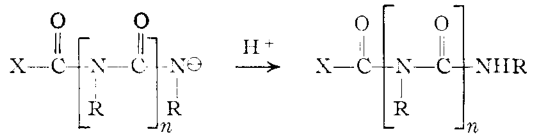
From a study of the polymerization conditions, it is observed that both these reactions do occur. The trimerization reaction is favored at high concentrations of initiator and high temperature. The polymerization reaction is favored by low temperatures, high monomer concentrations and low concentrations of initiator. These facts are consistent with the postulate that the amount of polymer formation is governed by the relative rate of cyclization. By decreasing the temperature the cyclization rate can be rendered small, to favor the linear polymer formation. The reaction is probably more complex than indicated here, since the depolymerization of 1-nylon as illustrated by the case of *p*-methoxyphenyl 1-nylon can also occur in solution.

The termination step most probably occurs during the isolation of the polymer and/or by reaction with adventitious water present in the reaction medium in a similar manner to the reaction termination step:



In this regard, it is of interest to note that the addition of 5% ethyl succinate, 10% acetonitrile or 5% methylene chloride does not markedly influence the polymerization. However, the addition of 1% formamide completely inhibited the polymerization.

Acknowledgment.—We wish to thank Drs. D. Akeley and R. Zbinden, both of Pioneering Research, E. I. du Pont de Nemours & Co., for their assistance in the light scattering molecular weight determinations and the measurement and interpretation of the infrared spectra, respectively.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Alkylation of Nitriles: Ketenimine Formation[1]

BY MELVIN S. NEWMAN, T. FUKUNAGA[2] AND T. MIWA

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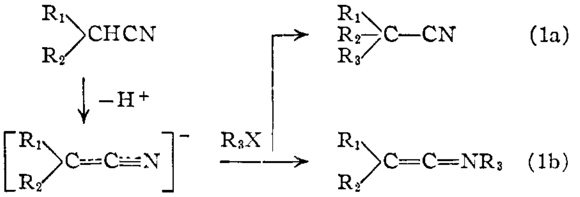
The alkylation of alkylacetonitriles to trialkylacetonitriles by reaction with alkali amides followed by treatment with alkylating agents is described. In the case of diisopropylacetonitrile, alkylation with isopropyl iodide yields moderate amounts of ketenimine as indicated by isolation after hydration as N-isopropyldiisopropylacetamide. In the case of *t*-butylisopropylacetonitrile, only ketenimine was obtained.

The alkylation of nitriles by (1) conversion to an ambident anion[3] with a strong base and (2) reaction of this anion with an alkyl halide, or other alkylating agent, has often been effected.[4-6] To our knowledge, only carbon alkylation has been reported, except for nitrogen alkylation in the case of trimethylchlorosilane.[7]

In connection with a program of synthesis and study of reactions of highly hindered nitriles[8] we had occasion to study the alkylation of highly branched nitriles with a variety of alkylating agents. We now report the formation of substituted ketenimines on alkylation of highly branched nitriles along with the more common carbon alkylation products.



The results of our alkylation studies are summarized in Table I.

In discussion of the factors involved in predicting and controlling the position at which an ambident anion reacts, several factors were mentioned[3] but steric factors were not stressed. The N-alkylation involved in silicoalkylation was explained mainly on steric grounds.[7] We agree that steric factors are largely responsible. Although we have not studied enough cases to define accurately the conditions for controlling the ratio of carbon to nitrogen alkylation of nitriles, it seems obvious that steric factors are important. In no case did N-alkylation occur when the disubstituted nitrile involved had a *six number*[9] of less than 12. For example, alkylation of *t*-butylmethylacetonitrile (expt. 20) with methyl bromide, *t*-butylethyl-

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[1] This research was supported largely by the United States Air Force under Contract No. AF33(616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center. Early support from the Research Corporation, 1956–1957, is gratefully acknowledged.

[2] Part of the material herein presented was taken from the Ph.D. Thesis, Ohio State University, 1959, of T. Fukunaga.

[3] We support the use of the term "ambident" for an anion capable of undergoing alkylation at two (or more) positions. See (a) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955); (b) D. Y. Curtin, R. J. Crawford and M. Wilhelm, *ibid.*, **80**, 1391 (1958); (c) N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

[4] For reviews see (a) A. C. Cope, H. L. Holmes and H. O. House, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1957, Vol. IX, p. 107; and (b) F. W. Bergstrom and W. C. Fernelius, *Chem. Revs.*, **20**, 451 (1937).

[5] C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).

[6] R. L. Jacobs and G. L. Goerner, *J. Org. Chem.*, **21**, 837 (1956).

[7] M. Prober, THIS JOURNAL, **78**, 2274 (1956), termed this alkylation "silicoalkylation."

[8] L. Tsai, T. Miwa and M. S. Newman, *ibid.*, **79**, 2530 (1957).

[9] For definition and discussion of the *six number* see M. S. Newman, *ibid.*, **72**, 4783 (1950), and M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 4, p. 203 ff.

TABLE I

ALKYLATION OF NITRILES

Run	R_1R_2CHCN		R_3X		Metal	Mole ratio of R_3X/R_1R_2-CHCN	Method[a]	Reaction time, hr.	Yield, %		Ratio of yields C-alkyl/N-alkyl
	R_1	R_2	R_3	X					C-Alkylation[b]	N-Alkylation	
					I. Triethylacetonitrile[c]						
1	C_2H_5	H	C_2H_5	Br	Na	2.0	A	23	58	0	..
2			C_2H_5	I	Na	2.1	A	19	49	0	..
3			C_2H_5	$C_2H_5SO_4$	Na	2.1	B	24	63	0	..
4			C_2H_5	CH_3SO_3	Na	2.1	A	30	0[d]	0	..
5			C_2H_5	$C_6H_5SO_3$	Na	2.2	A	24	0[d]	0	..
					II. Diisopropylmethylacetonitrile						
6	CH_3	H	i-C_3H_7	I	Na	2.1	A	27	59	0	..
7	i-C_3H_7	i-C_3H_7	CH_3	Br	Na	4.4	B	30	81	0	..
					III. Diisopropylethylacetonitrile[e]						
8	C_2H_5	H	i-C_3H_7	Br	Na	2.1	A	24	58	0	..
9			i-C_3H_7	I	Na	2.2	A	24	77	0	..
10	i-C_3H_7	i-C_3H_7	C_2H_5	Br	Na	1.5	B	30	78	0	..
					IV. Triisopropylacetonitrile						
11	H	H	i-C_3H_7	I	Na	3.3	A	25	18	14[f]	1.3
12	i-C_3H_7	H	i-C_3H_7	I	Na	2.2	A	30	34	12[f]	2.8
13	i-C_3H_7	i-C_3H_7	i-C_3H_7	I	Na	2.1	A	25	37	23[f]	1.6
14				I	Na	1.3	C	18	50	25[f]	2.0
15				I	K	1.3	C	30	42	26[f]	1.6
16				I	K	1.3	C	48	45	19[f]	2.4
17				I	Li	1.3	C	30	39	26[f]	1.5
18				Br	K	1.4	C	12	33	25[f]	1.3
					V. Miscellaneous						
19	i-C_3H_7	i-C_3H_7	i-C_4H_9	Br	K	1.1	C	15	84	Trace[f]	∞
20	t-C_4H_9	H	CH_3	Br	Na	4.4	B	35	78	0	..
21			C_2H_5	Br	Na	2.2	A	40	65	0	..
22			i-C_3H_7	I	Na	2.4	C[g]	30	0[h]	56[f]	..
23			i-C_3H_7	I	Na	3.6	A	30	0	28[i]	0
24	t-C_4H_9	i-C_3H_7	C_2H_5	Br	Na	1.2	A	24	56	Small[i]	Large
25			i-C_4H_9	Br	Na	1.1	A	24	39	12[i]	3.2

[a] See Experimental for descriptions of methods A, B and C. [b] Yields refer only to trialkylacetonitriles which boiled over a 3° range and had physicals constants which agreed with the literature values. The properties of the new compounds are reported in Table II and in the Experimental part. [c] K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932), reported a b.p. of 165–170°; C. Schuerch, Jr., and E. H. Huntress, THIS JOURNAL, **70**, 2824 (1948), reported $n^{20}D$ 1.4219. [d] Diethylacetonitrile was obtained in about 35% yield. [e] K. Ziegler and H. Ohlinger, ref. *c*, reported a b.p. of 85° at 12 mm. [f] Isolated as the corresponding amide after treatment with aqueous acid. [g] Both the nitrile and the alkylating reagent were added in ethereal solution. [h] t-Butylisopropylacetonitrile was obtained in 43% yield. [i] Isolated as ketenimine.

acetonitrile (expt. 21) with ethyl bromide, and the diethyl- or ethylisopropylacetonitriles (expts. 1–10) with various alkylating agents did not yield any ketenimines.[10] However, alkylations of diisopropylacetonitrile (six number, 12) with isopropyl iodide yielded appreciable ketenimine (expts. 11–18) while alkylation of t-butylisopropylacetonitrile (six number, 15) with isopropyl iodide yielded exclusively ketenimine (expts. 22, 23). We have not yet attempted to work out conditions for maximizing the yield of ketenimine in this or other cases. This work is being continued. It is possible that alkylation of di-t-butylacetonitrile will yield mainly ketenimine with all alkyl halides.[11]

Experimental[12]

Diisopropylacetonitrile.—Ethyl diisopropylcyanoacetate was prepared by alkylation of ethyl cyanoacetate (226 g.) as described[13] in 84% yield.[14] The ester (334.5 g.) was hydrolyzed[14] by refluxing with 100 ml. of ethanol and 1200 g. of 35% potassium hydroxide for 26 hours[15] until the mixture was homogeneous to give a 98% yield of crude diisopropylcyanoacetic acid. The cyanoacetic acid (282 g.) was heated at 180–200° with 2 g. of copper powder (Copper Metal, precipitated powder, J. T. Baker Chemical Co., Phillipsburg, N. J.). Vigorous evolution of carbon dioxide ensued and occasionally moderate cooling was necessary. After the evolution of gas had subsided, diisopropylacetonitrile was obtained by fractionation through a glass helices-

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(10) In some of the earlier experiments infrared examination of the crude reaction product was not made. Hence, small amounts of ketenimine may have been missed. Ketenimines absorb at 4.9–5.0μ; C. L. Stevens and J. C. French, THIS JOURNAL, **75**, 657 (1953). However, we do not believe appreciable amounts were formed as the amides resulting from treatment of ketenimines with water would have been detected; see footnote *f*, Table I.

(11) The synthesis of di-t-butylacetic acid has recently been accomplished in good yield. Its reactions will be the subject of a forthcoming paper.

(12) Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. All melting points are corrected. Acetonitrile, propionitrile and isovaleronitrile were purified by distillation.

(13) For the introduction of the second isopropyl group, the reaction mixture was heated at reflux for 2 hours and at about 80° overnight with continuous stirring.

(14) This procedure is essentially that of (a) F. C. B. Marshall, *J. Chem. Soc.*, 2754 (1930); (b) M. S. Newman and R. J. Harper, Jr., THIS JOURNAL, **80**, 6353 (1958).

(15) The time required for the hydrolysis appeared to be cut down by adding more alcohol to the reaction mixture.

TABLE II

NEW TRIALKYLACETONITRILES, $R_1R_2R_3CCN$

R_1	R_2	R_3	B.p., °C.[a]	$n^{25}D$	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
i-C_3H_7	i-C_3H_7	CH_3	186–187	1.4288	77.6	77.2	12.3	12.8	10.1	9.9
i-C_3H_7	i-C_3H_7	C_2H_5	80–81(10)[b]	1.4386	78.4	78.3	12.5	13.0	9.1	9.1
i-C_3H_7	i-C_3H_7	i-C_3H_7	220–221	1.4491	79.0	79.0	12.7	12.9	8.4	8.1
i-C_3H_7	i-C_3H_7	i-C_4H_9	82–83(3)	1.4443	79.5	79.6	12.8	13.0	7.7	7.7
t-C_4H_9	CH_3	CH_3	168–169[c]		76.7	76.7	12.1	12.1	11.2	11.2
t-C_4H_9	C_2H_5	C_2H_5	198–200	1.4350	78.4	78.6	12.5	12.5	9.1	9.0
t-C_4H_9	i-C_3H_7	C_2H_5	223–224	1.4497	79.0	78.8	12.7	13.1	8.4	8.2
t-C_4H_9	i-C_3H_7	i-C_4H_9	89.0–89.5	1.4490	79.9	80.1	12.9	13.1	7.2	7.3

[a] B.p. at atmospheric pressure except as noted in parentheses. [b] K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932), reported a b.p. of 85° at 12 mm., but gave no analytical data. [c] M.p. 133.6–134.2°; F. C. Whitmore, R. E. Marker and L. Plambeck, Jr., THIS JOURNAL, **63**, 1626 (1941), reported a m.p. of 131–132°, but gave no analytical data.

packed column as a colorless oil, b.p. 168–169°, $n^{22}D$ 1.4167 (reported[14a] b.p. 170°, $n^{23}D$ 1.4158), in 85% yield.

***t*-Butylacetonitrile.**—Ethyl *t*-butylcyanoacetate was prepared in 59% yield as described.[16] The ester was saponified and decarboxylated[17] to give *t*-butylacetonitrile, b.p. 135–137° (reported[17] b.p. 137°), in 72% yield.

***t*-Butylisopropylacetonitrile** was prepared according to the method described.[8] It may be noted that the crude alkylation product, ethyl *t*-butylisopropylcyanoacetate, had a medium infrared absorption band at 5.0 μ characteristic ketenimine.[10]

Alkylation of Nitriles.—A procedure similar to that described[18] was followed. Sodium,[19] lithium[12] and potassium[20] amides were prepared as described. When the cation was sodium a suspension of sodium amide in liquid ammonia was present; when lithium and potassium amides were involved the amide system appeared to be homogeneous. Three general methods of alkylation were used: method A: A mixture of nitrile and alkylating reagent was added to the alkali amide–liquid ammonia system. Method B: Nitrile was added first and immediately followed by addition of alkylating reagent. Method C: Nitrile was added first and after stirring for one hour the alkylating reagent was added.

A Dry Ice–acetone reflux condenser was used so that the reaction could be conveniently carried out for a long period at reflux temperature of ammonia.

After a certain period of refluxing, liquid ammonia was evaporated on the steam-bath and a sufficient amount of water was added to dissolve salts in the residue. The organic layer, to which ether–benzene extracts of the aqueous layer were added, was washed successively with 2 *N* hydrochloric acid, water and saturated sodium chloride solution and dried with anhydrous magnesium sulfate. After evaporating the solvent, the residue was distilled to yield trialkylacetonitrile (expts. 1–10, 20 and 21). The new trialkylacetonitriles are listed in Table II.

N-Isopropyldiisopropylacetamide (Expts. 11–18).—The reaction product was worked up as described above and after evaporating the solvent the residue was cooled in a Dry Ice–acetone-bath to separate crystalline amide, which was filtered and washed with cold petroleum ether (b.p. 35–55°) to give N-isopropyldiisopropylacetamide, m.p. 168–169°. The filtrate and washings were distilled to give triisopropylacetonitrile. Recrystallization of the amide from benzene–petroleum ether (b.p. 65–69°) afforded pure N-isopropyldiisopropylacetamide, m.p. 168.8–169.4°, undepressed by mixing with a sample of the amide, 168–169°, prepared from diisopropylacetyl chloride and isopropylamine.

Anal. Calcd. for $C_{11}H_{23}NO$: N, 7.6. Found: N, 7.6.

N-Isopropyldiisopropylacetonitrile was recovered unchanged after the following attempts at hydrolysis: refluxing with 35% potassium hydroxide for 24 hours; refluxing with 40% hydrobromic acid in acetic acid for 45 hours; and refluxing with concentrated hydrochloric acid in dioxane for 24 hours. Treatment with sodium nitrite in 75% sulfuric acid at 50° was without effect.

N-Isopropyl-*t*-butylisopropylacetamide (Expt. 22).—The reaction product was worked up as described above without acid washing. After removing the solvent the residue was dissolved in petroleum ether (b.p. 35–55°) and treated with 6 *N* hydrochloric acid with shaking in an ice–water-bath. A highly exothermic reaction took place and a large amount of white crystalline substance was formed. It was filtered and washed with cold petroleum ether (b.p. 35–55°) to yield N-isopropyl-*t*-butylisopropylacetamide, m.p. 150.3–150.8° (recrystallized from benzene–petroleum ether boiling at 65–69°), undepressed by mixing with a sample of the amide, m.p. 150.1–150.6°, prepared from *t*-butylisopropylacetyl chloride and isopropylamine.

Anal. Calcd. for $C_{12}H_{25}NO$: C, 72.3; H, 12.6; N, 7.0. Found: C, 72.4, 72.6; H, 12.8, 12.5; N, 7.0, 7.1.

The filtrate and washings were distilled to give *t*-butylisopropylacetonitrile (see Table II).

N-Isopropyl-*t*-butylisopropylketenimine (Expt. 23).—The reaction product was worked up in the usual manner without acid washing. After removing the solvent the residue was fractionally distilled to yield N-isopropyl-*t*-butylisopropylketenimine,[21] b.p. 73–74° (14 mm.), $n^{19}D$ 1.4481, d^{19} 0.7958.

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.5; H, 12.8; N, 7.7. Found: C, 78.9; H, 12.4; N, 7.8.

N-Isobutyl-*t*-butylisopropylketenimine (Expt. 25).—The reaction product was treated as for the above ketenimine. Fractional distillation of the organic residue afforded N-isobutyl-*t*-butylisopropylketenimine, b.p. 90.5–91.8° (14 mm.), $n^{24}D$ 1.4480, d^{24} 0.7960.

Anal. Calcd. for $C_{13}H_{25}N$: C, 79.9; H, 12.9; N, 7.2. Found: C, 79.7; H, 13.2; N, 7.0.

Isobutyl-*t*-butylisopropylacetonitrile was obtained as a higher boiling fraction (see Table II).

Pure samples of N-isopropyldiisopropylketenimine,[21] N-isobutyldiisopropylketenimine (expt. 19) and N-ethyl-*t*-butylisopropylketenimine (expt. 24) were not obtained either because of the small yield or because the boiling point was too close to that of the corresponding isomeric or dialkylated acetonitriles. The presence of these ketenimines was, however, confirmed by an infrared absorption band at 5.0 μ.

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[16] S. Wideqvist, *Acta Chem. Scand.*, **3**, 303 (1949); *Arkiv. Kemi*, **2**, 321 (1950).

[17] A. J. Birch, *J. Chem. Soc.*, 2721 (1949).

[18] F. W. Bergstrom and R. Agostinho, THIS JOURNAL, **67**, 2152 (1945).

[19] C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 122.

[20] R. S. Yost and C. R. Hauser, THIS JOURNAL, **69**, 2325 (1947).

[21] The ketenimine appeared to be quite stable. The crude ketenimine could be kept at room temperature for at least three months without any change in the infrared spectrum.