Communications

The Reaction of Lithium Naphthalenide with Quaternary Ammonium Salts

Summary: The reaction of aliphatic and aromatic trimethylammonium iodide salts with lithium naphthalenide occurs selectively with elimination of trimethylamine.

Sir: The reaction of aromatic radical anions with halogen containing organic compounds has been shown to produce radicals plus halide ions *via* dissociative electron transfer.[1,2] Although tosylates,[3] sulfonamides,[4] and polyphenylethanes[5] have been cleaved with sodium naphthalenide to form alcohols, amines, and polyphenylmethanes, reactions with other functional groups such as quaternary ammonium salts do not appear to have been studied.[6]

We are pleased to report that several alkyl- and aryltrimethylammonium iodide salts listed in Table I undergo reductive cleavage with lithium naphthalenide in tetrahydrofuran (THF). The carbon–nitrogen bond to the larger R group is cleaved preferentially to form radicals and trimethylamine.

The formation of radicals is inferred from the reaction of 5-hexenyltrimethylammonium iodide, **5**, where 4% of methylcyclopentane is formed together with 35% of 1-hexene. The reasons why formation of methylcyclopentane serves as evidence for the presence of 5-hexenyl radical have been given by Garst and his coworkers for reactions of 5-hexenyl halides with sodium naphthalenide.[7]

Analysis of the results on benzhydryltrimethylammonium iodide, **1**, to form *sym*-tetraphenylethane, **6**, also suggests that some of the **6** is formed by α coupling of two benzhydryl radicals (path A). Radicals formed in the presence of an aromatic radical anion are expected to be reduced to carbanions faster than they can couple to dimer.[1] Path B, summarized in eq 1, involves two sequential one-electron reductions during which benzhydryl radical is reduced by a second equivalent of naphthalenide ion to form a diphenylmethyl carbanion which then displaces trimethylamine from **1** yielding **6**.

$$\underset{\mathbf{1}}{(C_6H_5)_2CH\overset{+}{N}(CH_3)_3I^-} \xrightarrow{C_{10}H_8^{\cdot -}} (C_6H_5)_2CH\cdot \xrightarrow{C_{10}H_8^{\cdot -}}$$

$$(C_6H_5)_2CH:^- \xrightarrow{\mathbf{1}} \mathbf{6} \qquad (1)$$

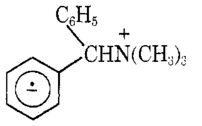
In experiments which use equimolar amounts of naphthalenide and **1**, if the mole percentage of unreacted salt (Table I) is a measure of the maximum amount of carbanion formed by path B, it can be concluded that 22% of **6** is formed by path B and 35% by path A. Additional support for path A was reported recently for benzylic halides analogous to **1** reacting with naphthalenide under conditions which militate against path B, namely, the slow dropwise addition of naphthalenide to halide.[8]

This reductive cleavage of a carbon–nitrogen bond by naphthalenide ion is analogous to the sodium in liquid ammonia fission of quaternary ammonium salts which have been studied systematically by Grovenstein.[9,10] The most surprising difference between our results with lithium naphthalenide and those reported earlier is that tetramethylammonium iodide did not react with lithium naphthalenide after 3 days at 25°. Sodium in liquid ammonia on the other hand readily cleaved tetramethylammonium bromide completely within 1.0–2.0 hr.[9b]

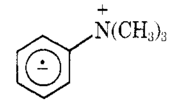
Whereas reductions with sodium in liquid ammonia can be complicated by the presence of strongly basic amide ions, aromatic radical anions are weakly basic and complications due to Sommelet–Hauser and Stevens rearrangements are not encountered.[12]

Normally in reductions with naphthalenide ion 1 equiv of naphthalene must be separated from the products. Although it is possible to use α-dimethylaminonaphthalene's radical anion as the reducing agent,[6] we have cleaved **1** (13.76 g, 0.039 mol) to give **6** (88–100% yields) using a catalytic amount of naphthalene (1 g) by the portionwise addition of 1 equiv of lithium to a suspension of **1** in THF (100 ml).

The reductive cleavage of a carbon–nitrogen bond by naphthalenide ion may form the same type of intermediate (*e.g.*, **1′** or **3′**) as is generated in the synthesis step of the radical anion chain mechanism[13] for substitution at tertiary carbon in *p*-nitrocumyl chloride and α,*p*-dinitrocumene by tertiary amines.[14] An alternate possibility is



1′



3′

that naphthalenide ion transfers the electron directly into the valence shell of the nitrogen atom to form an unstable intermediate which eliminates the more stable radical and a tertiary amine.

In summary, a new method for the chemical cleavage of the more complex organic grouping from a quaternary ammonium iodide salt has been discovered.

References and Notes

(1) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971), and earlier references therein.
(2) G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160

Table I
Reactions of Lithium Naphthalenide with Quaternary Ammonium Iodide Salts in THF[a]

$RN^+(CH_3)_3I^-$	No.	Reaction time, minutes	% RR	% RH	% recovd salt	% $(CH_3)_3N$	% $RN(CH_3)_2$
$(C_6H_5)_2CH$	**1**	<5	57[b]	22[c]	22	81–85[b]	5
$(C_6H_5)CH_2$	**2**	<5	6[c]	72[c]	9	87[b]	8[b]
C_6H_5	**3**	15	4[c]	39[c]	48	18[b]	10[c]
1-$C_{10}H_7$[d]	**4**	90	0.2[c]	45[c]	44	80[b]	17[c]
$CH_2{=}CH(CH_2)_4$	**5**	120		4[e] 35[f]	38	80[b]	. . .

[a] One equivalent of naphthalenide ion per each equivalent of salt; dry salt is added to naphthalenide ion in one portion. [b] Trimethylamine was distilled, derivatized with methyl iodide, and tetramethylammonium iodide was isolated. [c] Quantitative gas chromatography. [d] Lithium biphenylenide was used. [e] Methylcyclopentane. [f] 1-Hexene.

(1968); G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966); G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967); G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971); G. D. Sargent, C. M. Tatum, and S. M. Kastner, *J. Amer. Chem. Soc.*, **94**, 7174 (1972).

(3) W. D. Closson, P. Wriede, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 1581 (1966).

(4) (a) S. Ji, S. Schulenberg, and W. D. Closson, *J. Amer. Chem. Soc.*, **92**, 650 (1970); (b) S. Ji, L. B. Gortler, A. Waring, A. Tattisti, S. Bank, W. D. Closson, and P. Wriede, *ibid.*, **89**, 5311 (1967).

(5) J. J. Eisch, *J. Org. Chem.*, **28**, 707 (1963).

(6) For a recent literature summary, see S. Bank and M. Platz, *Tetrahedron Lett.*, 2097 (1973).

(7) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966).

(8) H. E. Zieger, I. Angres, and L. Maresca, *J. Amer. Chem. Soc.*, **95**, 8201 (1973).

(9) E. Grovenstein, Jr., and L. C. Rogers, *J. Amer. Chem. Soc.*, **86**, 854 (1964). (b) E. Govenstein, Jr., and R. W. Stevenson, *ibid.*, **81**, 4850 (1959). (c) E. Grovenstein, Jr., S. Chandra, C. Collum, and W. E. Davis, Jr., *ibid.*, **88**, 1275 (1966). (d) R. A. Rossi and J. F. Bunnett, *ibid.*, **96**, 112 (1974); **94**, 683 (1972).

(10) This reaction has some analogy to Emde reduction. The electrochemical degradation of quaternary ammonium salts by electrolysis of aqueous solutions has been reported.[11] However, the results differed substantially from those reported here owing to the use of water as solvent (*e.g.*, benzhydryltriethylammonium acetate was reduced to diphenylmethane).

(11) M. Finkelstein, R. C. Peterson, and S. D. Moss, *J. Amer. Chem. Soc.*, **81**, 2361 (1959).

(12) We have carried out Sommelet–Hauser and Stevens rearrangement studies on **1** and **2** using alkyllithium reagents. Use of trityllithium or benzhydryllithium in THF on **1** and **2** gives high yields of >90% of displacement products (pentaphenylethane, **6**, *unsym*-tetraphenylethane, and 1,1,2-triphenylethane).

(13) (a) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, J. W. Manthey, M. T. Musser, and R. T. Sweiger, *J. Amer. Chem. Soc.*, **90**, 6219 (1968); (b) N. Kornblum, *et. al.*, *ibid.*, **89**, 725 (1967); (c) R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, **87**, 4520 (1965); (d) *ibid.*, **86**, 3904 (1964); (e) G. A. Russell and W. C. Danen, *ibid*, **88**, 5663 (1966).

(14) N. Kornblum and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 1804 (1970).

(15) Doctoral Candidate at Brooklyn College of The City University of New York, 1971.

Department of Chemistry
Brooklyn College of the
City University of New York
Brooklyn, New York 11210

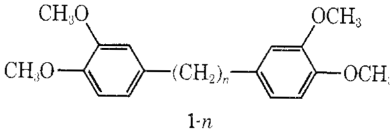
Isaac Angres[15]
Herman E. Zieger

Received January 16, 1974

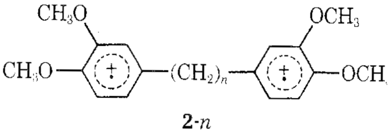
Electrosynthesis of Medium- and Large-Sized Rings by Oxidative Cyclization of Bis(3,4-dimethoxyphenyl)alkanes

Summary: On anodic oxidation in trifluoroacetic acid (TFA)-dichloromethane, diarylalkanes, $Ar(CH_2)_nAr$ where Ar = 3,4-dimethoxyphenyl and $n \geq 6$, undergo a novel dimerization–cyclization reaction with formation of a ($2n + 8$)-membered ring compound (**3**-*n*).

Sir: We report the anodic synthesis of cyclic compounds containing rings with as many as 40 members starting from the bis(3,4-dimethoxyphenyl)alkanes (**1**-*n*). These reactions involve two-electron oxidations to give the intermediate dication diradicals (**2**-*n*) which undergo coupling simultaneously at both ends with a neighboring ion. Dication diradicals have recently been implicated as intermediates in the intramolecular cyclization of methoxybibenzyls.[1] While the synthesis of medium- and large-sized rings has its own inherent interest, the results presented here are particularly novel since all previous attempts to prepare such compounds by anodic coupling reactions have been entirely unsuccessful.[2]

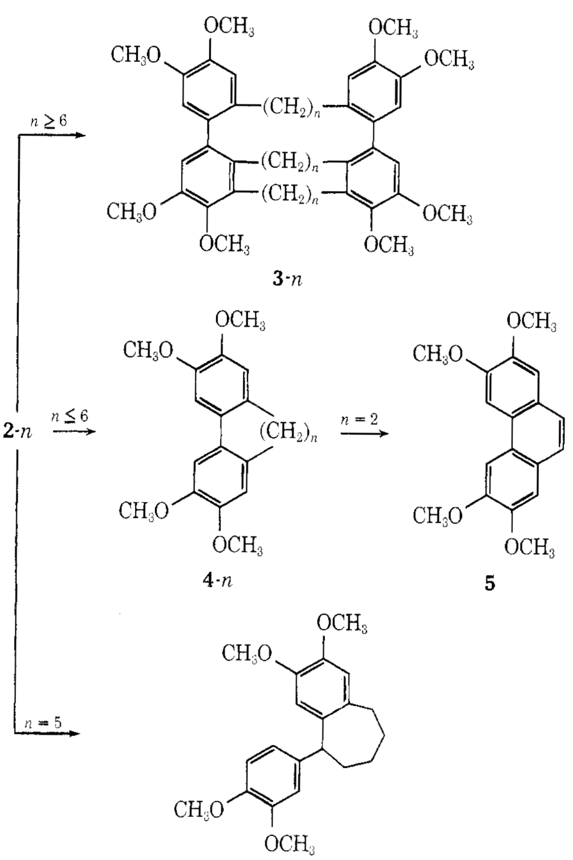


1-*n*



2-*n*

Scheme I



The synthesis were carried out by anodic oxidation of the substrates (5.0 mmol) in TFA–dichloromethane (1:3) containing n-Bu_4NBF_4 (1 g in 200 ml of solvent) in a closed two-compartment cell. Constant current (current density 0.16 mA/cm^2) oxidation was carried out at a platinum anode (150 cm^2) at −20° under nitrogen until 3.0 Faradays/mol had been passed. Zinc dust (3 g) was added and stirring was continued for an additional hour at −20°. After work-up, the oily residue was chromatographed on silica gel (200 g, toluene–ethyl acetate gradient, 25-ml fractions). The fractions were analyzed by tlc and nmr and mass spectroscopy. The results, along with those obtained by oxidation with manganic tris(acetylacetonate)[3,4] (MTA) are summarized in Table I.

Large-ring compounds (**3**-*n*) are only formed on the oxidation of compounds containing a saturated chain of six or more carbons. As indicated in Table I, both the yield and the nature of the oxidation products of **1**-*n* depend dramatically upon the carbon chain length. In spite of this, we feel that the initial oxidation product is *2-n* in all cases.[5] The reactions which the various dication diradicals (**2**-*n*) undergo are summarized in Scheme I. When *n* is 4 or smaller intramolecular cyclization giving the bridged biphenyls (**4**-*n*) is the exclusive reaction pathway. In the specific case of *n* = 2, the phenanthrene **5** is the product isolated.[1] The case where *n* = 5 (**1**-5) is unique. Cyclization here occurs between one ring and the position α to the other ring to give **6**. It is of interest that the yield of **3**-*n* is low for *n* = 6 or 7, reaches a maximum at *n* = 8 or 9, and diminishes sharply at *n* = 16. Also at *n* = 16 the