Anal. Calcd. for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91. Found: C, 84.26; H, 5.27; N, 5.01.

2-N-p-Dimethylaminobenzylideneaminofluoren-9-ol. To a boiling solution of 2-aminofluoren-9-ol (1 g., 0.005 mole) in 50% acetic acid (15 ml.), *p*-dimethylaminobenzaldehyde (0.76 g.) in 50% acetic acid (5 ml.) was added during a period of 5 min. The reaction solution was heated at 105–110° for 10 min. and diluted with an equal volume of water. The acid solution was rendered alkaline with concentrated ammonium hydroxide, and the product filtered and recrystallized from ethanol containing a small amount of acetic acid, yielding 1.2 g. (73%), m.p. 211–212°. Recrystallization from acetone gave m.p. 212–213°.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14. Found: C, 80.67; H, 6.05.

2-N-p-Nitrobenzylideneaminofluoren-9-ol. To a boiling solution of 2-aminofluoren-9-ol (7.9 g., 0.04 mole) in absolute ethanol (250 ml.) containing a few drops of glacial acetic acid, *p*-nitrobenzaldehyde (6 g., 0.04 mole) in hot absolute ethanol (30 ml.) was added dropwise within 5 min. The reaction solution was then concentrated until crystallization of the product took place. After cooling to room temperature the shiny yellow plates were filtered, yielding 11.6 g. (88%), m.p. 200–201°.

Anal. Calcd. for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.64; H, 4.44; N, 8.44.

2-N-Benzylideneamino-3-bromofluoren-9-ol. A mixture of 2-amino-3-bromofluoren-9-ol[3] (2.2 g., 0.008 mole), benzaldehyde (5.3 g., 0.05 mole), and glacial acetic acid (2 drops) was heated under reflux at 155–160° (bath) for 1 hr. and excess benzaldehyde removed under reduced pressure. The yellow solid residue was recrystallized from methanol giving 2.2 g. (76%) of light yellow needles, m.p. 175–178°. Two recrystallizations from methanol gave an analytical sample, m.p. 178.5–179.5°.

Anal. Calcd. for $C_{20}H_{12}BrNO$: C, 66.32; H, 3.34; N, 3.87. Found: C, 66.34; H, 3.89; N, 3.87.

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[CONTRIBUTION NO. 412 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENT STATION, E. I. DU PONT DE NEMOURS AND CO.]

Alkylidene Derivatives of 3-Pentenenitrile

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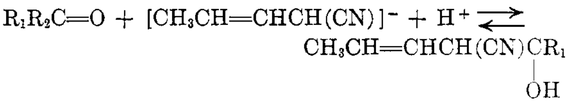
The synthesis of nine new alkylidene derivatives of 3-pentenenitrile (1-substituted-2-cyano-4-methyl-1,3-butadienes) by the condensation of 3-pentenenitrile with aldehydes and ketones is described. The compounds derived from aldehydes form low molecular weight polymers on heating.

The Knoevenagel modification of the Perkin reaction has been used previously to prepare unsaturated acids or nitriles by condensation of aldehydes or ketones with such active methylene compounds as phenylacetic acid, malonic acid, cyanoacetic acid, and benzyl cyanide in the presence of alkaline reagents.[1] Cope[2] prepared a series of alkylidene cyanoacetic esters, $R_1R_2C{=}C(CN)COOCH_3$, by condensing ketones with methyl cyanoacetate and interpreted the experimental evidence in favor of an aldol-type mechanism for the Knoevenagel reaction.

Compounds in which a methylene group is activated by a double bond and a nitrile group have now been found to undergo this reaction. Alkylidene derivatives of 3-pentenenitrile have been synthesized by condensation of aldehydes and ketones with 3-pentenenitrile, prepared by reaction of butadiene with hydrogen cyanide, in the presence of sodium alkoxides. The mechanism is similar to that proposed by Cope:[2] (*1*) formation of a carbanion of the 3-pentenenitrile, probably through dissociation of a hydrogen ion,

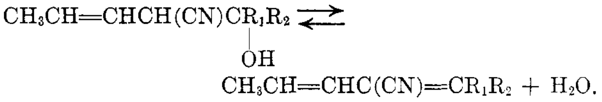
$$CH_3CH{=}CHCH_2CN \rightleftarrows H^+ + [CH_3CH{=}CHCH(CN)]^-;$$

(*2*) addition of the carbanion to the carbonyl compound,



$$R_1R_2C{=}O + [CH_3CH{=}CHCH(CN)]^- + H^+ \rightleftarrows CH_3CH{=}CHCH(CN)\underset{\underset{OH}{|}}{C}R_1R_2;$$

and (*3*) elimination of water from the aldol-like intermediate,



$$CH_3CH{=}CHCH(CN)\underset{\underset{OH}{|}}{C}R_1R_2 \rightleftarrows CH_3CH{=}CHC(CN){=}CR_1R_2 + H_2O.$$

A

The physical properties of the 2-alkylidene derivatives of 3-pentenenitrile are summarized in the table.

Structural assignment was based on elemental analysis, infrared and ultraviolet absorption, the high exaltation in molecular refraction, and the formation of a crystalline dibromide to which the structure, $CH_3CHBrCHBrC(CN){=}CR_1R_2$,[3,4] was assigned.

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[1] J. R. Johnson, *Org. Reactions*, **1**, 210 (1947).

[2] A. C. Cope, *J. Am. Chem. Soc.*, **59**, 2327 (1937).

[3] Mahan, U. S. Patent **2,384,630** (1945), describes an analytical method based on the fact that 3-pentenenitrile adds bromine whereas 2-pentenenitrile does not add bromine.

[4] Linstead, *J. Chem. Soc.*, 358 (1927), reports that bromine adds to $\beta\gamma$-unsaturated acids about 100 times faster than to $\alpha\beta$-unsaturated acids.

TABLE I

2-ALKYLIDENE DERIVATIVES OF 3-PENTENENITRILE $CH_3CH{=}CHC(CN){=}CR_1R_2$

	Substitution		Yield,	B.P.,			M_D			Analyses	
										Calcd.	Found
Cpd.	R_1	R_2	%	°C./Mm.	n_D^{25}	d_{25}^{25}	Calcd.	Obsd.	Formula	N	N
I	H	C_6H_5	70	135–137/4	1.6110	1.1040	52.83	53.50	$C_{12}H_{11}N$	8.28	8.30
II	H	C_4H_3O	52	117–118/6	1.6270				$C_{10}H_9NO$	8.81	8.87
III	H	$CH(CH_3)_2$	63	97–102/32	1.4627	0.8490	40.16	43.80	$C_9H_{13}N$	10.36	10.35
IV	H	CH_3	9	68–72/37	1.4360						
V	H	$CH{=}CHCH_3$	10	96–98/29	1.4309				$C_9H_{11}N$	10.52	10.65
VI	H	p-$CH_3OC_6H_4$	51	153–155/2					$C_{13}H_{13}NO$	7.04	7.11
VII	[a]	[a]	34	137–138/17	1.5170	0.9510	49.61	51.20	$C_{11}H_{15}N$[b]	8.68	8.51
VIII	CH_3	CH_3	66	81–81.5/13	1.4961	0.8766	37.96	40.40	$C_8H_{11}N$[c]	11.56	11.48
IX	CH_3	C_2H_5	55	102/20	1.4891	0.8760	42.58	44.40	$C_9H_{13}N$	10.36	10.17

[a] R_1R_2 = cyclohexylidene. [b] Calcd.: C, 81.93; H, 9.37. Found: C, 81.6; H, 9.87. [c] Calcd.: C, 79.29; H, 9.15. Found: C, 79.43; H, 9.3.

The hindered nitrile structure A was assigned to the compounds instead of the structure B, $R_1R_2C{=}C(CH_3){-}CH{=}CHCN$, on the basis of ultraviolet absorption spectra and the lack of reactivity of the nitriles. The hindered nitriles showed great resistance to reaction with thioglycolic acid, to hydrolysis to acids, to formation of tertiary butyl amides by reaction with *tert*-butyl alcohol in sulfuric acid as in the case of acrylonitrile, and where R_1 and R_2 are alkyl groups to formation of Diels-Alder adducts with maleic anhydride.

Maximum ultraviolet absorption in ethyl alcohol was observed at 2440 A. (ϵ = 15,250) for 2-isopropylidene-3-pentenenitrile. The low intensity favors the hindered conjugated nitrile structure, A, since an unhindered, conjugated, terminal nitrile, 2,4-pentadienenitrile, has $\lambda_{\max}^{\text{methanol}}$ 2410 A. (ϵ = 18,550). Values for the backbone hydrocarbon structure for each case are 2,4-hexadiene,[5] $\lambda_{\max}^{\text{hexane}}$ 2270 A. (ϵ = 22,500), and 1,3-butadiene,[6] $\lambda_{\max}^{\text{hexane}}$ 2170 A. (ϵ = 20,900).

A molecular model of the hindered nitrile structure, A, in which R_1 and R_2 are methyl groups has a *trans* form but cannot add maleic anhydride. Experimentally no crystalline Diels-Alder adduct was obtained by reaction of 2-isopropylidene-3-pentenenitrile with maleic anhydride. This observation is in agreement with that of Craig[7] which indicated that a similar *trans* form of piperylene did not add maleic anhydride.

Most of the 2-alkylidene-3-pentenenitrile derivatives polymerized when heated at about 200° even in the presence of antioxidants. The polymers had little unsaturation as judged by iodine-number determinations. The 2-benzylidene (I) and 2-furfurylidene (II) derivatives formed solid polymers. The 2-isobutylidene (III), 2-ethylidene (IV), and 2-cyclohexylidene (VII) derivatives formed viscous oils, while the 2-isopropylidene (VIII) and 2-(2-butylidene) (IX) derivatives did not polymerize. The highest molecular weight obtained for a polymer of the 2-benzylidene derivative was 440 by the boiling point method.

EXPERIMENTAL

3-Pentenenitrile. The method described by Coffman, Salisbury, and Scott[8] was employed. In a 1.3-l. Monel metal bomb chilled with solid carbon dioxide was placed a mixture of 146 g. (5.4 moles) of hydrogen cyanide, 298 g. (5.5 moles) of butadiene, and 1.07 g. (0.54 mole) of cuprous chloride. The bomb was rocked and heated for 2 hr. during which time the temperature increased to 102° and the gauge pressure rose to 285 pounds per square inch. The reaction became exothermic and in 3 min. the temperature surged to 128° and the gauge pressure reached 460 pounds per square inch. The temperature continued to rise during the next 4 min. to 182°, but the pressure dropped to 180 pounds per square inch. The crude product (345 g.) was isolated by steam distillation of the reaction mixture. The upper organic layer was separated, dried over anhydrous sodium sulfate, and distilled through a 110-cm. long, helix-packed column. The fraction boiling at 142–144.5° was collected; n_D^{25} 1.4199; 266 g. (yield 60%).

Anal. Calcd. for C_5H_7N: N, 17.29. Found: N, 17.03.

The infrared spectrum showed a distinct band at 4.45μ characteristic of the nitrile group and a pronounced band at 10.33μ characteristic of a *trans* internal double bond. The 3-pentenenitrile was treated with *tert*-butyl alcohol in sulfuric acid to form the *N-tert*-butyl amide, m.p. 48.5–50°.

Anal. Calcd. for $CH_3CH{=}CHCH_2CONHC(CH_3)_3$: N, 9.02. Found: N, 8.71.

2-Benzylidene-3-pentenenitrile[9] (I). A solution of 3 g. (0.13 mole) of sodium dissolved in 47 g. of absolute ethyl alcohol was added dropwise to a solution of 53 g. (0.5 mole) of freshly distilled benzaldehyde and 32.4 g. (0.4 mole) of 3-pentenenitrile in 316 g. of absolute ethyl alcohol. During the addition of the sodium ethoxide solution over a period of about 45 min., the reaction mixture was stirred and blanketed with nitrogen and the temperature rose from 21° to 36°. The reaction mixture was next heated on a steam bath under a reflux condenser for 3 hr. The crude reaction product was then poured into ice water and extracted with ethyl ether. This ether solution was dried over anhydrous sodium sulfate, filtered, and evaporated on the steam bath. Distillation of the residual oil under reduced pressure yielded 47 g. of 2-benzylidene-3-pentenenitrile (1-phenyl-4-methyl-2-cyano-1,3-butadiene), a light yellow oil, b.p.

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(5) Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940).

(6) Smakula, *Angew. chem.*, **47**, 657 (1934).

(7) Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

(8) Coffman, Salisbury, and Scott, U. S. Patent **2,509,859** (1950).

(9) Pratt, U. S. Patent **2,773,857** (1956).

160°/16 mm.; n_D^{25} 1.6112. On redistillation, through a 30-cm. Fenske ring-packed column at a reflux ratio of 1:10, the product obtained possessed the following constants: b.p. 135–137°/4 mm.; n_D^{25} 1.6110; d_{25}^{25} 1.1040.

2-Isopropylidene-3-pentenenitrile[9] (VIII). Acetone was condensed with 3-pentenenitrile in the same manner as described above for benzaldehyde. The product was distilled through a 76-cm. Nester spinning band column at a reflux ratio of 1:10. The liquid product melted at −8°. The compound added oxygen readily, and it was stored under nitrogen prior to analysis. Low results, particularly for carbon, were obtained until it was discovered that the analytical sample had to be burned very slowly.

The compound showed infrared absorption at 3.4μ for saturated CH, 3.5μ for unsaturated CH, 4.5μ for conjugated nitrile, 6.17μ for conjugated unsaturation, 7.25μ for CH_3, and 10.45μ for a *trans* internal double bond.

2-Isopropylidene-3-pentenenitrile proved difficult to hydrolyze. In contrast with 3-pentenenitrile, no acid or lactone formed when it was boiled with concentrated hydrochloric acid. The nitrile was hydrolyzed by boiling two days with 17% aqueous sodium hydroxide. On acidification and distillation, about 10% of 3-pentenoic acid and about 10% of crude liquid 2-isopropylidene-3-pentenoic acid were recovered. Following a procedure employed by Whyte and Cope[10] to hydrolyze hindered nitriles, 48 g. of 2-isopropylidene-3-pentenenitrile was stirred 15 hr. at reflux temperature with a mixture of 45 g. of potassium hydroxide, 20 g. of water, and 100 ml. of diethylene glycol. After acidification and fractional distillation, 1.7 g. of a straw-colored liquid acid was recovered, n_D^{25} 1.4489, b.p. 82–90°/5 mm.

Anal. Calcd. for $CH_3CH{=}CHC(COOH){=}C(CH_3)_2$: neut. equiv., 140. Found: neut. equiv., 137.3.

Some acetone was liberated, but most of the product was a solid polymer.

2-Isopropylidene-3-pentenenitrile was treated with two mole equivalents of bromine in chloroform at 3°, conditions employed by Craig[11] to prepare the tetrabromide of piperylene. From 4.4 g. of 2-isopropylidene-3-pentenenitrile there was obtained 6.1 g. of needles which were recrystallized from boiling heptane, m.p. 114–116°. No tetrabromide was formed.

Anal. Calcd. for $C_7H_{11}Br_2(CN)$: C, 34.20; H, 3.94; N, 4.99; Br, 56.95. Found: C, 34.26; H, 4.22; N, 5.06; Br, 56.95.

2-Isopropylidene-3-pentenenitrile, unlike 3-pentenenitrile, did not yield a solid *N-tert*-butylamide when reacted with *tert*-butyl alcohol and sulfuric acid in glacial acetic acid by the procedure used by Plaut and Ritter[12] to prepare amides from acrylonitrile.

There was no evidence of reaction when 2-isopropylidene-3-pentenenitrile was mixed with thioglycolic acid and hydrogen chloride in ethyl ether. Under these conditions, Shriner and Fuson[13] indicate that unhindered nitriles form solid α-iminoalkyl mercaptoacetic acid hydrochlorides.

The other compounds listed in the table, II from furfuraldehyde, III from isobutyraldehyde, IV from acetaldehyde, V from crotonaldehyde, VI from *p*-methoxybenzaldehyde, VII from cyclohexanone, and IX from methyl ethyl ketone, were prepared by the same procedure using 32 mole per cent sodium ethoxide, based on 3-pentenenitrile, as the condensing agent. Erroneous carbon and hydrogen results were obtained unless the samples were burned slowly and carefully. These compounds also added oxygen readily, and it was necessary to store samples in an inert atmosphere prior to analysis.

Polymerization. A soft, tacky polymer was obtained by heating 2-benzylidene-3-pentenenitrile with 0.1% of its weight of hydroquinone under nitrogen in a sealed glass tube for 48 hr. at 175°. The resulting benzene-soluble polymer possessed an iodine number 14.7. X-ray diffraction measurements indicated it to be noncrystalline.

Treatment of 2-benzylidene-3-pentenenitrile under 7500 atmospheres pressure at 200° for 5 hr. produced a tough, transparent, red-brown polymer which was harder and less tacky than the polymer prepared by heating for 48 hr. at 175° under atmospheric pressure. It was soluble in benzene and chloroform, but insoluble in ethyl alcohol or acetic acid. The iodine number was 6.4. The molecular weight determined by elevation of the boiling point of a benzene solution was 440.

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[10] Whyte and Cope, *J. Am. Chem. Soc.*, **65**, 1999 (1943).

[11] Craig, *J. Am. Chem. Soc.*, **65**, 1011 (1943).

[12] Plaut and Ritter, *J. Am. Chem. Soc.*, **73**, 4077 (1951).

[13] Shriner and Fuson, *Identification of Organic Compounds*, John Wiley & Sons, Inc., 1948, p. 205.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Some Reactions of Methanesulfinyl Chloride[1]

IRWIN B. DOUGLASS AND BASIL SAID FARAH[2]

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Methanesulfinyl chloride has been found to react with excess of alkanethiols to form mixtures of simple disulfides, with boiling alcohols to form alkyl chlorides, with benzene in the presence of anhydrous aluminum chloride to form methyl benzyl sulfone, and with aromatic amines to form methanesulfinamides.

The ease with which the alkanesulfinyl chlorides can be prepared by the controlled hydrolysis or alcoholysis of alkylsulfur trichlorides according to the equations:

$$RSCl_3 + H_2O \longrightarrow RSOCl + 2HCl$$

$$RSCl_3 + CH_3OH \longrightarrow RSOCl + HCl + CH_3Cl$$

has made these compounds readily available[3] and has led us to study certain reactions of methanesulfinyl chloride.

J. von Braun and Weisbach[4] have reported that some of the lower alkanesulfinyl chlorides are con-

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[1] This work has been supported in part by the Office of Naval Research.

[2] Taken from the Master's thesis of Basil Said Farah.

[3] I. B. Douglass and Donald Poole, *J. Org. Chem.*, **22**, 536 (1957).

[4] J. von Braun and K. Weisbach, *Ber.*, **63B**, 2836 (1930).