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REACTIONS OF ORGANIC ANIONS—IX

COMPETITIVE ALKYLATION OF ACETONITRILE DERIVATIVES

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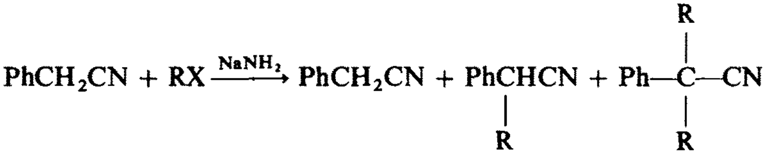
Abstract—Factors determining the relative proportions of mono and dialkylated products have been discussed. Selectivity of alkylation in liquid ammonia may be controlled by varying the amount of $NaNH_2$. Other factors of interest in the control of mono *versus* dialkylation are indicated.

THE alkylation of phenylacetonitrile, malonic ester and other compounds containing active methylene groups yields mono and dialkyl derivatives, the latter sometimes being formed in considerable amounts.[1] When stoichiometric quantities of the substrates—the alkylated compounds and the alkylating agents—are used the products consist of mono and dialkyl derivatives, together with starting material, e.g.



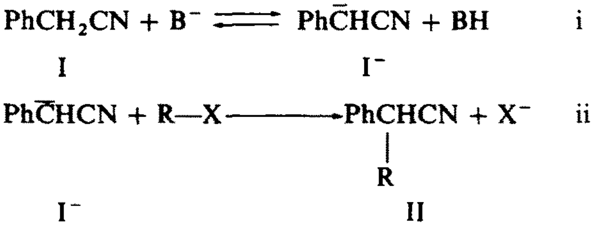
$$\underset{\mathrm{I}}{\mathrm{PhCH_2CN}} + \mathrm{RX} \xrightarrow{\mathrm{NaNH_2}} \underset{\mathrm{I}}{\mathrm{PhCH_2CN}} + \underset{\mathrm{II}}{\mathrm{Ph}\underset{\underset{\mathrm{R}}{|}}{\mathrm{C}}\mathrm{HCN}} + \underset{\mathrm{III}}{\mathrm{Ph{-}}\overset{\overset{\mathrm{R}}{|}}{\underset{\underset{\mathrm{R}}{|}}{\mathrm{C}}}\mathrm{{-}CN}} \qquad (1)$$

The amount of III, and consequently of I, is often quite considerable, whereby the yield of II is substantially reduced and its purification becomes a complex operation.

The ratio in which I, II and III are produced depends on various factors, such as the kind of the alkylating agent, the nature of the base and solvent, the reaction procedure, etc.

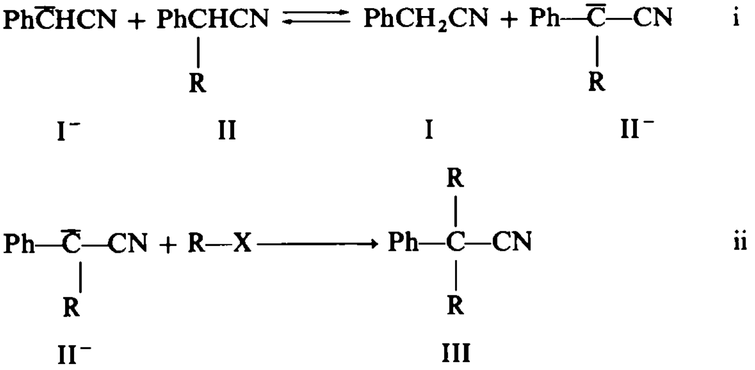
Alkylation of I carried out in liquid ammonia in the presence of sodium amide with benzyl chloride ($R = PhCH_2$-) and methyl iodide ($R = Me$) yielded[2] 29 and 21% I, 33 and 50% II, and 30 and 19% III respectively. The catalytic method[3] yielded 22 and 5% I, 50 and 89% II, and 19 and 4% III respectively. Since iodine ions inhibit this reaction, methyl chloride or bromide were used instead of MeI. Only II was formed in both methods when α-phenylchloroethane ($R = PhMeCH$—) or benzhydryl chloride ($R = Ph_2CH$—) were used as alkylating agents.

The alkylation of phenylacetonitrile (I) proceeds generally in two main stages:



$$\begin{aligned} &\underset{\mathrm{I}}{\mathrm{PhCH_2CN}} + \mathrm{B^-} \rightleftharpoons \underset{\mathrm{I^-}}{\mathrm{Ph\bar{C}HCN}} + \mathrm{BH} && \mathrm{i} \\ &\underset{\mathrm{I^-}}{\mathrm{Ph\bar{C}HCN}} + \mathrm{R{-}X} \longrightarrow \underset{\mathrm{II}}{\mathrm{Ph}\underset{\underset{\mathrm{R}}{|}}{\mathrm{C}}\mathrm{HCN}} + \mathrm{X^-} && \mathrm{ii} \end{aligned} \qquad (2)$$

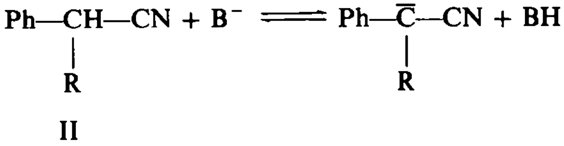
As alkylation proceeds, the concentration of II increases, the following equilibrium is established and, consequently, a dialkylated product is formed



$$\underset{\mathrm{I}^-}{\mathrm{Ph\bar{C}HCN}} + \underset{\mathrm{II}}{\mathrm{PhCH}\underset{\textstyle \mathrm{R}}{|}\mathrm{CN}} \rightleftharpoons \underset{\mathrm{I}}{\mathrm{PhCH_2CN}} + \underset{\mathrm{II}^-}{\mathrm{Ph{-}}\underset{\textstyle \mathrm{R}}{\bar{\mathrm{C}}}\mathrm{{-}CN}} \qquad \mathrm{i} \tag{3}$$

$$\underset{\mathrm{II}^-}{\mathrm{Ph{-}}\underset{\textstyle \mathrm{R}}{\bar{\mathrm{C}}}\mathrm{{-}CN}} + \mathrm{R{-}X} \longrightarrow \underset{\mathrm{III}}{\mathrm{Ph{-}}\overset{\textstyle \mathrm{R}}{\underset{\textstyle \mathrm{R}}{\mathrm{C}}}\mathrm{{-}CN}} \qquad \mathrm{ii}$$

The alkylated nitrile can also produce an anion directly under the influence of base B$^-$, either when the latter is in excess or when the equilibrium (2 i) is not completely shifted to the right. In both aforementioned cases the reaction mixture contains some base B$^-$.



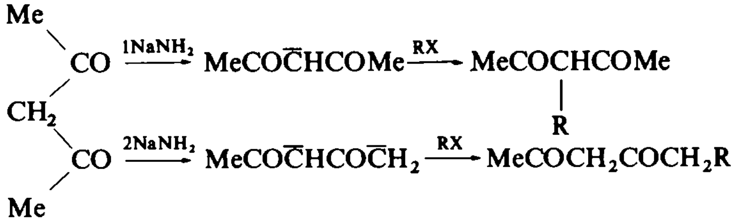
$$\underset{\mathrm{II}}{\mathrm{Ph{-}}\underset{\textstyle \mathrm{R}}{\mathrm{CH}}\mathrm{{-}CN}} + \mathrm{B}^- \rightleftharpoons \mathrm{Ph{-}}\underset{\textstyle \mathrm{R}}{\bar{\mathrm{C}}}\mathrm{{-}CN} + \mathrm{BH} \tag{4}$$

Thus there are two nitrilic anions in the reaction mixture, viz., I$^-$ and II$^-$:, their activity and their concentration in the system are decisive factors determining which will react with R—X.

Base B$^-$ in excess considerably increases the concentration of II$^-$ soon after the beginning of the reaction (2 ii). As such an excess is seldom used, only the equimolar quantities will be considered. In this case anion II$^-$ is formed owing to the equilibrium (3 i). This equilibrium should be considered as acid—base equilibrium, depending on the relative strength of the acids I and II, as well as on the strength of the respective conjugated bases I$^-$ and II$^-$. The "acidity" of the nitrile II is determined by the nature of the substituent R.

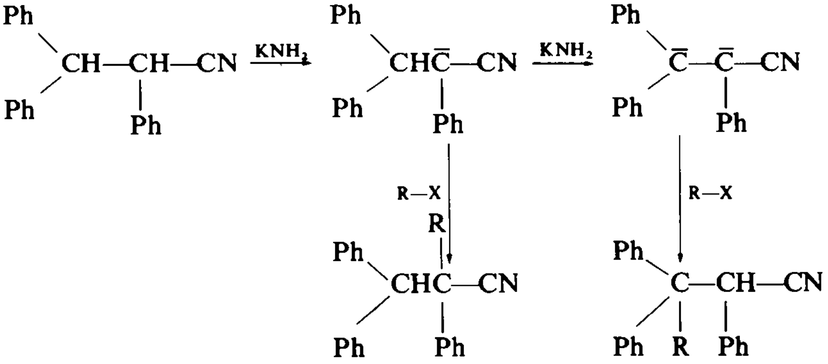
The alkylic substituent most frequently encountered, decreases the "acidic" properties of II as compared with those of I. Consequently, the equilibrium (3 i) is shifted to the left despite the higher concentration of II, which always occurs when the reaction follows the scheme (2 ii). Nevertheless, several cases are known when the substituent R— stimulates the "acidity" of nitrile II, thus shifting the equilibrium (3 i) to the right.[4]

The differences in the activities of anions I$^-$ and II$^-$ also depend on the substituent R. As was established by Hauser *et al.*, when an organic molecule is capable of forming anions in two positions under the influence of strong bases, these positions often differ in acidic strength. Consequently, the monoanion formed in the reaction of a substrate with one molecule of a base reacts differently than does the dianion formed under the action of two molecules of the base. This has been shown in the alkylation of acetylacetone.[5]



(5)

and of 2,3,3-triphenylpropionitrile.[6]



(6)

Similar phenomena were observed in many other instances[7, 8]. The following general conclusion may be advanced: when a compound having two active "acidic" hydrogen atoms is able to form dianions, the anion derived from the more "acidic" position is less active than that derived from the less "acidic" position. When this is applied to the nitriles forming monoanions, one may assume that anions of less "acidic" nitriles, i.e. these ionized less readily, should be more active in alkylation than the nitrile anions formed more readily.

However, this discussion should not be limited only to electronic factors. Steric effects certainly have their influence on the first and second stage of alkylation (2 i and 2 ii).

Introduction of the substituent R— into the molecule I hinders the approach of the anion B^- or I^- to II, thus making the formation of anion II^- more difficult. Similarly, the presence of substituent R— in anion II^- hinders the approach of anion II^- to the R—X molecule.

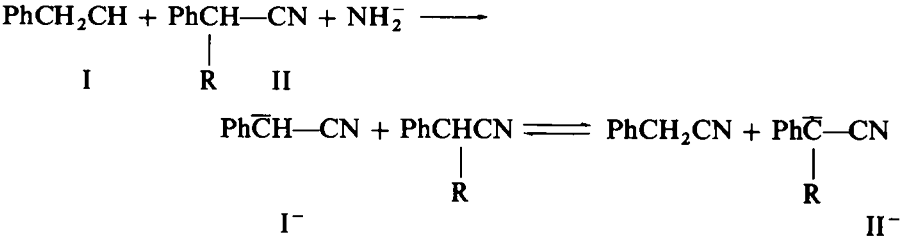
To sum up, the electronic effects of the substituent R— has an opposite action in each stage of alkylation (2 i and 2 ii). The electron-donor substituents (particularly alkyls), hinder anion formation, deactivating the nitrile in the first stage (2 i) and simultaneously activating the anion (II^-) in the reaction with alkyl halogenide. On the contrary, the electron-acceptor substituents stimulate the nitrile anionization, simultaneously deactivating the newly formed anion.

The steric effects of the substituent R— have a deactivating action in both stages of the reaction (2 i and 2 ii).

These considerations hold true only in homogeneous systems when anions I^- and II^-, nitriles I and II, and R—X are in solution, in which the equilibria 2 i, 3 i and 4 are established continuously. These conditions are best preserved in liquid ammonia which is a good solvent for sodium nitrile derivatives. The high electric conductivity of these solutions points to their high degree of dissociation; hence the presence of the sodium derivative as an ion pair is negligible.[9]

Sodium amide seems to be the most convenient base for use in liquid ammonia. Owing to the high basicity of the latter, the equilibrium (2 i), when $B^- = NH_2^-$, is shifted to the right even for the least "acidic" dialkylacetic nitriles.[10] Since kinetic measurements in liquid ammonia are difficult, we investigated the activity of nitriles I and II and their anions by means of the competitive alkylation method.

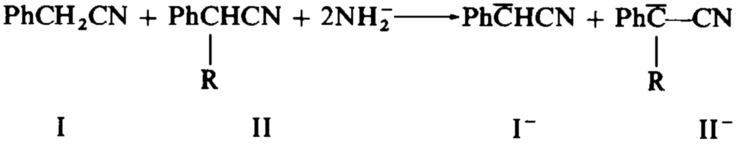
By applying equimolar quantities of two nitriles with one mole of sodium amide in liquid ammonia only half of the nitrile molecules can form anions and the equilibrium is established:



$$\underset{\mathrm{I}}{\mathrm{PhCH_2CH}} + \underset{\mathrm{II}}{\underset{\mathrm{R}}{\mathrm{PhCH{-}CN}}} + \mathrm{NH_2^-} \longrightarrow \underset{\mathrm{I^-}}{\mathrm{Ph\bar{C}H{-}CN}} + \underset{\mathrm{R}}{\mathrm{PhCHCN}} \rightleftharpoons \mathrm{PhCH_2CN} + \underset{\mathrm{II^-}}{\underset{\mathrm{R}}{\mathrm{Ph\bar{C}{-}CN}}} \qquad (7)$$

The ratio of $\mathrm{I^-}$ to $\mathrm{II^-}$ depends on the "acidity" of I and II. A more acidic nitrile forms anions in a higher degree, and these anions undergo alkylation under the action of the alkylating agent R—X.

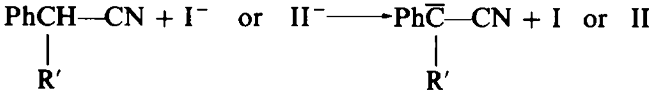
However, when two moles of sodium amide are used all the nitrile molecules become anionized



$$\underset{\mathrm{I}}{\mathrm{PhCH_2CN}} + \underset{\mathrm{II}}{\underset{\mathrm{R}}{\mathrm{PhCHCN}}} + 2\mathrm{NH_2^-} \longrightarrow \underset{\mathrm{I^-}}{\mathrm{Ph\bar{C}HCN}} + \underset{\mathrm{II^-}}{\underset{\mathrm{R}}{\mathrm{Ph\bar{C}{-}CN}}} \qquad (8)$$

Treatment of such a mixture with one mole of the alkylating agent R′—X will bring about mainly the alkylation of the more active anion.

In the case of alkylation of the mixture of anions $\mathrm{I^-}$ and $\mathrm{II^-}$ with R′—X, the following equilibrium between the product of alkylation of I and the anions $\mathrm{I^-}$ and $\mathrm{II^-}$ can occur, e.g.

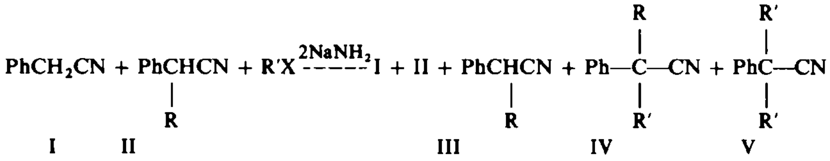


$$\underset{\mathrm{R'}}{\mathrm{PhCH{-}CN}} + \mathrm{I^-} \text{ or } \mathrm{II^-} \longrightarrow \underset{\mathrm{R'}}{\mathrm{Ph\bar{C}{-}CN}} + \mathrm{I} \text{ or } \mathrm{II} \qquad (9)$$

thus furnishing symmetrically the dialkylderivative of I. This has been observed several times.

The above suppositions have been fully confirmed by experiment. The results of competitive alkylation are presented in Table 1. All experiments were carried out in liquid ammonia in the presence of sodium amide prepared from metallic sodium and a catalytic amount of ferric chloride shortly before addition of the nitriles. The products were analysed by distillation and gas-chromatography. Pure reference nitriles for identification were prepared by catalytic alkylation.[11] Diisopropylphenylacetonitrile was prepared by alkylation of monoisopropylphenylacetonitrile with isopropyl bromide in the presence of sodium amide in liquid ammonia.[12]

TABLE 1. RESULTS OF COMPETITIVE ALKYLATION EXPERIMENTS[a]



$$\underset{I}{PhCH_2CN} + \underset{II}{\underset{R}{PhCHCN}} + R'X \xrightarrow{2NaNH_2} I + II + \underset{III}{\underset{R}{PhCHCN}} + \underset{IV}{Ph\overset{R}{\underset{R'}{C}}CN} + \underset{V}{Ph\overset{R'}{\underset{R'}{C}}CN}$$

No.	R in PhCHRCN	R'X	$NaNH_2$ moles	Composition of resulting mixture mole %				
				I	II	III	IV	V
1	Et	iso-$C_5H_{11}Br$	1	10	50	35	5	
2	Et	iso-$C_5H_{11}Br$	2	44	14	7	39	
3	i-Pr	n-$C_5H_{11}Br$	1	8	92^b			
4	i-Pr	n-$C_5H_{11}Br$	2	73	27^b			
5	i-Pr	iso-PrBr	1	5	95			
6	i-Pr	iso-PrBr	2	32	42·5		25·5	
7	Ph	EtBr	1	91		9^b		
8	Ph	EtBr	2	22		55^b		23
9	II=MeCN	iso-$C_5H_{11}Br$	1	2		98		
10	II=MeCN	iso-$C_5H_{11}Br$	2	52		0	29 + 12^c	
11	$PhCH_2$	EtBr	1	32		68^b		
12	$PhCH_2$	EtBr	2	70		20^b		10
13^d	$PhCH_2$	EtBr	1	85		15^b		
14^d	$PhCH_2$	EtBr	2	30·5		69·5		
15	Ph	Et	NaOH + TEBA chloride	94		6^b		
16	Et	Et		10·3		87·4	2·3	

[a] Initial mixture contained equimolar quantities of I and II.

[b] Lower-boiling nitriles were separated from the reaction mixture by vacuum distillation and analysed gas-chromatographically.

[c] Yield of dialkylated acetonitrile.

[d] Nitrile I was 2-phenylbutyronitrile, in this case III was 2-phenyl-2-ethylbutyronitrile.

TABLE 2. DEGREE OF DIALKYLATION OF PHENYLACETONITRILE (I) IN RELATION TO THE SUBSTRATE PROPORTION, AND THE REACTION PROCEDURE

No.	RX	Solvent	Moles of			Content after alkylation mole—%		
			I	$NaNH_2$	RX	I	II	III
1	EtBr	NH_3	1	1	1	15	70	15
2	EtBr	NH_3	1·2	1	1	6^a	89	5
3	EtBr	NH_3	1	1·8	1	48	2	50
4	$PhCH_2Cl$	NH_3	1	1	1	31	37	32
5	$PhCH_2Cl$	$NH_3{}^b$	1	1	2	29	43	28
6	$PhCH_2Cl$	ether[b]	1	1	2	21	59	20

[a] After substracting the excess of I; Mixture after alkylation contained I 22%, II 74%, III 4%.

[b] Solution of nitrile sodium derivative was added to the solution of R—X.

The experiments 1 and 2 show an electrostatic influence of the substituent R=Et in both stages of alkylation: anion formation (2 i) and its subsequent reaction with the alkylating agent (2 ii). In these experiments the alkylating agent of low activity (isoamylbromide) was used; hence the difference in anion activities played an important role.

The experiments 3–6 (when R = i—Pr) show the marked steric influence occurring in the stage of the anion reaction with R′—X (2 ii) independently of the electrostatic factor mentioned above (experiments 1–2). This is particularly evident in experiments 5 and 6 when secondary isopropyl bromide was used as alkylating agent. However, the electrostatic effect was stronger than the steric hindrances. When a mixture of I and II (R = i—Pr) was alkylated with isopropyl bromide in the presence of 2 moles of $NaNH_2$, II was preferently alkylated.

The Ph group (R = Ph), contrary to the alkyl group, favours anion formation, simultaneously decreasing their activity. The first conclusion was confirmed by experiment 7, when a mixture of I and II (R = Ph) was alkylated in the presence of 1 mole of sodium amide, yielding mainly the derivative of II. On the other hand, the electrostatic deactivating influence of the Ph in the diphenylacetonitrile anion is strengthened by the steric factor. This conclusion is supported by the fact that in the alkylation of the mixture of anions I^- and II^-, reacted I^- (experiment 8). Analysis of the product obtained from this experiment disclosed the presence of a considerable quantity (23% of low-boiling nitriles) of dialkyl derivatives of I. This fact confirms an equilibrium of type (9). The total balance shows that the degree of alkylation of II does not exceed 1–2%. The unreacted diphenylacetonitrile isolated from the reaction mixture was almost quantitative.

A similar strong electrostatic influence of the Ph group was established in the competitive alkylation of I and acetonitrile with isoamyl bromide (experiments 9 and 10). In the presence of 1 mole of $NaNH_2$ only I was alkylated, whereas with 2 moles of sodium amide the reaction product contained isoamylacetonitrile. diisoamylacetonitrile and I. No alkyl derivative of I was found in the product.

In another series, in order to confirm our observations in the case of the catalytic method of alkylation, experiments were carried out with nitriles: I and II where R = Ph— and I and II R = Et Table 1. In experiments 15 and 16, diphenylacetonitrile were alkylated. In both cases the more acidic nitriles underwent alkylation. These results prove that in the catalytic method anion formation is caused by a small quantity of the base. Therefore, it may be assumed that it is ammonium hydroxide (formed from chloride by the action of conc. NaOH solution) that acts as the base. An excess of sodium hydroxide continuously regenerates ammonium hydroxide.

These facts explain the higher selectivity of the catalytic method of phenylacetonitrile alkylation as compared with the methods applying stoichiometric quantities of the base, e.g. sodium amide.[3]*

All these experimental facts throw new light upon the problem of mono and dialkylation. As shown above, the quantity of III depends on the concentration

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* According to the data presented by Hauser, by the author of the present paper and by some other authors,[13] owing to the close boiling temperatures of I, II and III (R = Me), the synthesis of pure monomethylic derivatives of phenylacetonitrile by methylation in the presence of sodium amide is almost impossible. It seems that the authors who claimed to have obtained monomethylic derivatives of phenylacetonitrile analogues, were probably dealing with mixtures of I, II and III (R = Me).[13a]

ratio of I^- and II^- and their activities. The equilibrium (2 i) determining the concentration of I^- and II^- depends on the "acidity" of nitriles I and II, which in turn depends on the character of the substituent R in II. The activity of II^- is also determined by R. The electrostatic influence of the substituents on the "acidity" of the nitriles and on the activity of their anions have opposite directions, compensating each other to some extent in the total alkylation reaction. The extent of this compensation is still unknown, it seems however, that it is high. Hence the conclusion that usually in mono *versus* dialkylation of I with R—X (when R— is electron-donor substituent) it is the steric effects which play the more decisive role. It is true that the intensity of the steric effects is less pronounced than the electrostatic, nevertheless, they strengthen each other in both stages of the reaction.

When the alkylation is carried out with an electron-acceptor substituent R, increasing the "acidity" of nitrile II as compared with I, the equilibrium (3 i) is shifted to the right with increased amounts of II so that the concentration of II^- surpasses that of I^-. In such cases dialkylation takes place—the monoalkyl derivatives are sometimes difficult to obtain.

The results of our work give the following practical indications for obtaining satisfactory yields of monoalkylated nitriles.

1. When the substituent R decreases the acidity of the nitrile, the alkylation should be carried out so as to prevent the establishment of equilibrium (3 i) or shift it to the left. This can be effected by the use of excess alkylated nitrile (application of 20% excess of phenylacetonitrile in ethylation lowers the amount of dialkylated product).

On the other hand, when sodium amide is used in excess, high concentration of the anion II^- is produced (equilibrium 4), and the yield of the monoethylated product (II) is therefore negligible. (The resulting mixture contains I and III (R = Et) in nearly equimolar quantities, and ca. 2% of II, see Table 2). It is thought that by adding sodium derivative of I to an excess of active alkylating agent (benzyl chloride), the establishment of equilibrium could be prevented, but this procedure did not change the proportion between mono and dialkylation (Table 2). This may serve as proof that the base–acid equilibrium (3 i) is more rapid than the alkylation of an anion. A more pronounced change in this proportion was observed by using ether (a poor solvent for the sodium derivative) instead of liquid ammonia. Better results can be obtained by the catalytic method.

2. When the substituent, e.g. cyanomethyl or carbalcoxymethyl, increases the "acidity" of the nitrile, the reaction should be carried out with sodium amide in excess, at possibly low temperature. The reaction then follows the scheme (3 i) or (4) with the formation of II and finally II^-. An excess of the base yields I, formed in reaction (3 i), to be reconverted to the anion I^-. In the competition of anions I^- and II^-, the alkylation takes place with the more active anion I^-, thus mainly the mono-alkylated product II is formed. This is a defence of the active hydrogen in nitrile II by the metal.

The foregoing conclusion has been confirmed experimentally by the alkylation of phenylacetonitrile (I) with chloroacetonitrile. So far, the condensation of the above named compounds effected in the presence of sodium amide[4b] or by the catalytic[14] method gave exclusively the nitrile of β-phenylcarballylic acid (III, R = —CH_2CN), without formation of the monoalkyl derivative (phenylsuccinic nitrile).

Alkylation of I (1 mole) with chloroacetonitrile (1 mole) in the presence of $NaNH_2$

(1·7 mole) gave the monoalkylated product II (phenylsuccinic nitrile) in a 41% yield. The phenyltricarballylic nitrile was formed in minute quantity (ca. 9%).

EXPERIMENTAL

GLC apparatus. Perkin–Elmer, Model 154-L chromatograph with 2 m long column filled with Ucon-Lb-550X (polypropylene glycol), a thermal conductivity detector, and H_2 as carrier gas, were used throughout the experiments.

2-Phenylbutyronitrile, 2-phenyl-3-methylbutyronitrile and 2,3-diphenylpropionitrile were prepared by catalytic alkylation of phenylacetonitrile. The purity of the first and second compounds was checked gas-chromatography.

2-Phenyl-2-isopropylbutyronitrile, 2-phenyl-2-isoamylbutyronitrile and *2-phenyl-2-ethylbutyronitrile* used as reference substances for gas-chromatographic analysis were prepared by catalytic alkylation of 2-phenylbutyronitrile.

The competitive alkylation was effected according to the method described below.

Competitive alkylation of phenylacetonitrile and 2-phenylbutyronitrile in the presence of 1 mole of sodium amide. Liquid ammonia (70 ml), Na metal (1·15 g; 0·05 g at.) and a small crystal of $FeCl_3$ were mixed in a 3-necked flask. When the initial dark-blue colour disappeared, phenylacetonitrile (5·86 g; 0·05 mole) mixed with 2-phenylacetonitrile (7·25 g; 0·05 mole) was added, and all was stirred for 30 min, cooled, treated with isoamyl bromide (7·45 g) diluted with an equal volume of anhydrous ethyl ether, and stirred for a further 60 min. The mixture was left at room temp till all the NH_3 evaporated, washed with acidified water, the organic layer was extracted with benzene, dried and distilled, and the nitrile fraction boiling at 104–155° 9 mm (14·9 g) was collected. The results of gas-chromatographic analysis of the collected fraction are shown in Table 1.

Synthesis of phenylsuccinonitrile. To $NaNH_2$ formed from Na (19·6 g, 0·85 g at. in 400 ml liquid ammonia) phenylacetonitrile (58·5 g; 0·5 mole) was added dropwise with stirring. The flask contents were cooled to −65° and chloroacetonitrile (38 g) dissolved in an equal volume of anhydrous ether was added dropwise. When the reaction was complete, the cooling bath was removed and the reaction mixture was left at ambient temp till all the NH_3 evaporated. The residue was treated with a small amount of MeOH, diluted with water and filtered off. The filtrate was extracted twice with benzene, the extract was dried and distilled. Phenylsuccinonitrile, b.p. 150–160°/1·5 mm (32 g; 41%) was collected. Repeated distillation gave the product boiling at 129°/0·1 mm, m.p. 64° from light petroleum; lit.[4b] 64°. Phenylacetonitrile (15 g) was recovered. β-Phenyltricarballylic (9 g; 9·2%), m.p. 131° (from benzene—lit.[4b] 132°) was recovered from the filtration and distillation residues.

Alkylation of acetonitrile with isoamyl bromide. To the suspension of $NaNH_2$ (4·6 g; 0·2 mole) in liquid ammonia, acetonitrile (10·2 g; 0·2 mole) was added. The stirring was continued for 30 min, followed by the addition of isoamyl bromide (30·2 g; 0·2 mole) in an equal volume of anhydrous ether. When the reaction was complete, the mixture was left at room temp till the NH_3 evaporated. The residue was treated with water and the organic layer was extracted with benzene. The benzene extract after removal of the solvent was distilled, the following fractions being collected: I b.p. 65–72°/12 mm (8·4 g; 37%) II b.p. 116–123°/12 mm (5·6 g; 15·5%). The first fraction contained 5-methylcaproic nitrile—its analytical sample boils at 68°/12 mm, n_D^{20} 1·4136. (Found: N, 12·4; 12·6 calc. for $C_7H_{13}N$: N, 12·6%.)

The second fraction contains 2-isoamyl-5-methylcaproic nitrile. Its analytical sample boils at 120°/12 mm, n_D^{20} 1·4306. (Found: N, 7·9; 7·8. $C_{12}H_{23}N$ requires: N, 7·74%).

Catalytic alkylation of phenylacetonitrile and 2-phenylbutyronitrile mixture with ethyl bromide. In a 3-necked flask 5·86 g (0·05 m) phenylacetonitrile, 7·25 (0·05 m) 2-phenylbutyronitrile, 5·6 g (0·052 m) EtBr, 15 ml of 50% NaOHaq and 0·13 g (0·0005 m) triethylbenzylammonium chloride were placed. The reaction was carried out at 33° for 3 hr with vigorous stirring. The reaction mixture was then diluted with distilled water. The organic layer was separated, washed twice with water, the washings were added to the aqueous layer and the whole was analyzed for Br^-. The analysis showed 98% conversion. The organic product was distilled b.p. 110–125°/12 mm affording 13·7 g (94%) nitriles and analyzed by gas-chromatography.

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[*] Concentrated NaOHaq was used as condensing agent in the presence of catalytic amounts of triethylbenzylammonium chloride.[3]