from hexane, but recovery was low. The triazine is very soluble in water and most organic solvents.

4-Amino-2,6-dimethylpyrimidine (III) was identified by direct comparison of it, its picrate (m.p. 216–217°),[14] and its N-acetyl derivative[15] (IV) with authentic samples. The authentic sample of the pyrimidine was prepared by a modification[16] of the method of Ronzio and Cook.[9] A mixture of 196 g. of acetonitrile and 4.0 g. of sodium methoxide was heated for 12 hours at 150° in a 1-l. rocking, stainless-steel bomb. The reaction mixture from the cooled bomb was co-distilled with 1800 ml. of kerosene as described by Ronzio and Cook. The 4-amino-2,6-dimethylpyrimidine weighed 168 g. (86% yield). It gave 4-acetamido-2,6-dimethylpyrimidine[15] when heated with acetic anhydride.

N-(2,6-Dimethyl-4-pyrimidyl)-acetamidine (V) was most conveniently obtained as described in experiment D above. It was purified by a rapid recrystallization from water followed by recrystallization from benzene and sublimation at 0.5 mm. (pot temp. 130°). It crystallized from water as a **dihydrate** which lost its water at 50–65°. **An N-acetyl derivative** of the amidine was obtained by refluxing a solution of 0.10 g. of the amidine in 1.0 ml. of acetic anhydride for 30 minutes, removing acetic acid and anhydride at reduced pressure, and recrystallizing the residue successively from water and cyclohexane. **The hydrochloride monohydrate** of the amidine was obtained by saturating its ether solution with hydrogen chloride. N-(2,6-Dimethyl-4-pyrimidyl)-acetamidine was hydrolyzed to 4-acetamido-2,6-dimethylpyrimidine (IV) with evolution of ammonia by refluxing a solution of 0.40 g. of the amidine in 1.5 ml. of water for 20 hours; cooling the solution caused the precipitation of 4-acetamino-2,6-dimethylpyrimidine, which weighed 0.18 g. after two recrystallizations from water.

The properties of the above-described compounds are listed in Table II.

Trimerization of Other Nitriles to *s*-Triazines.—Table I gives the results of experiments in which propionitrile, *n*-valeronitrile, α,α-dichloropropionitrile[17] or benzonitrile dissolved in an equal weight of methanol or other alcohol were heated for 18 hours under an initial pressure of 7500 atm. The final pressure was generally 6300–7000 atm. The *s*-triazines were isolated as follows: 2,4,6-triethyl-*s*-triazine and 2,4,6-tri-*n*-butyl-*s*-triazine, by distillation; 2,4,6-tris-(1,1-dichloroethyl)-*s*-triazine (II), by removal of the low-boiler at reduced pressure, sublimation of the residue at 0.5 mm. (pot temp. 110–130°), and recrystallization of the sublimate from 95% ethanol; 2,4,6-triphenyl-*s*-triazine, by dilution with two parts of hexane, filtration, sublimation of the filtered solid at 0.5 mm. (pot temp. 150–175°), and recrystallization from toluene.

The physical properties of the *s*-triazines are listed in Table II.

2,4,6-Triethyl-*s*-triazine from 2,4,6-Tris-(1,1-dichloroethyl)-*s*-triazine.[8]—A solution of 176 g. of 2,4,6-tris-(1,1-dichloroethyl)-*s*-triazine[17] (II) in 500 ml. of 95% ethanol was refluxed and stirred while 525 g. of zinc dust was added during one hour. Refluxing and stirring were continued for 3 hours, 375 ml. of ethanol was removed by distillation, and 800 ml. of ether was added. Zinc and zinc salts were removed by filtration and the ether extract was washed with 1.0 l. of 40% potassium hydroxide. The ether layer was separated and the aqueous layer, a thick slurry of zinc salts, was extracted with two 200-ml. portions of ether. The combined extracts were dried over potassium hydroxide and distilled to give 42 g. (54% yield) of 2,4,6-triethyl-*s*-triazine,

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(12) T. L. Cairns, A. W. Larchar and B. C. McKusick (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,503,999 (1950).

(13) C. Grundmann and G. Weisse, *Ber.*, **84**, 684 (1951); C. Grundmann, G. Weisse and S. Seide, *Ann.*, **577**, 77 (1952).

(14) J. Schmidt, *ibid.*, **35**, 1575 (1902), reports m.p. 214°.

(15) A. Pinner, *ibid.*, **22**, 1600 (1889).

(16) A. W. Larchar (to E. I. du Pont de Nemours and Company), U. S. Patent 2,540,826 (1951); *cf.* W. Schwarze (to Deutsche Golde- und Silber-Scheideanstalt), German Patent 819,692 (1951).

(17) R. Otto and G. Holst, *J. prakt. Chem.*, **41**, 460 (1890).

b.p. 75–80° (10 mm.). Purification by redistillation gave material melting at 24–25°.

The Rearrangement of 2,4,6-Trialkyl-*s*-triazines to 4-Aminopyrimidines.—A mixture of equal weights of 2,4,6-triethyl-*s*-triazine (I) and methanol was saturated with gaseous ammonia, and 7.58 g. of the resultant solution was held at 150° and 8500–8300 atm. for 17 hours. By distillation, 2.01 g. (53%) of the triazine was recovered. 4-Amino-2,6-diethyl-5-methylpyrimidine (VI, 1.21 g., 32% yield) was isolated by sublimation of the distillation residue. After recrystallization from ethanol it melted at 189–190°[18] alone or mixed with an authentic specimen prepared by the method of Larchar.[16]

A solution of 2.84 g. of 2,4,6-trimethyl-*s*-triazine in 4.80 g. of methanol was held at 150° and 8500 atm. for 18 hours. 4-Amino-2,6-dimethylpyrimidine (III, 0.35 g., 12% yield) and 2,4,6-trimethyl-*s*-triazine (1.9 g., 66% recovery) were separated from the reaction mixture by fractional sublimation.

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(18) R. Schwarze, *ibid.*, **42**, 1 (1890), reports m.p. 190°.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 299 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

The Reaction of Acetylene with Acrylic Compounds[1]

BY T. L. CAIRNS, V. A. ENGELHARDT, H. L. JACKSON, G. H. KALB AND J. C. SAUER

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Reaction of acetylene with acrylic compounds was found to give high yields of heptatrienoic acid derivatives. The structures of these compounds were demonstrated and their reactivity in Diels–Alder and dimerization reactions investigated. Methyl 2,4,6-heptatrienoate was converted to the corresponding acid and alcohol.

A new reaction involving the condensation of two molecules of acetylene with one molecule of an α,β-unsaturated compound has been discovered during investigation of the behavior of acetylene in the presence of complex nickel-containing catalysts. Thus, interaction of acetylene and methyl acrylate gives in high yield a new compound proven to be methyl 2,4,6-heptatrienoate (I)

$$2C_2H_2 + CH_2{=}CH{-}CO_2CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CO_2CH_3$$

I

The reaction proceeds readily also with acrylonitrile to form 2,4,6-heptatrienenitrile (II). This synthesis provides a convenient new route to otherwise difficultly accessible, highly conjugated aliphatic compounds.

Proof of Structure.—The ester I and nitrile II absorbed three moles of hydrogen under mild conditions forming the well known corresponding saturated compounds and proving the linear arrangement of the seven chain carbon atoms. The nitrile failed to form a solid derivative with copper or mercury salts and this fact, coupled with the absence of absorption at 3 μ in the infrared, excludes the possibility of a terminal acetylenic function. Ozonization of the nitrile yielded hydrogen cyanide, formic acid and oxalic acid, indicating the presence of a double bond alpha, beta to the nitrile group[2] and the presence of terminal unsaturation. No higher dibasic acids, acetic acid or cyanoacetic acid, products to be expected from analogous compounds having allenic or acetylenic functions, were observed. Finally, the ultraviolet and infrared absorption spectra of the nitrile and the Raman and infrared spectra of the ester as well as reactivity in Diels–Alder condensations, Michael-type additions and polymerization are all in accord with the heptatriene structure.

Synthesis Conditions, Catalysts and Reaction Mechanism.—The most effective type of catalyst found for synthesis of these heptatrienes was a compound of nickel modified by the addition of a phosphine or a phosphite. The catalyst was ordinarily prepared by adding nickel carbonyl and triphenylphosphine to the acrylic compound. Such a mixture probably gives rise to the complexes, $Ni(CO)_2[(C_6H_5)_3P]_2$ and $Ni(CO)_3[(C_6H_5)_3P]$.[3] Other nickel compounds, such as nickel cyanide, in combination with triethyl phosphite were also active as catalysts.

The reaction was conducted by treating the acrylate containing nickel carbonyl and triphenylphosphine with acetylene at pressures up to about 15 atm. and temperatures of 70–90°. Yields of about 80% methyl heptatrienoate and about 70% heptatrienenitrile were regularly obtained. An induction period was frequently observed after which a smooth, exothermic reaction took place with absorption of approximately the theoretical amount of acetylene. The induction period could be reduced or eliminated by starting the reaction at temperatures around 100° followed by rapid cooling to about 70°. Great care must be exercised to prevent uncontrolled increases in temperature during these reactions since occasional violent decompositions have been encountered.

There is at present insufficient evidence on which to base a reaction mechanism for the synthesis of these heptatrienes. However, in postulating a probable mechanism the following must be taken into account. (1) One of the preferred catalysts for the synthesis of heptatrienes is the complex from nickel carbonyl and triphenylphosphine, the same catalyst reported to be effective for the conversion of acetylene to benzene.[3]

(2) We have found that nickel cyanide, which in the presence of inert solvents or weak electron

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(1) This paper was presented at the New York Meeting of the American Chemical Society, Sept., 1951. See abstracts page 14 M.

(2) A. van Dormael, *Bull. soc. chim. Belg.*, **52**, 100 (1943), shows that α,β-unsaturated nitriles yield hydrogen cyanide while β,γ-unsaturated nitriles form cyanoacetic acid when ozonized.

(3) W. Reppe and W. J. Schweckendieck, *Ann.*, **560**, 104 (1948).