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REACTIONS OF CALCIUM AND MAGNESIUM NAPHTHALENIDES WITH ETHYL ESTERS OF 2-BROMOPROPIONIC AND 2-BROMOBUTYRIC ACID IN LIQUID AMMONIA

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Summary

The reaction in liquid ammonia of magnesium naphthalenide with the ethyl esters of 2-bromopropionic and 2-bromobutyric acid gives after hydrolysis the corresponding 2,2'-dialkylsuccinic acids, whereas calcium naphthalenide reacts to give in the former case 2,2'-dimethyl anhydride, and 2-hexene-3,4-dicarboxylic acid in the latter. Possible reaction mechanisms are discussed.

Introduction

Earlier investigation [1] of the reaction of some aliphatic bromoesters with magnesium in liquid ammonia showed the formation of products of dimerization and ammonolysis. It was found that in the case of 2-bromopropionic acid ethyl ester the formation of a Wurtz-type product is favored by the replacement of magnesium with magnesium naphthalenide. Similar behaviour is also shown by benzyl chloride towards sodium or sodium naphthalenide [2,3].

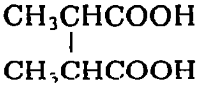
The present study was undertaken to gain further insight into the influence of the metal in the reaction. We have carried out more comprehensive experimental investigations upon the behaviour of magnesium and calcium naphthalenide towards the ethyl esters of 2-bromopropionic acid and 2-bromobutyric acid.

Results and discussion

The experiments were performed under the reaction conditions used previously [1], except that the mole ratio ester/naphthalenide used here is 1/1.

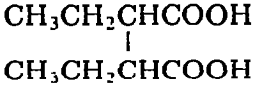
When magnesium naphthalenide is used, good yields of *meso* and racemic forms of dimethyl-(I) and diethyl-(II) succinic acid were obtained after hydrolysis.

Treatment of the ethyl ester of 2-bromopropionic acid with calcium naphthalenide afforded after hydrolysis the anhydride of 2,2′-dimethylmaleic acid (III). The analogous reaction of calcium naphthalenide with the ethyl ester of 2-bromobutyric acid gave 2-hexene-3,4-dicarboxylic acid (IV). The structural assignments of IV are based on elemental and spectral analysis. The IR spectrum shows a characteristic band at 800 cm^{-1} assignable to the deformation vibrations of C—H in a trisubstituted ethylenic system. The melting point of IV differs from that given in ref. 20, possibly due to geometrical isomerism.



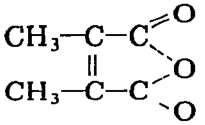
$$\begin{array}{l}CH_3CHCOOH\\ \quad|\\ CH_3CHCOOH\end{array}$$

(I)

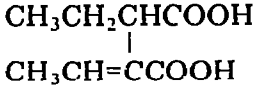


$$\begin{array}{l}CH_3CH_2CHCOOH\\ \qquad\quad|\\ CH_3CH_2CHCOOH\end{array}$$

(II)



(III)



$$\begin{array}{l}CH_3CH_2CHCOOH\\ \qquad\quad|\\ CH_3CH{=}CCOOH\end{array}$$

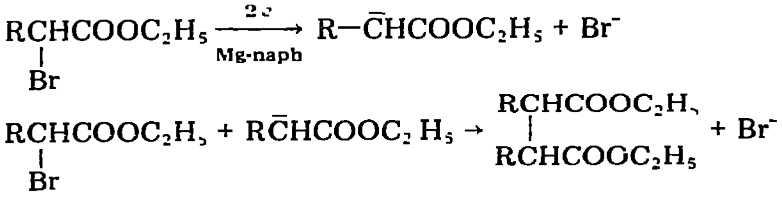
(IV)

In a parallel experiment we detected by chromatography in the non-saponified reaction mixture the diethyl ester of 3-hexene-3,4-dicarboxylic acid, whose structure is confirmed by elemental analysis and spectral data. The IR spectrum shows no band at 800 cm^{-1}, it is thus clear that the reaction between calcium naphthalenide and 2-bromobutyric acid ethyl ester gives 3-hexene-3,4-dicarboxylic acid diethyl ester which, after hydrolysis, yields the isomeric acid IV. The corresponding 3-hexene-3,4-dicarboxylic acid is not known in the free state.

At present not enough is known concerning the nature of the reaction(s) leading to formation of dimeric products I and II to permit any definite mechanistic proposal

A considerable amount of work has been carried out on the interaction between organic halides and sodium naphthalenide in various organic solvents. Garst et al. [4—7] have shown that the reaction produces organic radicals plus halide ions by electron transfer from the radical anion to the halide, and proved that the formation of the dimerization products involved free radical intermediates Sargent and Lux [8] found that the formation of the corresponding dimer is related to the appearance of alkylated dihydronaphthalenes. According to Sargent and Lux these results unequivocally establish the radical—radical anion combination mechanism. In conclusion, we feel that the radical—radical anion combination provides clear evidence for the intermediate formation of free radicals However, it seems that in the present case the radical—radical anion combination does not occur, due to the absence of acids containing the dihydronaphthalene nucleus. The available experimental data do not allow one to identify the mechanistic pathway for the reaction between organic halides and sodium naphthalenide discussed here. There is no apparent way, as yet, of distinguishing between the radical mechanism outlined in refs. 4—9 and a simple nucleophilic displacement as presented in Scheme 1

SCHEME 1



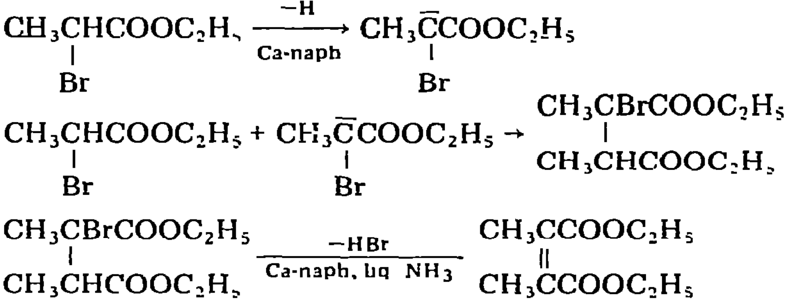
$$\underset{\displaystyle Br}{\underset{|}{RCHCOOC_2H_5}} \xrightarrow[\text{Mg-naph}]{2e} R{-}\bar{C}HCOOC_2H_5 + Br^-$$

$$\underset{\displaystyle Br}{\underset{|}{RCHCOOC_2H_5}} + R\bar{C}HCOOC_2H_5 \rightarrow \begin{array}{l}RCHCOOC_2H_5\\ \quad|\\ RCHCOOC_2H_5\end{array} + Br^-$$

On the other hand, it is hard to imagine an S_N2 displacement by the anion formed on another bromoester molecule, at a rate competitive with the reductive cleavage of the carbon—bromine bond by naphthalenide in the chosen reaction conditions.

For the reaction of the initial bromoesters with calcium naphthalenide Scheme 2 seems to be more probable.

SCHEME 2



$$\mathrm{CH_3}\underset{\underset{\mathrm{Br}}{|}}{\mathrm{C}}\mathrm{HCOOC_2H_5} \xrightarrow[\text{Ca-naph}]{-\mathrm{H}^+} \mathrm{CH_3}\underset{\underset{\mathrm{Br}}{|}}{\bar{\mathrm{C}}}\mathrm{COOC_2H_5}$$

$$\mathrm{CH_3}\underset{\underset{\mathrm{Br}}{|}}{\mathrm{C}}\mathrm{HCOOC_2H_5} + \mathrm{CH_3}\underset{\underset{\mathrm{Br}}{|}}{\bar{\mathrm{C}}}\mathrm{COOC_2H_5} \rightarrow \begin{matrix}\mathrm{CH_3CBrCOOC_2H_5}\\ |\\ \mathrm{CH_3CHCOOC_2H_5}\end{matrix}$$

$$\begin{matrix}\mathrm{CH_3CBrCOOC_2H_5}\\ |\\ \mathrm{CH_3CHCOOC_2H_5}\end{matrix} \xrightarrow[\text{Ca-naph, liq NH}_3]{-\mathrm{HBr}} \begin{matrix}\mathrm{CH_3CCOOC_2H_5}\\ \|\\ \mathrm{CH_3CCOOC_2H_5}\end{matrix}$$

The assumption that the reagent in the reactions investigated is the radical anion of naphthalene is in accord with the paramagnetic properties of the magnesium and calcium adducts of dimethylnaphthalene or anthracene in liquid ammonia[10].

If Scheme 2 is operative, the proton abstraction process in principle can be visualize as a reaction of radical anions or dianions of naphthalene. However, it may also be supposed that the abstraction of the proton is a result of the reaction of the amide anion which may be formed as a result of ammonolysis of the calcium naphthalenide

In order to obtain more detailed information about the mechanism, the interaction between the ethyl ester of 2-bromobutyric acid and calcium in liquid ammonia has been studied. It was established that IV is not formed in detectable amounts Since the formation of calcium amide has been proved to occur [11] in the chosen reaction, the result obtained clearly rules out the amide anion as a base in the process, represented in Scheme 2.

The disproportionation of radical anions to a dinegative ion and a hydrocarbon is thought to be energetically unfavourable[12, 13]. From this point of view there is little evidence for a dianion attack on the α-hydrogen atom from the bromine-containing compound, nevertheless, the reaction of hydrocarbon radical anions with proton-donors has been found useful for the formation of carbanions under very mild conditions[14].

The possibility that III and IV are formed as a result of dimerization of the respective ethoxycarbonylcarbenes must be ruled out because there is no evidence[15] for α-elimination of hydrogen chloride from α-halogeno esters of aliphatic acids.

It is of interest to find experimental proof of the apparent difference in the reactivity of the two metal naphthalenides. The proton-abstracting properties of calcium naphthalenide are clearly demonstrated by the presence of 1,4-dihydronaphthalene (detected by VPC) in the reaction mixture, whereas in the corresponding reaction with magnesium naphthalenide no 1,4-dihydronaphthalene could be detected.

The marked difference in the behaviour of the calcium and magnesium adducts of naphthalene towards the ethyl esters of 2-bromopropionic and 2-bromobutyric acids remains unexplained at present, hence the exact state of the two naphthalenides in liquid ammonia remains uncertain. If we turn our attention to the difference in coordinating abilities of calcium and magnesium and its influence on the state of the species involved, we suggest that the calcium adduct exists as an unpaired ionic species, in contrast to magnesium naphthalenide. The reaction pathway (Scheme 1 or Scheme 2) will depend upon the relative freedom of the negatively-charged particles.

The formation of the diethyl ester of 2-hexene-3,4-dicarboxylic acid (IV) instead of the diethyl ester of 2,2'-diethylmaleic acid is governed probably by steric factors; the van der Waals repulsion forces between the substituents at the carbon atoms, forming the double bond in diethylmaleic acid ethyl ester, must be greater than those in the diethyl ester of 2-hexene-3,4-dicarboxylic acid.

Experimental

All melting points were measured using a Koffler hot stage apparatus fitted with a polarizing microscope, and are uncorrected. A Fractovap, model B apparatus produced by Carlo Erba, Italy was used for VPC analysis with stationary phase (PEGA) 8% w/w of the inert support (Chromosorb W) Nitrogen was used as carrier gas. The IR spectra were obtained with Karl Zeiss (Jena) UR-10 spectrophotometer.

Reactions of magnesium naphthalenide with ethyl esters of 2-bromopropionic and 2-bromobutyric acid

To 0.1 mol of magnesium naphthalenide[16], 0.1 mol of the bromoester was added. The deep green solution of the magnesium naphthalenide turned colourless and a crystalline product was obtained The reaction was allowed to continue at −33° for 60 min Ammonia was evaporated while simultaneously adding 200 ml dry ether. The reaction mixture was acidified with 3*N* hydrogen chloride and extracted thoroughly with ether (200 ml). The ether extract was dried (Na_2SO_4) and evaporated. The residue was saponified with 10% KOH and, after the usual work up, mixtures of racemic and *meso* forms of the respective dialkylsuccinic acids were obtained. Yields: 2,2'-dimethylsuccinic acid, 4.2 g (58%), 2,2'-diethylsuccinic acid 4.5 g (52%). Separation of the mixtures was carried out as follows: 2,2'-dimethylsuccinic acid (I) The crude product was refluxed in dry benzene (50 ml), and the insoluble crystalline residue (m.p. 200—203°) was collected by filtration, and recrystallization from water afforded *meso*-2 2'-dimethylsuccinic acid as a colourless crystalline solid melting at 205—206° (lit [17] m.p. 193°), IR (nujol) 1700 cm^{-1} [ν(COOH)]. (Found: C, 49 68; H, 6.89. $C_6H_{10}O_4$ calcd · C, 49 31; H, 6.90%.)

Cooling the benzene extract gave a crystalline precipitate melting at 120—124° which was recrystallized once from water to give (±)-2,2'-dimethylsuccinic acid, m.p. 126—127° (lit. [17] 129°), IR (nujol) 1700 cm^{-1} [ν(COOH)]. (Found: C, 49.52, H, 6.94. $C_6H_{10}O_4$ calcd.: C, 49.31; H, 6.90%.)

The same general procedure was used with the mixture of *meso*- and (±)-2,2'-diethylsuccinic acid (II). (±)-2,2'-Diethylsuccinic acid has m.p. 133—134°

(lit. 133° [17], 129° [18]. IR (nujol) 1700 cm^{-1} [ν(COOH)]. (Found. C, 55.06; H, 8.02. $C_8H_{14}O_4$ calcd. C, 55.16, H, 8.10%.)

Meso-2,2'-diethylsuccinic acid was recrystallized from water to give colourless crystals, m.p. 211—212°(lit. 195° [17], 190°[18]), IR (nujol) 1700 cm^{-1} [ν(COOH)]. (Found: C, 55.33, H, 8.00. $C_8H_{14}O_4$ calcd.: C, 55.16; H, 8.10%.)

Reactions of calcium naphthalenide with ethyl esters of 2-bromopropionic and 2-bromobutyric acid

To the blue solution of calcium in liquid ammonia [2 g(0.05 mol) calcium and 700 ml liquid ammonia], a solution of 12.80 g (0.1 mol) naphthalene in 50 ml dry ether was added. The deep blue colour turned pale green. The mixture was kept at —33° (b.p. NH_3) for 3 h, then a solution of 0.1 mol of the appropriate ester in 30 ml ether was added dropwise in 30 min. The reaction mixture was allowed to stand for 2 h. Ammonia was evaporated while simultaneously adding 200 ml ether. The resulting precipitate was worked up following a procedure similar to that given above.

2,2'-Dimethylmaleic anhydride (III). M.p. 93—94° (lit. [19] 95.5°), IR (nujol) 1790 and 1820 cm^{-1} [ν(anhydride)]. (Found: C, 57.41, H, 5.04. $C_6H_6O_3$ calcd.: C, 57.14; H, 4.80%) Yield: 2.50 g (40%)

2-Hexene-3,4-dicarboxylic acid (IV). Yield 4.9 g (57%). It was purified by crystallization from water, m.p. 235—236° (lit. [20] 236°). IR (nujol) 1695 cm^{-1} (conjugated COOH) and 1630 cm^{-1} (conjugated C=C). (Found: C, 55.93; H, 6.80. $C_8H_{12}O_4$ calcd.: C, 55.80, H, 7.03).

3-Hexene-3,4-dicarboxylic acid ethyl ester. The isolated reaction mixture was not saponified. Surplus naphthalene was removed by filtration. The residue was chromatographed on a neutral alumina column, eluted with hexane and benzene to afford a pale yellow oil, b.p. 53—55°/20 mm. IR ($CHCl_3$): 1730 cm^{-1} (COOR) and 1650 cm^{-1} (C=C). (Found, C, 62.99, H, 8.85. $C_{12}H_{20}O_4$ calcd.: C, 63.13; H, 8.83%.)

Reaction of 2-bromobutyric acid ethyl ester with calcium in liquid ammonia

To 2 g (0.05 mol) calcium dissolved in 1000 ml anhydrous ammonia was slowly added 19.50 g (0.1 mol) of the ethyl ester of 2-bromobutyric acid, diluted with 30 ml dry ether. The reaction was allowed to continue at —33° for 2 h. The deep blue solution turned colourless. Ammonia was evaporated while adding 200 ml dry ether, and the reaction mixture was acidified with 3*N* hydrogen chloride and extracted several times with ether. The ether extracts were combined, dried (Na_2SO_4), and thenconcentrated to afford 11.50 g liquid product. Within 1 h there appeared a (1.50 g) crystalline precipitate, which after recrystallization from ethanol had m.p. 110—111° (lit. [21] m.p. of 2-bromobutyric acid amide 112°). (Found: C, 29.31; H, 5.04. C_4H_8BrNO calcd.: C, 28.90; H, 4.84%.) The liquid residue was distilled in vacuo to give two products: 2.60 g, b.p. 53—55°/12 mm and 2.50 g, b.p. 80—90°/12mm. First fraction: found. C, 43.61; H, 6.83. Second fraction, found: C, 51.30; H, 7.69%.)

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