Anal. Calcd. for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 63.11, 63.35; H, 8.33, 8.18; N, 4.08; 3.95 (Dumas); N, 5.64, 5.55 (Kjeldahl). The infrared spectrum showed strong peaks at 1558 cm.$^{-1}$ and 1720–30 cm.$^{-1}$; lesser peaks appeared at 1340 cm.$^{-1}$ and 1137 cm.$^{-1}$

The *bisphenylhydrazone*, prepared in the usual manner,[28] melted at 151.8–154.8° after thorough washing with 95% ethanol.

Anal. Calcd. for $C_{26}H_{33}N_5O_2$: C, 69.76; H, 7.43. Found: C, 69.41, 69.51; H, 7.37, 7.52.

The *bis-2,4-dinitrophenylhydrazone* was prepared by allowing 0.05 g. of the ketone to react with 5.4 ml. of 2,4-dinitrophenylhydrazine solution (5% sulfuric acid in ethanol; 66 ml. contain 1 g. of 2,4-dinitrophenylhydrazine) at room temperature for 18 hours. The red-orange solid, washed three times with cold 95% ethanol, melted at 117.5–119.5°.

Anal. Calcd. for $C_{26}H_{29}N_9O_{10}$: C, 49.74; H, 4.66. Found: C, 50.12, 50.20; H, 4.78, 5.06.

1-Keto-1,2-bis(2-ketocyclohexyl)ethane (X). A suspension of 1.0 g. (0.0038 mole) of 1-nitro-1,2-bis(2-ketocyclohexyl)ethane (IXa) in 20 ml. of absolute ethanol was cooled under a nitrogen atmosphere. To the magnetically stirred suspension was added over a period of 30 min. a solution resulting from the reaction of 0.15 g. (0.0075 mole) of sodium with 15 ml. of absolute ethanol.[15] The resulting yellow sodio-salt solution was stirred for 1 hr. with cooling under the nitrogen atmosphere.

The cold sodio-salt solution was added, over a period of 30 min., to a chilled solution of 0.5 ml. (0.008 mole) of concd. hydrochloric acid in 5 ml. of water and 4 ml. of ethanol. Stirring of the yellow solution was continued for 1 hr., after which 50 ml. of water was added. The organic material was recovered by four extractions with 35-ml. portions of ether. The ether extracts were washed twice with 5% sodium carbonate solution and four times with water. The residual yellow oil obtained from the dried ether extracts could not be crystallized. The infrared spectrum of the oil showed a very strong carbonyl band at 1707 cm.$^{-1}$, a less strong band at 1542 cm.$^{-1}$, and a weak band at 1605 cm.$^{-1}$

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-ketophenanthrene (XI). The same procedure[15] used above to obtain triketone X was followed, using 2.0 g. of dodecahydro-9-nitrophenanthrene (Ia). The ether was removed from the dry extracts without heat; a stream of nitrogen aided the process. The infrared spectrum of the residual oil had strong bands at 1705 cm.$^{-1}$ and 1542 cm.$^{-1}$; there was a weak band at 1660 cm.$^{-1}$ An ultraviolet spectrum (in iso-octane) showed a plateau at 265–290 mμ (ε 147).

Reaction of some of the ethereal extracts with chilled 2,4-dinitrophenylhydrazine solution for 20 min. at 0° produced a yellow-orange precipitate which was removed by filtration and washed once with 5% potassium carbonate solution and three times with water.[16] This *yellow 2,4-dinitrophenylhydrazone* melted at 158.0–158.6° after recrystallization from ethyl acetate and ethanol.

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29. Found: C, 62.16, 62.40; H, 6.27, 6.02. The ultraviolet spectrum (in chloroform) had a slight inflection at 260 mμ.

A red 2,4-dinitrophenylhydrazone, identical with that obtained below, was isolated by allowing the ketonic oil to react with acidic 2,4-dinitrophenylhydrazine solution at room temperature for several hours.

1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-9-ketophenanthrene (XII). A solution of 2.5 g. (0.01 mole) of dodecahydro-9-nitrophenanthrene and 1 g. (0.025 mole) of sodium hydroxide in 40 ml. of ethanol was cooled for 30 min.[29] The yellow solution was poured rapidly into 70 ml. of cold 1:6 hydrochloric acid. The resulting mixture was stirred with cooling for 1.5 hr.; it was allowed to warm to room temperature overnight.

The organic material was extracted from the solution with ether; the ether was removed from the dry extracts by heating on a steam bath. The residual brown oil could not be crystallized; its infrared spectrum had a strong band at 1660 cm.$^{-1}$ and weak peaks at 1707 and 1545 cm.$^{-1}$ Its ultraviolet spectrum (in isooctane) showed maxima at 235 mμ (ε 3,880) and 280 mμ (ε 940).

A *brick-red 2,4-dinitrophenylhydrazone*, melting at 233.5–234.1° after recrystallization from ethyl acetate and ethanol (1:1), was isolated.

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29. Found: C, 62.37, 62.33; H, 6.17, 6.44. Its chloroform solution showed an inflection at 293 mμ and a maximum at 260 mμ (ε 20,400) in the ultraviolet.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophenanthrene (Ia) from its sodio salt. Sodio salt was prepared from 2.0 g. of dodecahydro-9-nitrophenanthrene (Ia) by reaction with ethanolic sodium ethoxide at 0° under a nitrogen atmosphere. To the sodio-salt solution was added over a period of 20 min. a chilled solution of 1.25 g. (0.018 mole) of hydroxylamine hydrochloride[17] in 25 ml. of water. The mixture was stirred with cooling.

The weight of recovered product (from aqueous ethanol) was 0.82 g. (41%); it was identical with the adduct in melting point, mixed melting point, and infrared spectrum.

COLLEGE PARK, MD.

---

(28) R. Shriner and R. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 1948 (3rd ed.), p. 116.

(29) A. B. Ross, Ph.D. thesis, University of Maryland, 1957.

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

A Study of the Alkylation of β,β,β-Trialkylpropionitriles

NORMAN RABJOHN AND P. R. STAPP[1]

Received May 9, 1960

A study has been made of the alkylation of β,β,β-trialkylpropionitriles (I) by means of alkyl halides and sodamide. It has been found that α-alkylated nitriles (II), N-α-dialkyl substituted ketenimines (III) and α,α-dialkylated nitriles (IV) are formed in varying proportions depending upon conditions.

In view of the recent report[2] of the isolation of ketenimines from the alkylation of dialkylacetonitriles, we wish to describe our results on the alkylation of β,β,β-trialkylpropionitriles (I) which confirm and

---

(1) Phillips Petroleum Fellow, 1959–60.

(2) M. S. Newman, T. Fukunaga, and T. Miwa, *J. Am. Chem. Soc.*, **82**, 873 (1960).

TABLE I

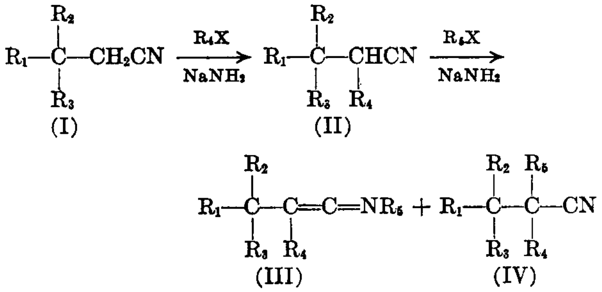
ALKYLATION OF 3,3-DIPROPYLHEPTANONITRILE WITH *n*-BUTYL BROMIDE IN VARIOUS SOLVENTS

Solvent	Moles Halide[a] /Moles Nitrile	Reflux Time, Hr.	% Yield of Alkylated Product, IIa + IIIa + IVa	Composition of Alkylated Product, Weight % IIa	IIIa	IVa
Liquid ammonia	1.1	3	89	94	6.0	Trace
Benzene	3.0	48	93	70	9.6	19.9
Benzene	3.0	24	14	100	Trace	0
Benzene	1.1	48	71	98	1.6	0
Ether	1.1	48	84	96	4.3	0
Ether	1.1	24	85	96	4.2	0
Toluene	1.1	24	57	78	22[b]	0
Tetrahydrofuran	1.1	24	23	84	16[c]	0

[a] Equimolar amounts of alkyl halide and sodamide were employed in each experiment. [b] Determined by titration with standard bromine solution. [c] The percentage ketenimine as determined by titration with standard bromine solution was 15%.

supplement the work of Newman and his associates.

Preliminary experiments on the alkylation of several β,β,β-trialkylpropionitriles (I), by means of alkyl halides and commercial sodamide in varying proportions and in different solvents, led to α-alkylated nitriles (II) in poor yields, and/or inseparable mixtures of II, ketenimines (III), α,α-dialkylated nitriles (IV) and unidentified by-products with infrared absorptions at 6.2 μ, which were probably amidines.[3] The presence of ketenimines was inferred on the basis of a strong absorption band at 5.0 μ in the spectra of the reaction mixtures.[4] In addition, hydrolysis of the mixtures caused the disappearance of the band at 5.0 μ with the appearance of bands at 3.0, 6.1, and 6.5 μ, which are characteristic of *N*-alkylamides[5]; however, the amides could not be isolated in a pure state. The use of a large excess of sodamide and alkyl halide, as well as higher reaction temperatures, increased significantly the amount of the unidentified by-products. Attempts at preforming the carbanion from the nitrile by heating a mixture of the latter with sodamide in the solvent, before adding the alkyl halide, apparently resulted also in increased amidine formation with no noticeable increase in yield of alkylated materials.



Ia = Ib = Ic

Ia–IVa
$R_1 = R_4 = R_5 = n\text{-}C_4H_9$
$R_2 = R_3 = n\text{-}C_3H_7$

IIb–IVb
$R_1 = n\text{-}C_4H_9$
$R_2 = R_3 = n\text{-}C_3H_7$
$R_4 = R_5 = n\text{-}C_8H_{17}$

IIc–IVc
$R_1 = n\text{-}C_4H_9$
$R_2 = R_3 = n\text{-}C_3H_7$
$R_4 = R_5 = i\text{-}C_4H_9$

In an effort to obtain higher yields of alkylated products, a systematic investigation was undertaken of the alkylation of 3,3-dipropylheptanonitrile (Ia) with *n*-butyl bromide in a number of solvents. Relatively mild conditions were employed, as compared with those in the preliminary study, and the products were analyzed by gas chromatography. Mixtures of unchanged starting material (Ia), 2-butyl-3,3-dipropylheptanonitrile (IIa), the ketenimine, 5-aza-7-butyl-8,8-dipropyl-5,6-dodecadiene (IIIa) and 2,2-dibutyl-3,3-dipropylheptanonitrile (IVa) were obtained as summarized in Table I. No amidine formation was observed under these conditions.

It appears that when dialkylation occurred, IIIa was formed almost to the exclusion of IVa in most cases. The relative ease of alkylation of Ia in ether as compared with the higher boiling solvents was of interest also. Since alkylation in liquid ammonia gave results comparable to commercial sodamide in ether, further studies were carried out with the latter system as a matter of convenience.

The structure of IIIa was determined by hydrolysis of the mixture from Run 7 and removal of IIa by distillation. The residual *N*,2-dibutyl-3,3-dipropylheptanamide was shown to be identical with a sample of the amide prepared from 2-butyl-3,3-dipropylheptanoic acid.

A series of alkylations of Ia was performed then using different alkyl halides. The mixtures of α-alkylated nitriles and ketenimines were analyzed again either by gas chromatography or by titration with standard bromine solution. The results are tabulated in Table II.

---

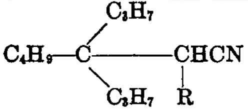
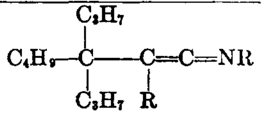
[3] N. Sperber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70**, 3091 (1948); C. J. Eby and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 723 (1957).

[4] C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953).

[5] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., J. Wiley and Sons, Inc., New York, 1958, p. 211.

TABLE II

ALKYLATION OF 3,3-DIPROPYLHEPTANONITRILE WITH VARIOUS HALIDES IN ETHER

Halide	% Yield of Alkylated Products	Composition of Alkylated Product, Weight %	
			 $C_4H_9-\underset{C_3H_7}{\overset{C_3H_7}{C}}-\underset{R}{C}=C=NR$
C_2H_5Br	89	96.7	3.3[a,b]
n-C_4H_9Br	85	95.8	4.2[a]
i-C_4H_9Br	75	88.1	11.9[b]
i-C_4H_9Cl	38	85.6	14.4[b]
s-C_4H_9Br	30	79.6	20.4[b]
i-$C_5H_{11}Br$	73	93.6	6.4[b]
n-$C_8H_{17}Br$	93	92.4	7.6[c]
$C_6H_{11}Br$	5	87.3	12.7[b]
C_6H_5Br	10	100	0
$CH_2{=}CHCH_2Cl$	Trace	—	—
$C_6H_5CH_2Cl$	0	—	—
$C_6H_5CH_2Cl$	31[d]	100	0

[a] Determined by gas chromatographic analysis. [b] Determined by titration with standard bromine solution. [c] Determined by isolation. [d] Run in refluxing toluene for 24 hr.

In contrast to the findings of Goerner and Holzschuh,[6] it was observed that, with the butyl bromides, the yields of alkylated nitriles varied in the order: normal > iso > secondary. The alkylations with ethyl, isoamyl, and n-octyl bromides proceeded normally to give the expected mixtures of α-alkylated nitriles and ketenimines in essentially the same ratios as those obtained by alkylation with n-butyl bromide. Since the boiling points of 2-octyl-3,3-dipropylheptanonitrile (IIIb) and the ketenimine, 8-aza-6-octyl-5,5-dipropyl-6,7-hexadecadiene (IIIb) are fairly far apart, it was possible to separate the mixture by fractional distillation. No isolable amount of the α,α-dialkylated nitrile, 2,2-dioctyl-3,3-dipropylheptanonitrile (IVb), was present.

Phenylation of Ia by means of bromobenzene and sodamide in refluxing ether was accomplished, though in low yield, with no evidence of ketenimine formation. This is in agreement with the results of Bunnett and Brotherton[7] and Bergstrom and Agostinho[8] who found that aliphatic nitriles can be phenylated in liquid ammonia.

In view of the many successful alkylations of aliphatic nitriles with both benzyl and allyl chlorides,[9] the data for these reactions of Ia given in Table II are of interest. Attempted alkylation of Ia with benzyl chloride in refluxing ether for twenty-four hours afforded a nearly quantitative recovery of unchanged starting materials. In a similar experiment, employing allyl chloride, 89% of Ia was recovered along with a considerable amount of polymeric material (presumably from the reaction of allyl chloride with sodamide). A vapor phase analysis of the Ia indicated a purity of 99%, with only trace amounts of 2-allyl-3,3-dipropylheptanonitrile present. The alkylation of Ia with benzyl chloride was accomplished in 31% yield, however, by carrying the reaction out in refluxing toluene.

The observation that no ammonia was liberated on refluxing an ether solution of Ia with sodamide supports the view that the α-hydrogen atoms would be expected to be less acidic than those in a simple monosubstituted acetonitrile. Apparently the formation of the carbanion is an equilibrium process. Likewise, the α-alkylated nitriles (II) must afford ambident anions; otherwise, it would be difficult to account for the presence of ketenimines.

The dialkylation of Ia was undertaken then with a large excess of isobutyl bromide and sodamide in order to obtain a sufficient amount of a relatively pure ketenimine for further study. After careful fractionation, there was obtained a 63% yield of 4-aza-6-isobutyl-2-methyl-7,7-dipropyl-4,5-undecadiene (IIIc) in 88% purity (contaminated by 12% of IVc). A sample of this material was hydrolyzed to an amide which was shown to be identical with authentic N,2-diisobutyl-3,3-dipropylheptanamide. An attempt to characterize the ketenimine (IIIc) by conversion to an α-bromoamide, by treatment with bromine followed by hydrolysis with aqueous acetic acid, resulted in the formation of N,2-diisobutyl-3,3-dipropylheptanamide. The reaction was not investigated further, but it seems possible that the α-bromoimino bromide suffered loss of bromine and reverted to the ketenimine which then was hydrolyzed.

In Table III are recorded the results of alkylation studies on two 2-alkyl-3,3-dipropylheptanonitriles (II). The reactions were performed under the same conditions as were employed previously with 3,3-dipropylheptanonitrile (Ia). The mixtures of II, ketenimines (III), and 2,2-dialkyl-3,3-dipropylheptanonitriles (IV) were analyzed also by gas chromatography. The data illustrate the steric

---

[6] G. L. Goerner and A. A. Holzschuh, *J. Org. Chem.*, **23**, 1346 (1958).

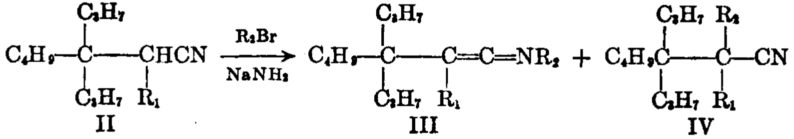
[7] J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **23**, 904 (1958).

[8] F. W. Bergstrom and R. Agostinho, *J. Am. Chem. Soc.*, **67**, 2152 (1945).

[9] A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, **9**, 294 (1957).

TABLE III

ALKYLATION OF 2-ALKYL-3,3-DIPROPYLHEPTANONITRILES WITH VARIOUS HALIDES



$$C_4H_9-\underset{C_3H_7}{\overset{C_3H_7}{C}}-\underset{R_1}{CHCN} \xrightarrow[NaNH_2]{R_2Br} C_4H_9-\underset{C_3H_7}{\overset{C_3H_7}{C}}-\underset{R_1}{C}=C=NR_2 + C_4H_9\underset{C_3H_7}{\overset{C_3H_7}{C}}-\underset{R_1}{\overset{R_2}{C}}-CN$$

II III IV

R_1	R_2	Solvent	% Yield II	III	IV	Ketenimine/Dialkylated Nitrile
n-C_4H_9	*n*-C_4H_9	Ether	16.7	43.6	37.5	1.16
n-C_4H_9	*i*-C_4H_9	Ether	50.1	32.7	13.8	2.37
i-C_4H_9	*i*-C_4H_9	Ether	65.3	28.4	06.2	4.58
n-C_4H_9	*n*-C_4H_9	Tetrahydrofuran	34.0	39.0	27.2	1.44

influence of carbon *vs.* hydrogen atoms in evaluating steric hindrance by the "rule of six."[10] All of the monoalkylated nitriles (II) have a "six number" of 12, and all of the dialkylated nitriles (IV) have a "six number" of 15, yet the ratio of nitrogen to carbon alkylation (which is undoubtedly related to steric factors), approximately doubles upon increasing the number of carbon atoms in the six position from 4 to 5 (Experiments 2 and 3, Table III).

An attempt to isolate 2,2-dibutyl-3,3-dipropylheptanonitrile (IVa) from Experiment 1, Table III met with only partial success. The reaction mixture was hydrolyzed to convert the ketenimine to an amide and then distilled. Three careful fractionations finally produced a small amount of pure IVa.

EXPERIMENTAL[11]

3,3-Dipropylheptanonitrile (Ia) was prepared in 42% yield from 4-heptanone according to the method of Rabjohn, Phillips, and DeFeo[12]; b.p. 137–138° (20 mm.), n_D^{25} 1.4420.

Anal. Calcd. for $C_{13}H_{25}N$: C, 79.93; H, 12.90. Found: C, 80.36; H, 13.08.

Alkylation of Ia *with n-butyl bromide in various solvents.* A mixture of Ia, commercial sodamide, *n*-butyl bromide, and 100 ml. of the appropriate dry solvent for each 0.1 mole of nitrile was refluxed for the specified time in a 1-l. three necked flask fitted with a sealed stirrer and a reflux condenser protected with a drying tube. After cooling, the mixture was filtered with suction through a sintered glass filter, the solvent was removed, and any unchanged starting material was removed by careful fractionation through a modified Podbielniak column.[13] The resulting mixtures of 2-butyl-3,3-dipropylheptanonitrile (IIa), 5-aza-7-butyl-8,8-dipropyl-5,6-dodecadiene (IIIa), and 2,2-dibutyl-3,3-dipropylheptanonitrile (IVa) were analyzed by gas chromatography[14] or by titration with standard bromine solution[15,16] with the results shown in Table I.

Alkylation of Ia *with n-butyl bromide in liquid ammonia.* To a suspension of sodamide from 3.8 g. (0.165 g.-atom) of sodium in 200 ml. of liquid ammonia, was added 29.3 g. (0.15 mole) of Ia and the mixture was stirred for 15 min. Then 22.6 g. (0.165 mole) of *n*-butyl bromide was added dropwise over a period of 30 min., the mixture was stirred for 3 hr., 150 ml. of dry ether was added, and the ammonia was allowed to evaporate at room temperature. The mixture was filtered through a sintered glass filter, the ether was removed, and the residue was distilled under reduced pressure. There was obtained 35.1 g. of material, b.p. 140–175°/1 mm., which was analyzed by gas chromatography. The composition of the product is indicated in Table I.

Isolation of 2-butyl-3,3-dipropylheptanonitrile (IIa) *and N,2-dibutyl-3,3-dipropylheptanamide.* A mixture of 13.8 g. of IIa and IIIa (from treatment of 0.1 mole of Ia with 0.11 mole of sodamide and 0.11 mole of *n*-butyl bromide in toluene for 24 hr.) was boiled with 100 ml. of 95% ethanol, 10 ml. of water, and 1 ml. of 10% hydrochloric acid for 4 hr. The ethanol was removed by distillation, the residue was poured into 200 ml. of water, and the mixture was extracted several times with ether. The combined ether extracts were washed with water, 10% sodium bicarbonate solution, again with water, and then were dried over magnesium sulfate. The solution was filtered, the ether was removed, and the residue was distilled under reduced pressure. There was obtained 9.4 g. (37.5% based on Ia) of IIa as a viscous, colorless oil, b.p. 165–167°/20 mm., n_D^{25} 1.4520.

Anal. Calcd. for $C_{17}H_{33}N$: C, 81.20; H, 13.23. Found: C, 81.33; H, 13.28.

The high boiling residue in the distillation flask solidified on cooling. This was recrystallized from acetonitrile and 2.0 g. (16% based on Ia) of *N*,2-dibutyl-3,3-dipropylheptanamide was obtained as fluffy, colorless needles, m.p. 118–122°. One additional recrystallization from acetonitrile raised the melting point to 122–124°. A mixed melting point with authentic *N*,2-dibutyl-3,3-dipropylheptanamide (see below) melted at 123–125°, and the infrared spectra were also identical.

No 2,2-dibutyl-3,3-dipropylheptanenitrile (IVa) was detected in either the distillate or the residue.

Preparation of 2-butyl-3,3-dipropylheptanoic acid. A modi-

---

[10] M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950); M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, p. 206.

[11] All melting points are uncorrected. The carbon, hydrogen, and nitrogen analyses were performed by Drs. Weiler and Strauss of Oxford, England.

[12] N. Rabjohn, L. V. Phillips, and R. J. DeFeo, *J. Org. Chem.*, **24**, 1964 (1959).

[13] J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall Inc., New York, 1950, p. 237.

[14] The gas chromatographic analyses were performed on a Perkin-Elmer Model 154 Vapor Fractometer using Column C (Silicone Oil) at a temperature of 225°. Helium was used as a carrier gas with a flow rate of 40 ml./min.

[15] G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *J. Am. Chem. Soc.*, **81**, 4878 (1959).

[16] A 1–2 g. sample was dissolved in 15 ml. of carbon tetrachloride and titrated with a standard (*ca.* 0.1*M*) solution of bromine in carbon tetrachloride until the bromine color persisted. A solvent blank was titrated also with the standard bromine solution in order to determine the correction for excess titrant added. It was determined that neither Ia or IIa reacted appreciably with the bromine solution upon standing at room temperature up to 4 hr.

TABLE IV

2-ALKYL-3,3-DIPROPYLHEPTANONITRILES (II) ISOLATED FROM REACTION MIXTURES

R	B.P. (Mm.)	n_D^{25}	% Carbon		% Hydrogen	
			Calcd.	Found	Calcd.	Found
C_2H_5	151–153 (20)	1.4508	80.64	80.44	13.09	12.71
n-C_4H_9	165–167 (20)	1.4520	81.20	81.33	13.23	13.28
i-C_4H_9	160–162 (20)	1.4511	81.20	81.17	13.23	13.00
s-C_4H_9	156–158 (20)	1.4540	81.20	80.92	13.23	13.18
i-C_5H_{11}	174–175 (20)	1.4517	81.43	81.17	13.29	13.08
n-C_8H_{17}	186–188 (1)	1.4553	82.01	82.29	13.44	13.24
C_6H_5	146–148 (1)	1.5004	84.07	84.06	10.77	10.84
$C_6H_5CH_2$	230–231 (1)	1.5002	84.14	84.55	10.95	10.90

TABLE V

N,2-DIALKYL-3,3-DIPROPYLHEPTANAMIDES (IV) ISOLATED FROM REACTION MIXTURES

R	M.P.	Recrystallized Solvent	% Carbon		% Hydrogen	
			Calcd.	Found	Calcd.	Found
n-C_4H_9	125–126	Acetonitrile	77.48	77.74	13.32	13.19
i-C_4H_9	108–109	Ethyl acetate	77.48	77.57	13.32	13.16
i-C_5H_{11}	127.5–129	Acetonitrile	78.12	77.84	13.40	13.35

fication of the procedure of Sarel and Newman[17] was used. A mixture of 25.1 g. (0.10 mole) of IIa and 100 g. of 75% (by weight) sulfuric acid was heated at 100–125° for 8 hr. with vigorous stirring. After standing overnight, the dark, gummy mass was poured into 500 ml. of ice water, and extracted several times with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, filtered, and the ether was evaporated. The residue was distilled under reduced pressure from a Claisen flask and 24.5 g. (91%) of 2-butyl-3,3-dipropylheptanamide was obtained as a nearly colorless, very viscous oil, b.p. 185–187°/1 mm., n_D^{25} 1.4720. The amide could not be induced to crystallize.

Anal. Calcd. for $C_{17}H_{35}NO$: C, 75.77; H, 13.09. Found: C, 75.91; H, 12.96.

A stirred suspension of 20 g. (0.074 mole) of 2-butyl-3,3-dipropylheptanamide in 125 g. of 75% sulfuric acid was prepared, and the mixture was heated to 80°. The source of heat was removed, and 34.5 g. (0.5 mole) of sodium nitrite was added in small portions so that the temperature was maintained at 80–90°. After cooling to room temperature, the mixture was poured into 500 ml. of ice water and extracted several times with ether. The combined ether extracts were washed twice with water, dried over magnesium sulfate, filtered, and the ether was removed at atmospheric pressure. The residue was distilled under reduced pressure and 17.2 g. (86%) of 2-butyl-3,3-dipropylheptanoic acid was obtained as a light yellow, viscous oil; b.p. 173–174°/1 mm., n_D^{25} 1.4570.

Anal. Calcd. for $C_{17}H_{34}O_2$: C, 75.50; H, 12.67; neut. equiv., 270.4. Found: C, 75.74; H, 12.76; neut. equiv., 275.3.

Preparation of N,2-dibutyl-3,3-dipropylheptanamide. A mixture of 15.0 g. (0.055 mole) of 2-butyl-3,3-dipropylheptanoic acid and 17.9 g. (0.15 mole) of thionyl chloride was refluxed for 2 hr., cooled, 50 ml. of dry benzene was added, and the benzene and excess thionyl chloride were removed at reduced pressure. The crude acid chloride was added dropwise to a solution of 11.6 g. (0.165 mole) of n-butylamine in 100 ml. of dry benzene at ice-bath temperature. After standing for 2 days, the mixture was worked up in the usual fashion to give 12.2 g. (69%) of *N*,2-dibutyl-3,3-dipropylheptanamide as fine, white needles, m.p. 122–124°. An analytical sample was obtained after several recrystallizations from acetonitrile as fluffy, white needles, m.p. 125–126°.

Anal. Calcd. for $C_{21}H_{43}NO$: C, 77.48; H, 13.32. Found: C, 77.74; H, 13.19.

Alkylation of Ia *with various halides in ether.* A mixture of Ia, 0.11 mole of sodamide, 0.11 mole of the halide, and 100 ml. of dry ether for each 0.10 mole of Ia, was refluxed for 24 hr. in a three necked flask fitted with a sealed stirrer and a reflux condenser protected by a drying tube. After cooling, the mixture was filtered with suction through a sintered glass filter, and the ether was removed. Unchanged Ia was removed by fractionation through a Modified Podbielniak Column, and the remaining mixtures were distilled as long as volatile material could be obtained. The resulting mixture of monoalkylated nitrile and ketenimine was analyzed then with the results shown in Table II.

Isolation of nitriles and amides from the above alkylations. The mixtures of monoalkylated nitriles and ketenimines from 0.15 mole of Ia were refluxed with 150 ml. of 95% ethanol, 10 ml. of water, and 2 ml. of 10% hydrochloric acid for 4 hr., and the ethanol was removed by distillation. The residues were poured into 200 ml. of water and extracted several times with ether. The combined ether extracts were washed with water, 10% sodium bicarbonate solution, again with water, dried over magnesium sulfate, and filtered. The ether was removed at atmospheric pressure and the residues were distilled at reduced pressure. The nitriles obtained are listed in Table IV.

The residues from the distillations were recrystallized to constant melting point when they could be induced to crystallize. The amides obtained are recorded in Table V.

Preparation of 2-octyl-3,3-dipropylheptanonitrile (IIb) *and 8-aza-6-octyl-5,5-dipropyl-6,7-hexadecadiene* (IIIb). A mixture of 29.3 g. (0.15 mole) of Ia, 6.4 g. (0.165 mole) of sodamide, 31.8 g. (0.165 mole) of n-octyl bromide, and 150 ml. of dry ether was refluxed for 24 hr. After work-up and distillation, there were obtained 39.4 g. (85%) of 2-octyl-3,3-dipropylheptanonitrile, b.p. 186–188°/1 mm., n_D^{25} 1.4553; and 4.4 g. (7%) of crude ketenimine, b.p. 248–250°/1 mm.

Anal. Calcd. for $C_{21}H_{41}N$: C, 82.01; H, 13.44. Found: C, 82.89; H, 13.24.

The crude ketenimine was fractionated carefully through a 24-in. spinning band column, and 3.0 g. of pure material, n_D^{25} 1.4654, was obtained.

Anal. Calcd. for $C_{29}H_{57}N$: C, 82.98; H, 13.69. Found: C, 82.50; H, 13.76.

Preparation of 4-aza-6-isobutyl-2-methyl-7,7-dipropyl-4,5-undecadiene (IIIc). In a 1-l. three necked flask fitted with a sealed stirrer and a reflux condenser protected with a drying

---

[17] S. Sarel and M. S. Newman, *J. Am. Chem. Soc.*, 78, 5416 (1956).

tube were placed 29 g. (0.2 mole) of Ia, 11.7 g. (0.31 mole) of sodamide, 41.1 g. (0.31 mole) of isobutyl bromide, and 150 ml. of dry benzene, and the mixture was refluxed for 6 hr. An additional 11.7 g. (0.3 mole) of sodamide and 41.1 g. (0.3 mole) of isobutyl bromide were added, and refluxing was continued for 16 hr. Still a third portion of 11.7 g. (0.3 mole) of sodamide, and 41.1 g. (0.3 mole) of isobutyl bromide was added, and refluxing was continued for an additional 10 hr. The flask was cooled in an ice bath and the mixture was decomposed by cautiously adding 250 ml. of cold water. The layers were separated, the aqueous layer was extracted with ether, and the combined organic solutions were washed with water and dried over magnesium sulfate. After filtration, the solvents were removed at atmospheric pressure and the residue was fractionated under reduced pressure. There was obtained 38.6 g. (63%) of the ketenimine as a colorless oil, b.p. 183–185°/20 mm., n_D^{25} 1.4650, having a characteristic isocyanide odor. The purity of the product was 88% as determined by gas chromatography, with the remaining 12% being 2,2-diisobutyl-3,3-dipropylheptanonitrile (IVc).

Anal. Calcd. for $C_{21}H_{41}N$: C, 82.01; H, 13.14; N, 4.55. Found: C, 82.04; H, 13.49; N, 4.44.

Hydrolysis of 4-aza-6-isobutyl-2-methyl-7,7-dipropyl-4,5-undecadiene (IIIc). A mixture of 17.8 g. (0.058 mole) of the ketenimine, 75 ml. of glacial acetic acid, and 25 ml. of water was refluxed for 4 hr., cooled, and poured into 250 ml. of cold water. The layers were separated, the aqueous layer was extracted three times with ether, and the combined organic layers were washed with water, then with 10% sodium hydroxide solution until neutral, again with water, and dried over magnesium sulfate. The solution was filtered, the ether was removed at atmospheric pressure, and the residue was distilled at reduced pressure. There was obtained 12.2 g. (65%) of *N*,2-diisobutyl-3,3-dipropylheptanamide, b.p. 169–171°/1 mm., which crystallized in the receiver. An analytical sample was recrystallized from ethyl acetate as fine white needles, m.p. 108–109°.

Anal. Calcd. for $C_{21}H_{43}NO$: C, 77.48; H, 13.32. Found: C, 77.57; H, 13.16.

Preparation of 2-benzyl-3,3-dipropylheptanonitrile. A mixture of 17.5 g. (0.09 mole) of Ia, 3.9 g. (0.10 mole) of sodamide, 12.7 g. (0.10 mole) of benzyl chloride, and 100 ml. of dry toluene was refluxed for 24 hr. After filtration, the solvent and a trace of unchanged benzyl chloride were removed at reduced pressure. An infrared spectrum of the residue indicated the presence of amines, ammonium salts, and nitrile, but with no band at 5.0 μ characteristic of a ketenimine.[4] The residue was taken up in ether and washed several times with 10% hydrochloric acid, twice with water, dried over magnesium sulfate, and filtered. The ether was removed at atmospheric pressure and the residue was distilled under reduced pressure. There were obtained 7.7 g. (44%) of Ia, and 8.0 g. (31%) of crude 2-benzyl-3,3-dipropylheptanonitrile, b.p. 230–236°/1 mm., which was contaminated by a trace of solid material. The residue in the flask, presumably tetrabenzylammonium chloride, amounted to about 4 g. and was not investigated further. The crude 2-benzyl-3,3-dipropylheptanonitrile was filtered with suction through a sintered glass filter and fractionated carefully through a spinning band column. There was obtained 7.0 g. of a colorless, very viscous oil, b.p. 230–231°/1 mm., n_D^{25} 1.5002.

Anal. Calcd. for $C_{20}H_{31}N$: C, 84.14; H, 10.95. Found: C, 84.55; H, 10.90.

The aqueous solution and washings were combined and made alkaline with 10% sodium hydroxide solution. The mixture was extracted several times with ether, the ether solutions were combined, washed twice with water, and dried over potassium hydroxide pellets. The ether was removed and 2.0 g. of a mixture of benzylamine, dibenzylamine, and tribenzylamine (as indicated by infrared spectra) was obtained.

Preparation of N,2-diisobutyl-3,3-dipropylheptanamide. The hydrolysis of 16 g. (0.06 mole) of 2-isobutyl-3,3-dipropylheptanonitrile to 2-isobutyl-3,3-dipropylheptanoic acid was accomplished by heating with 120 g. of 96% sulfuric acid at 100–120° for 8 hr., followed by treatment with 16.6 g. (0.24 mole) of sodium nitrite. The reaction was accompanied by considerable charring and tar formation. After work-up and distillation, there was obtained 7.1 g. of material, b.p. 161–162°/1 mm., which appeared to be a mixture of amide and acid. The mixture was treated with thionyl chloride, followed by isobutylamine, to give, after purification, 2.7 g. (13%) of *N*,2-diisobutyl-3,3-dipropylheptanamide; m.p. 107–108° (from ethyl acetate). A mixed melting point with the amide from hydrolysis of IIIc was not depressed.

Anal. Calcd. for $C_{21}H_{43}NO$: C, 77.48; H, 13.32. Found: C, 77.39; H, 13.01.

Attempted preparation of 2-bromo-N,2-diisobutyl-3,3-dipropylheptanamide. A solution of 4.8 g. (0.03 mole) of bromine in 25 ml. of carbon tetrachloride was added dropwise to a solution of 8.1 g. (0.026 mole) of 4-aza-6-isobutyl-2-methyl-7,7-dipropyl-4,5-undecadiene (IIIc) in 25 ml. of carbon tetrachloride while maintaining the temperature at −5 to 0° in an ice-salt bath. The bromine color was discharged immediately. The addition of the bromine solution was discontinued as soon as the bromine color persisted (about 2 ml. of solution was unused). The contents of the flask were allowed to warm to room temperature overnight and the solvent was removed under reduced pressure. There remained an intractable oil which was mixed with 100 ml. of 50% acetic acid and refluxed for 3 hr. The resulting mixture was poured into 500 ml. of cold water and extracted several times with ether. The combined ether extracts were washed with water, then with 10% sodium hydroxide solution, again with water, dried over magnesium sulfate, and filtered. The ether was evaporated, leaving a light brown oil which crystallized on standing. This was recrystallized from acetonitrile to give 4.6 g. (54%) of slightly yellow crystals, m.p. 83–88°. Repeated recrystallizations, first from acetonitrile, then from ethyl acetate, gave an analytical sample in the form of fine, colorless needles, m.p. 108.5–109.5°. The melting point was not depressed on admixture with authentic *N*,2-diisobutyl-3,3-dipropylheptanamide, and the infrared spectra were identical. A sodium fusion gave a negative test for bromine.

Alkylation of 2-alkyl-3,3-dipropylheptanonitriles with various halides. A mixture of 0.10 mole of the appropriate 2-alkyl-3,3-dipropylheptanonitrile (II), 0.11 mole of sodamide, 0.11 mole of the halide, and 100 ml. of the solvent was refluxed for 24 hr. After filtration, removal of solvent, and distillation, the resulting mixtures of unchanged starting material (II), dialkylated nitrile (IV), and ketenimine (III), were analyzed by gas chromatography. The results are shown in Table III.

Isolation of 2,2-dibutyl-3,3-dipropylheptanonitrile (IVa). A mixture of 29.1 g. of the reaction mixture from the alkylation of 2-butyl-3,3-dipropylheptanonitrile (IIa) with *n*-butyl bromide in ether, 150 ml. of 95% ethanol, 10 ml. of water, and 2 ml. of 10% hydrochloric acid was refluxed for 4 hr. After removal of the ethanol, extraction, and distillation in the usual manner, there were obtained 3.3 g. (13%) of unchanged 2-butyl-3,3-dipropylheptanonitrile, b.p. 137–140°/1 mm., and 10.3 g. (33%) of crude 2,2-dibutyl-3,3-dipropylheptanonitrile, b.p. 176–178°/1 mm., which was contaminated by traces of amide. After fractionation twice through a spinning bond column, a sample of pure 2,2-dibutyl-3,3-dipropylheptanonitrile, b.p. 176–177°/1 mm., n_D^{25} 1.4650, was obtained.

Anal. Calcd. for $C_{21}H_{41}N$: C, 82.01; H, 13.44. Found: C, 82.29; H, 13.35.

The original distillation residue solidified on cooling. This was recrystallized from acetonitrile to give 8.3 g. (27%) of *N*,2-dibutyl-3,3-dipropylheptanamide, m.p. 123–125°.

COLUMBIA, MO.