α,α'-Dimetalations of Dimethylarenes with Organosodium Reagents. The Catalytic Effect of Certain Tertiary Amines[1]

GEORGE B. TRIMITSIS,* A. TUNCAY, R. D. BEYER, AND K. J. KETTERMAN

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001

Received January 15, 1973

It has been found that *N,N,N',N'*-tetramethylethylenediamine (TMEDA) exerts a marked catalytic influence on α,α'-dimetalations of certain dimethylarenes. Reaction of 1,2-, 1,3-, 1,6-, and 1,8-dimethylnaphthalene and *o*- and *m*-xylene with 2.1–4.0 molar equiv of *n*-amylsodium in the presence of TMEDA produced the corresponding α,α' dianions in quantitative yield. 1,3- and 1,8-dimethylnaphthalene and *m*-xylene dianions were subjected to alkylation and/or carbonation and aldol condensation, to produce the expected α,α'-dicondensation products in high yield. 1,4-Dimethylnaphthalene and *p*-xylene could not be converted to their α,α' dianions. The reactivity of the above dimethylarenes toward α,α'-dimetalation was established and arguments are presented to account for the observed results. The catalytic effect of certain substances other than TMEDA on metalations with *n*-amylsodium has been examined and the results are discussed.

Among the various transformations in organic chemistry, those leading to carbon–carbon bond formation have always been considered to be of the utmost fundamental interest and immense practical importance.[2] A large proportion of the carbon–carbon bond forming reactions proceed through carbanion intermediates:[2,3] aldol and Claisen condensations, Grignard reactions, alkylations of enolates and other anions, and metal acetylide reactions are just a few examples of such reactions.

Since most carbon acids are only weakly acidic,[4] the demand for strong bases capable of transforming such substrates to the corresponding carbanions under mild conditions and reasonably short reaction times is great. Among the strongest and most suitable bases presently available is the family of lithium alkyls,[5] which either alone or in conjunction with certain tertiary amine catalysts[6] have revolutionized the area of carbanion chemistry.

Although sodium and potassium alkyls[7] have been known for a long time to be much stronger bases than organolithium reagents, their use in the formation of carbanions has so far been relatively limited. The main reason for this is the high insolubility of organosodium and organopotassium reagents in hydrocarbon solvents, resulting in heterogeneous reaction mixtures and unacceptably low yield metalations even at high temperatures and prolonged reaction times.[8]

We have observed[1] that metalations with *n*-amylsodium, the most commonly used organosodium reagent, can be improved tremendously by performing these reactions in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). Just as in the case of metalations with organolithium reagents,[6] this tertiary amine appears to have a profound catalytic effect on metalations with organosodium reagents.

The present report describes the use of this new base–catalyst system in the quantitative α,α'-dimetalation of certain dimethylnaphthalenes and xylenes, and the subsequent reaction of these dianions with representative electrophilic reagents to give a variety of α,α'-dicondensation products in high yield. In addition, the reactivity of the three isomeric xylenes as well as certain isomeric dimethylnaphthalenes toward α,α' dianion formation has been studied and arguments are presented in order to explain the observed trends. Finally, the catalytic effect of certain substances other than TMEDA on metalations with *n*-amylsodium has been examined and the results are discussed.

Results

Formation of the *n*-Amylsodium–TMEDA Complex.—Addition of an approximately equimolar amount of TMEDA (see Experimental Section) to a suspension of *n*-amylsodium in hexane at −15° resulted in an apparent solubilization of the solid to give a bright blue solution. Centrifugation of a portion of this solution, however, gave a clear, supernatant liquid and a dark blue precipitate, indicating that the amine had a dispersing rather than a solubilizing effect on *n*-amylsodium in hexane.

The *n*-amylsodium–TMEDA mixture was found to be an exceedingly powerful metalating agent capable of quantitatively converting certain dimethylarenes to their α,α' dianions at room temperature within 2 hr. The dimetalations of certain dimethylnaphthalenes and those of the three isomeric xylenes are described below.

Metalation of Certain Dimethylnaphthalenes.—The reactions of 1,2-, 1,3-, 1,4-, 1,6-, and 1,8-dimethylnaphthalene with *n*-amylsodium were studied under a variety of experimental conditions and their reactivities toward α,α'-dimetalation were compared. Of the five isomers examined, 1,3-dimethylnaphthalene was found to be the most reactive toward α,α'-dimetalation. Thus, treatment of this hydrocarbon at room temperature with 2.1–2.4 equiv of *n*-amylsodium[9] in the presence of 2 equiv of TMEDA for 2 hr produced the insoluble brick-red 1,3-dimethylnaphthalene dianion **1** (Scheme I) in practically quantitative yield, as evidenced by quenching the reaction mixture with deuterium oxide followed by nmr analysis of the deuterated product **2a**.

---

[1] For a preliminary account of part of this work, see G. B. Trimitsis, A. Tuncay, and R. D. Beyer, *J. Amer. Chem. Soc.*, **94**, 2152 (1972).

[2] W. Carruthers, "Some Modern Methods of Organic Synthesis," Cambridge University Press, London, England, 1971, pp 1–70.

[3] H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 492–816.

[4] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 1–45.

[5] J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

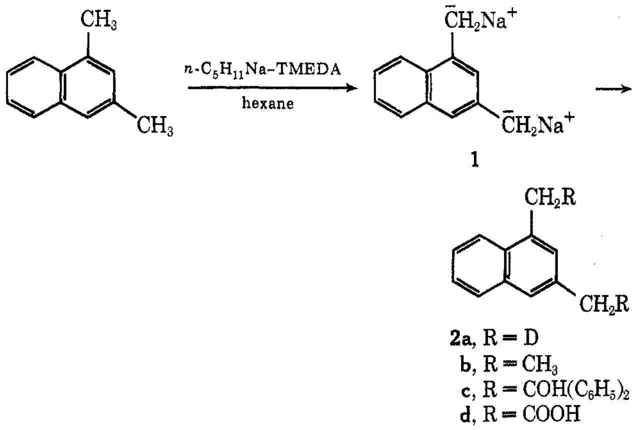
[6] (a) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964); (b) A. W. Langer, Jr., *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965); (c) C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965).

[7] R. A. Benkeser, D. J. Foster, and D. M. Sauve, *Chem. Rev.*, **57**, 867 (1957).

[8] A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., *J. Amer. Chem. Soc.*, **65**, 1339 (1943).

[9] The reaction of *n*-amyl chloride with sodium metal to give *n*-amylsodium proceeds to the extent of 70–80% yield, and the amount of base used in this experiment was that produced from 3 equiv of *n*-amyl chloride and excess sodium. For more details see Experimental Section.

SCHEME I

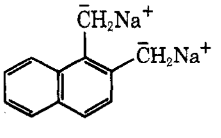


1

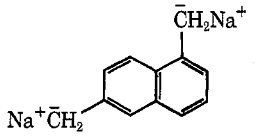
2a, R = D
b, R = CH_3
c, R = $COH(C_6H_5)_2$
d, R = COOH

1,3-Dimethylnaphthalene dianion **1** was found to react quite readily at room temperature with electrophilic reagents to give α,α'-dicondensation products in high yield. For example, reaction with excess methyl iodide converted dianion **1** almost exclusively to 1,3-diethylnaphthalene (**2b**), as shown by vapor phase chromatographic (vpc) analysis of the crude reaction mixture. Only trace amounts of a second component, most likely the monoalkylation product, could be detected, and no starting material was recovered. Similarly, reaction of dianion **1** with 2.5 equiv of benzophenone gave the new carbonyl addition product **2c**, in 50% yield, while carbonation with excess solid carbon dioxide produced the new dicarboxylic acid **2d**, in 74% yield. Structural assignments for products **2c** and **2d** were based on C, H analyses and on spectral data (see Experimental Section).

Reaction of 1,2-, 1,6-, and 1,8-dimethylnaphthalene with n-amylsodium–TMEDA under conditions identical with those employed for the quantitative dimetalation of 1,3-dimethylnaphthalene, followed by deuteration with deuterium oxide and nmr analysis of the resulting products, showed the incorporation of 1.8 atoms of deuterium per molecule of 1,2- and 1,6-dimethylnaphthalene, and 1.5 atoms of deuterium per molecule of 1,8-dimethylnaphthalene, thereby indicating that only partial dimetalation of these substances had occurred under these conditions. Most interestingly, however, when the amount of n-amylsodium was increased to 3.5–4.0 equiv,[10] and the amount of TMEDA to 3.4 equiv, complete dimetalation was achieved in all three cases, to give α,α'-dimethylnaphthalene dianions **3**, **4**, and **5**, respectively, in quantitative yield, as shown by deuteration.

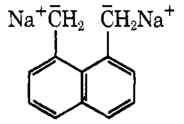


3

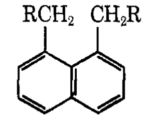


4

In addition to deuteration, 1,8-dimethylnaphthalene dianion **5** was found to undergo facile dicondensation reactions with a variety of typical electrophilic reagents. For example, treatment of **5** with 2.5 equiv of benzophenone afforded the new diol **6a**, in 52% yield, while reaction with excess carbon dioxide produced the new dicarboxylic acid **6b**, in 40% yield. The identity of products **6a** and **6b** was established by C, H analysis and by their nmr and ir spectra (see Experimental Section).



5

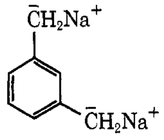


6a, R = $COH(C_6H_5)_2$
b, R = COOH

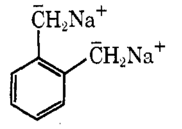
Unlike the isomeric naphthalenes discussed above, reaction of 1,4-dimethylnaphthalene with up to 4.0 equiv of n-amylsodium–TMEDA followed by deuteration resulted in the incorporation of only one deuterium atom per molecule of hydrocarbon, clearly indicating that 1,4-dimethylnaphthalene had been converted only to its monoanion.

Metalation of *o*-, *m*-, and *p*-Xylene.—The three isomeric xylenes had been previously dimetalated in low yield[8] by heating with n-amylsodium in octane for 3 hr. Their reactivity toward α,α'-dianion formation,[8] as indicated by subsequent carbonation of the reaction mixtures, was reported to be m-xylene ≅ p-xylene > o-xylene.

Reaction of o-, m-, and p-xylene with n-amylsodium in the presence of TMEDA under the conditions employed in the previous section established a completely different reactivity sequence for the above hydrocarbons and clearly showed that m-xylene was much more reactive toward α,α'-dimetalation than either of the other two isomers. Thus, reaction of m-xylene with 2.1–2.4 equiv of n-amylsodium[9] in the presence of 2.0 equiv of TMEDA in hexane at room temperature for 2 hr produced the insoluble α,α'-disodio-m-xylene **7** in practically quantitative yield, as determined by subsequent quenching with deuterium oxide and quantitative nmr analysis. In addition treatment of dianion **7** with an excess of methyl iodide afforded almost exclusively 1,3-diethylbenzene, with only a minor amount of the monocondensation product 1-ethyl-3-methylbenzene being produced, as shown by vpc analysis of the crude reaction mixture.



7



8

Reaction of o-xylene with n-amylsodium–TMEDA under the above conditions followed by deuteration with deuterium oxide resulted in the incorporation of only 1.64 deuterium atoms per molecule of hydrocarbon. As in the case of 1,2-dimethylnaphthalene, however, when the amount of base was increased to 3.5–4.0 equiv[10] complete α,α'-dimetalation occurred to give dianion **8** in quantitative yield.

Finally it was found that unlike m- and o-xylene p-xylene failed to afford an α,α' dianion even when treated with 4.0 equiv of n-amylsodium in the presence of TMEDA. Instead, only α-monometalation occurred, as indicated by quenching the reaction mixture

---

[10] The amount of base used in these experiments was that produced from the reaction of 5.0 equiv of n-amyl chloride and excess sodium. For more details see footnote 9 and Experimental Section.

with deuterium oxide, followed by nmr analysis of the resulting product.

Next, an effort was made to investigate whether substances other than TMEDA might serve as catalysts in the α,α′-dimetalation of dimethylarenes by means of *n*-amylsodium in hydrocarbon solvents. For this purpose, the effect of 1,4-diazabicyclo[2.2.2]octane (DABCO), a tertiary amine which has been used extensively as a catalyst in metalations with organolithium reagents,[6a,11] and sodium *tert*-butoxide, which has been occasionally used to promote metalations with *n*-amylsodium,[12] were tested.

Reaction of *m*-xylene with 2.1–2.4 equiv of *n*-amylsodium[9] in the presence of 2.2 equiv of DABCO, under conditions identical with those described earlier, followed by treatment of the reaction mixture with an excess of methyl iodide afforded a mixture of products, consisting of starting material, 1-ethyl-3-methylbenzene, and 1,3-diethylbenzene in the ratio of 2.8:1.0:1.1.

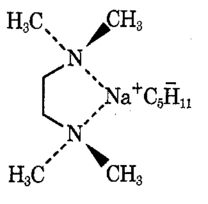
Similar results were obtained when dimethylation of *m*-xylene was attempted in the presence of sodium *tert*-butoxide as a catalyst. Thus, treatment of this hydrocarbon with 2.1–2.4 equiv of *n*-amylsodium[9] and 2.8 equiv of sodium *tert*-butoxide at room temperature for 2 hr, followed by methylation of the reaction mixture with excess methyl iodide, again afforded starting material, 1-ethyl-3-methylbenzene and 1,3-diethylbenzene, this time in a ratio of 1.0:1.1:4.6.

Finally, it was found that reaction of *m*-xylene or 1,3-dimethylnaphthalene with *n*-amylsodium under the above conditions, but in the *absence* of a catalyst, produced only low yield α-monometalation, and no dimetalation at all.

Discussion

Catalytic Effect of TMEDA on Metalations with *n*-Amylsodium.—The results described in the previous section clearly indicate that unlike DABCO and sodium *tert*-butoxide, TMEDA is an exceedingly effective catalyst in metalations of weak carbon acids by means of *n*-amylsodium.

Conceivably TMEDA can catalyze metalations with organosodium reagents in at least two different ways. First, it can coordinate with the sodium ion (structure 9) and in so doing it can cause the large *n*-amylsodium aggregates to disintegrate into smaller particles, thereby providing a much larger surface area for the reaction to occur. That a peptizing action does indeed occur when TMEDA is added to the organosodium reagent is quite evident, since an *n*-amylsodium slurry in hexane appears as a true solution upon addition of TMEDA. As pointed out earlier, high-speed centrifugation of the reaction mixture afforded a dark blue precipitate and a clear supernatant layer, thereby confirming that the effect of TMEDA was to peptize rather than to solubilize the *n*-amylsodium aggregates in the hydrocarbon solvent.



9

In addition to its peptizing action, TMEDA may also catalyze metalations with *n*-amylsodium in another way. Complex formation between the sodium ions and TMEDA will undoubtedly help diffuse the polarizing power of the metal ion, thus weakening the carbon–sodium bond. As a result the carbanion will become more basic and therefore more reactive. Similar theories have been proposed in order to explain the catalytic effect of TMEDA and other tertiary amines on metalation reactions with organolithium reagents.[6]

The inability of DABCO to catalyze metalations with *n*-amylsodium is quite interesting, especially since this diamine has been found to be almost as effective[6a] in catalyzing metalations with alkyllithium reagents as TMEDA. The ineffectiveness of DABCO as a catalyst in metalations with *n*-amylsodium is most likely due to the fact that unlike TMEDA this diamine cannot act as a bidentate ligand.[13] Its coordinating power is therefore much lower than that of TMEDA, and its ability to disintegrate the tightly packed organosodium aggregates is considerably weaker. Although organolithium reagents also exist in a polymeric form[14] in hydrocarbon solvents, these compounds are much less ionic than organosodium compounds and the monomer units are held much less tightly in the aggregates. Consequently, even monodentate ligands such as DABCO and triethylamine have been shown to be capable of disrupting the polymeric alkyllithium species,[6c] thereby catalyzing metalations by means of these reagents.

Morton[12b] in 1955, and more recently Benkeser[12a] and his coworkers, have demonstrated that sodium *tert*-butoxide can serve as an effective catalyst in certain metalations with organosodium reagents. For example, it was found that, while treatment of *tert*-butylbenzene with *n*-amylsodium in nonane for 20 hr afforded only a 17% yield of ring metalation,[12a] an identical reaction in the presence of sodium *tert*-butoxide increased the yield of metalation to 70%. Under the reaction conditions employed during the present study the catalytic properties of sodium *tert*-butoxide in organosodium metalations were found to be slightly better than those of DABCO but definitely poorer than those of TMEDA.

Relative Reactivity of Isomeric Dimethylarenes toward α,α′-Dimetalation.—The fact that not all of the isomeric xylenes and dimethylnaphthalenes could be converted to their α,α′ dianions with equal facility is of particular interest and merits further discussion. Deuteration experiments during the present study clearly established that the ease of α,α′-dimetalation in the case of the xylenes is *m*-xylene > *o*-xylene ≫ *p*-xylene. This reactivity sequence is quite different from that reported by Morton[8] and his coworkers, who found *p*-xylene to be just as reactive as *m*-xylene toward α,α′-dimetalation, and *o*-xylene to be the least reactive of the three.

The reactivity sequence established during the

---

[11] E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

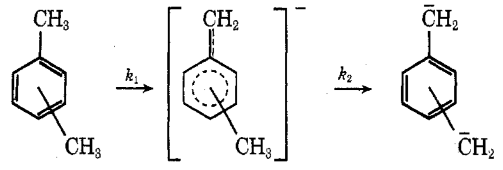
[12] (a) R. A. Benkeser, T. F. Crimmins, and Wen-hong Tong, *J. Amer. Chem. Soc.*, **90**, 4366 (1968); (b) A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955); (c) A. A. Morton and A. E. Brachman, *J. Amer. Chem. Soc.*, **73**, 4363 (1951); (d) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

[13] R. W. Parry in "The Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold, New York, N. Y., 1956, pp 220–252.

[14] T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965).

present study for the α,α'-dimetalation of the three isomeric xylenes can be best explained by means of a two-step mechanism as shown in Scheme II.

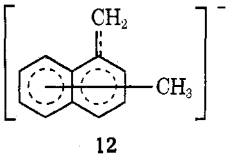
SCHEME II



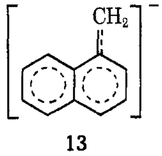
10 11

According to this mechanism the hydrocarbon is envisioned to react first with 1 equiv of base to produce the benzylic monoanion **10**, which in turn reacts with a second molecule of base to form the dianion **11**. Undoubtedly, the negative charge in monoanion **10** will make ionization of the second methyl group much more difficult than that of the first ($k_1 > k_2$), and therefore k_2 will be the rate-determining step. Furthermore, the ease of ionization of the second methyl group is not expected to be the same for all three isomeric xylene monoanions, but instead should depend on the electron density accumulation on the carbon bearing each of the methyl groups. Since delocalization in benzylic anions such as **10** is known to result in the largest charge accumulation at the para position of the benzene ring, with the ortho and meta positions receiving progressively less charge,[15] it would reasonably follow that the tendency of the three isomeric xylene monoanion toward dianion formation would be in the order meta > ortho > para, a conclusion which is in excellent agreement with our experimental results.

Similar arguments can be proposed to account for the results obtained in the case of the five isomeric dimethylnaphthalenes. Their reactivity toward latteral dimetalation as determined in the present study was shown to be 1,3-dimethylnaphthalene > 1,2-dimethylnaphthalene $\sim$ 1,6-dimethylnaphthalene > 1,8-dimethylnaphthalene $\gg$ 1,4-dimethylnaphthalene. Assuming that dianion formation proceeds through a monoanion such as that represented by structure **12**, the above results are, for the most part, in good qualitative agreement with Adamov's[16] self-consistent field (scf) calculations concerning the electron-density distribution in 1-methylnaphthalene monoanion **13**. These calculations predict that charge accumulation in monoanion **13** decreases in the order α-carbon > C_4 > C_2 > C_7 > C_5 > C_6 > C_3 > C_8. On the basis of these electron-density distributions, the high reactivity of 1,3-dimethylnaphthalene and the low reactivity of 1,4-dimethylnaphthalene toward α,α'-dianion formation can be easily rationalized. The lower than expected reactivity of 1,8-dimethylnaphthalene toward α,α'-dianion formation is most likely due to the inability of the incipient 1,8-dimethylnaphthalene dianion to acquire a completely flat configuration because of steric interactions between the peri hydrogens, thereby rendering the transition state leading to the 1,8-dimethylnaphthalene dianion **5** somewhat less stable than that leading to the other dimethylnaphthalene dianions. Alternatively, the close proximity of the two negative charges may cause 1,8-dimethylnaphthalene dianion **5** and the transition state leading to it to be less stable than the other dimethylnaphthalene dianions.



12



13

Finally, the equal reactivity of 1,2- and 1,6-dimethylnaphthalene toward α,α'-dianion formation suggests that C_6 of monoanion **13** must bear much more negative charge than Adamov's[16] calculations would seem to indicate.

Conclusions

The introduction of TMEDA as a catalyst in metalations of weak carbon acids by means of *n*-amylsodium in hydrocarbon solvents is seen to exert a profound influence on the yield of these reactions. For the first time metalations with organosodium reagents are made to proceed in high yields, mild conditions, and short reaction times. Unlike TMEDA, sodium *tert*-butoxide was found to be only weakly effective as a catalyst in metalation reactions, while DABCO was found to be totally ineffective.

The reactivity of a number of isomeric dimethylarenes toward α,α'-dianion formation has been established and the observed results were explained on the basis of a two-step mechanism involving the conversion of the hydrocarbon into a monoanion, first, which subsequently reacts with a second equivalent of base to produce the dianion. The dominant influence of the negative charge of the monoanion toward dianion formation appears to have been either totally overlooked or greatly deemphasized in the past.[8]

Of all the dianion intermediates formed during the present study the most interesting from a synthetic and theoretical point of view is that derived from 1,8-dimethylnaphthalene. It should be noted that previous attempts to obtain this intermediate were unsuccessful.[17] We are presently investigating the reactions of this dianion with a number of difunctional electrophilic reagents, which are expected to produce a series of unusual cyclic products.

Experimental Section

General.—Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Vapor phase chromatographic (vpc) analyses were carried out on a Varian Aerograph, series 2700 gas chromatograph equipped with a thermal conductivity detector, and using helium as a carrier gas. A 5 ft × 0.25 in. column packed with 3% SE-30 on Varaport 30 was used. Infrared spectra (ir) were taken on a Beckman IR-8 infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates A-60 spectrometer. Chemical shifts, relative to internal tetramethylsilane, were measured to the center of a singlet or multiplet and are reported in parts per million. An IEC International, Size 2, Model K centrifuge was used. All organosodium reactions were carried out under a nitrogen atmosphere, in a Morton flask equipped with a high-speed stirrer (Stir-O-Vac), purchased from Lab-Line Instruments, Melrose Park, Ill.

---

(15) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

(16) M. N. Adamov, A. A. Kane, and I. F. Tupitsyn, *Teor. Eksp. Khim.*, **3** (4), 437 (1967).

(17) L. D. Kershner, J. M. Gaidis, and H. H. Freedman, *J. Amer. Chem. Soc.*, **94**, 985 (1972).

Materials.—1,2- and 1,4-dimethylnaphthalene were purchased from Chemicals Procurement Laboratories, Inc., College Point, N.Y.

1,3-Dimethylnaphthalene was prepared essentially by the method of Canonne, *et al.*[18] 1,8-Dimethylnaphthalene was obtained by a modification of the method of Denisova, *et al.*,[19] as described below. *o*- and *m*-xylene were purchased from Matheson Coleman and Bell, Norwood, Ohio, while *p*-xylene was purchased from J. T. Baker Chemical Co., Phillipsburg, N. J. All three xylenes were distilled from sodium metal immediately before use. Sodium *tert*-butoxide was obtained from MSA Research Corporation, Evans City, Pa., and was used without further purification. Sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) was purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis., as a 70% solution in benzene.

1,8-Bishydroxymethylnaphthalene.—Sodium bis(2-methoxyethoxy)aluminum hydride (0.638 mol) dissolved in 2200 ml of benzene was charged into a three-necked round-bottomed flask equipped with a heating mantle, a magnetic stirrer, an addition funnel, and a reflux condenser connected to a high-purity nitrogen tank by means of a T tube. Stirring was initiated and a solution of 62.4 g (0.255 mol) of 1,8-dimethyl naphthalate[19,20] in 650 ml of benzene was added dropwise at room temperature over a period of 40 min. The reaction mixture was then refluxed for 1.5 hr. After cooling to room temperature, 150 ml of water were cautiously added followed by 500 ml of 9 *N* HCl. The resulting precipitate was collected by filtration, washed with water, and dried to afford 33.2 g (69.4%) of 1,8-bishydroxymethylnaphthalene, mp 154–156° (lit.[19,21] mp 156.5–157°).

1,8-Dimethylnaphthalene.—A solution of 14.92 g (0.0793 mol) of 1,8-bishydroxymethylnaphthalene, prepared as described above, in 250 ml of methanol containing a few drops of concentrated hydrochloric acid and 0.91 g of palladium black was shaken with hydrogen at room temperature in a Parr low-pressure hydrogenator at 3.5 atm. After the theoretical amount of hydrogen was absorbed (12 min), the catalyst was removed by filtration and the solvent was evaporated. There was obtained 10.2 g (82%) of crude 1,8-dimethylnaphthalene: mp 57.5–59° and 61.5–62.5° after one recrystallization from methanol (lit.[19,21c] mp 63.5–64.5°); ir (CCl$_4$) 3040 (C=C) and 2980 cm^{-1} (C–C); nmr (CCl$_4$) δ 7.35 (m, 6 H, aromatic), and 2.88 (s, 6 H, CH$_3$).

Preparation of *n*-Amylsodium.—This reagent[22] was prepared by the slow addition of *n*-amyl chloride to a stirred (10,000–12,000 rpm) sodium dispersion in hexane at −15°. After all of the *n*-amyl chloride had been added, the mixture was stirred for an additional 0.5 hr to ensure complete reaction. A 70–80% yield of *n*-amylsodium formation was assumed.[23]

Effect of TMEDA on the Solubility of *n*-Amylsodium in Hexane.—*n*-Amylsodium was prepared as described above from 3.21 g (0.03 mol) of *n*-amyl chloride and 1.38 g (0.06 mol) of a sodium dispersion in 80 ml of dry hexane. Approximately one-half of the reaction mixture was transferred into a centrifuge tube and centrifuged for 5 min at 1500 rpm. A clear supernatant layer and a blue precipitate resulted. The remaining one-half of the reaction mixture was treated with 0.01 mol of TMEDA before it was centrifuged. Upon centrifugation this portion of the reaction mixture also afforded a clear supernatant liquid and a dark blue precipitate.

Formation of 1,3-Dimethylnaphthalene Dianion 1 by Means of *n*-Amylsodium in the Presence of TMEDA.—To a stirred (9,000–10,000 rpm) suspension of *n*-amylsodium prepared from 3.21 g (0.03 mol) of *n*-amyl chloride and 1.38 g (0.06 mol) of sodium in 80 ml of anhydrous hexane was added at −15°, over a period of 8 min, a solution of 1.56 g (0.01 mol) of 1,3-dimethylnaphthalene and 2.32 g (0.02 mol) of TMEDA in 15 ml of dry hexane. The cold bath was then removed and the reaction mixture was allowed to warm slowly to room temperature. Dimetalation was completed by stirring for an additional 2 hr at room temperature and the resulting brick-red, insoluble 1,3-dimethylnaphthalene dianion 1 was employed as described below.

Deuteration of Dianion 1.—A suspension of dianion 1 (0.01 mol) in hexane was prepared as described above and subsequently quenched with 10 ml of deuterium oxide. Water (50 ml) was then added to the reaction mixture, and the layers were separated. The organic layer was washed three times with 20-ml portions of 6 *N* hydrochloric acid, three times with 20-ml portions of aqueous saturated sodium bicarbonate, and once with 50 ml of water; it was then dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure to give 1,3-dimethylnaphthalene-d_2 (**2a**), as shown by quantitative nmr analysis, nmr (CCl$_4$) δ 7.40 (m, 6 H, aromatic), 2.50 (m, 2 H, CH$_2$D), and 2.32 (m, 2 H, CH$_2$D). Vpc analysis of the crude reaction mixture showed no impurities.

Alkylation of Dianion 1 with Methyl Iodide.—To a stirred suspension of 0.01 mol of dianion 1 in 80 ml of hexane at 1–5° was added 5.67 g (0.04 mol) of methyl iodide over a period of 8–10 min. The cold bath was then removed and the reaction mixture was allowed to stir (8000 rpm) for 45 min at room temperature. Water (50 ml) was then added, the layers were separated, and the organic layer was washed three times with 20-ml portions of 6 *N* hydrochloric acid, three times with 20-ml portions of aqueous saturated sodium bicarbonate, and once with 50 ml of water; it was then dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. Vpc analysis of the residue revealed the presence of two components in a ratio of 19:1. The predominant component was shown to be 1,3-diethylnaphthalene (**2b**), picrate mp 99–100° (lit.[24] mp 100.5°). No attempt was made to identify the minor component.

Condensation of Dianion 1 with Benzophenone.—To a stirred suspension of 0.01 mol of dianion 1 in 80 ml of hexane at room temperature was added dropwise a solution of 4.55 g (0.025 mol) of benzophenone in 50 ml of dry hexane. After 1 hr of stirring (8000 rpm) at room temperature 50 ml of water was added. The resulting yellow solid was collected by filtration, washed with water, and dried to afford 2.60 g (50%) of crude diol **2c**: mp 176–181° (several recrystallizations of the crude product **2c** from ethanol–water raised the melting point to 192–193°); ir (KBr) 3540 cm^{-1} (OH); nmr (DMSO-d_6) δ 7.33 (m, 26 H, aromatic), 5.48 (s, 1 H, CH$_2$COH), 5.39 (s, 1 H, CH$_2$COH), 3.83 (s, 2 H, CH$_2$COH), and 3.49 (s, 2 H, CH$_2$COH).

Anal. Calcd for C$_{38}$H$_{32}$O$_2$: C, 87.69; H, 6.16. Found: C, 87.61; H, 6.26.

Carbonation of Dianion 1 with Excess Solid Carbon Dioxide.—A suspension of 0.02 mol of dianion 1 in hexane was prepared in the usual manner and then syringed onto a large excess of moisture-free, solid carbon dioxide. The resulting slurry was allowed to stand overnight at room temperature; 300 ml of water was then introduced with stirring, the layers were separated, and the aqueous layer was washed twice with 50-ml portions of hexane and twice with 50-ml portions of ethyl acetate and acidified with 12 *N* HCl. Upon cooling (ice bath) the acidic solution afforded a yellow-white precipitate, which was collected by filtration and dried to give 3.62 g (74%) of crude 1,3-naphthalenediacetic acid (**2d**): mp 215–217°, and 224–225° after several recrystallizations from ethyl acetate–petroleum ether (bp 30–60°); ir (KBr) 3000 (OH) and 1700 cm^{-1} (C=O); nmr (DMSO-d_6) δ 7.65 (m, 6 H, aromatic), 4.05 (s, 2 H, CH$_2$COOH), and 3.76 (s, 2 H, CH$_2$COOH).

Anal. Calcd for C$_{14}$H$_{12}$O$_4$: C, 68.85; H, 4.91. Found: C, 69.03; H, 4.78.

Metalation and Subsequent Deuteration of 1,3-Dimethylnaphthalene with *n*-Amylsodium in the Absence of a Catalyst.—To a stirred (9,000–10,000 rpm) suspension of *n*-amylsodium prepared from 1.38 g (0.06 mol) of sodium and 3.21 g (0.03 mol) of *n*-amyl chloride in 80 ml of anhydrous pentane was added, at −15°, 1.56 g (0.01 mol) of 1,3-dimethylnaphthalene over a period of 5 min, and stirring was continued for 2 hr at room temperature. The reaction mixture was then quenched with 5 ml of deuterium oxide and processed as described above to give 1,3-dimethylnaphthalene-d_1 as shown by quantitative nmr analysis, nmr (CCl$_4$) δ 7.40 (m, 6 H, aromatic), 2.55 (s, 2.6 H, CH$_2$D and CH$_3$), and 2.36 (s, 2.4 H, CH$_2$D and CH$_3$).

---

[18] P. Canonne, P. Holm, and L. C. Leitch, *Can. J. Chem.*, **45**, 2151 (1967).

[19] L. I. Denisova, N. A. Morozova, V. A. Plakhov, and A. I. Tochilkin, *Zh. Obshch. Khim.*, **34** (2), 519 (1964).

[20] T. A. Geissman and L. Morris, *J. Amer. Chem. Soc.*, **66**, 716 (1944).

[21] (a) W. J. Mitchell, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 2526 (1962); (b) W. B. Whalley and J. A. Corran, *ibid.*, 4719 (1958); (c) R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.*, **74**, 1406 (1952).

[22] (a) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Amer. Chem. Soc.*, **72**, 3785 (1950); (b) A. A. Morton and M. E. T. Holden, *ibid.*, **69**, 1675 (1947); (c) A. A. Morton, J. B. Davidson, and H. A. Newey, *ibid.*, **64**, 2240 (1942); (d) A. A. Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939); (e) A. A. Morton and D. M. Knott, *ibid.*, **13**, 650 (1939).

[23] M. Schlosser in "Newer Methods of Preparative Organic Chemistry," Vol. 5, W. Foerst, Ed., Verlag Chemie, Weinheim/Bergstr., Germany, and Academic Press, New York, N. Y., 1968, p 299.

[24] H. S. Desai and B. D. Tilak, *J. Sci. Ind. Res., Sect. B*, **20**, 22 (1961).

Formation of 1,2-, 1,6-, and 1,8-Dimethylnaphthalene Dianions 3, 4, and 5 and Subsequent Deuteration with Deuterium Oxide.—Treatment of 1.56 g (0.01 mol) of 1,2-, 1,6-, and 1,8-dimethylnaphthalene with *n*-amylsodium prepared from 2.30 g (0.10 mol) of sodium and 5.33 g (0.05 mol) of *n*-amyl chloride in the presence of 3.94 g (0.034 mol) of TMEDA under the same conditions used in the case of 1,3-dimethylnaphthalene produced dianions **3** (dark brown), **4** (dark red), and **5** (orange-brown), respectively, in quantitative yield, as shown by subsequent treatment of each reaction mixture with deuterium oxide followed by nmr analysis: nmr (CCl_4) for 1,2-dimethylnaphthalene-d_2, δ 7.53 (m, 6 H, aromatic), 2.45 (m, 2 H, CH_2D), and 2.37 (m, 2 H, CH_2D); nmr (CCl_4) for 1,6-dimethylnaphthalene-d_2, δ 7.48 (m, 6 H, aromatic), 2.60 (m, 2 H, CH_2D), and 2.45 (m, 2 H, CH_2D); nmr (CCl_4) for 1,8-dimethylnaphthalene-d_2, δ 7.36 (m, 6 H, aromatic) and 2.87 (m, 4 H, CH_2D).

When 1.56 g (0.01 mol) of 1,2-, 1,6-, and 1,8-dimethylnaphthalene was treated with *n*-amylsodium prepared from 1.38 g (0.06 mol) of sodium and 3.21 g (0.03 mol) of *n*-amyl chloride in the presence of 2.32 g (0.02 mol) of TMEDA followed by deuteration with deuterium oxide, 1.80 deuterium atoms were incorporated in each molecule of 1,2- and 1,6-dimethylnaphthalene, and 1.5 deuterium atoms were incorporated in each molecule of 1,8-dimethylnaphthalene, as established by nmr analysis.

Condensation of Dianion 5 with Benzophenone.—1,8-Dimethylnaphthalene dianion **5** (0.01 mol) was prepared as described above and subsequently treated with 4.55 g (0.025 mol) of benzophenone under conditions similar to those used in the case of 1,3-dimethylnaphthalene. There was obtained 2.75 g (52%) of crude diol **6a**: mp 177–181° and 198–199° after several recrystallizations of the crude product **6a** from ethanol; ir (KBr) 3540 cm^{-1} (OH); nmr ($CDCl_3$) δ 7.19 (m, 26 H, aromatic), 4.40 (s, 4 H, CH_2COH), and 2.30 (s, 2 H, CH_2COH).

Anal. Calcd for $C_{38}H_{32}O_2$: C, 87.69; H, 6.16. Found: C, 87.92; H, 6.30.

Carbonation of Dianion 5 with Excess Solid Carbon Dioxide.—Dianion **5** (0.01 mol) was carbonated with excess moisture-free solid carbon dioxide as described in the case of 1,3-dimethylnaphthalene dianion **1** to give 1.0 g (40%) of crude 1,8-naphthalenediacetic acid (**6b**), mp 229° dec. Compound **6b** was purified by recrystallization from ethyl acetate–petroleum ether (bp 30–60°): ir (KBr) 3000 (OH) and 1690 cm^{-1} (C=O); nmr (DMSO-d_6) δ 7.79 (m, 6 H, aromatic) and 4.18 (s, 4 H, CH_2COOH).

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.91. Found: C, 68.57; H, 4.96.

Attempted Dimetalation of 1,4-Dimethylnaphthalene.—1,4-Dimethylnaphthalene (1.56 g, 0.01 mol) was treated with a mixture of *n*-amylsodium, prepared from 2.30 g (0.10 mol) of sodium and 5.33 g (0.05 mol) of *n*-amyl chloride, and 3.94 g (0.034 mol) of TMEDA. After 2 hr of stirring the reaction mixture was quenched with deuterium oxide and processed as described above. Nmr analysis of the crude reaction mixture showed that only one deuterium atom per molecule of 1,4-dimethylnaphthalene had been incorporated: nmr (CCl_4) δ 7.55 (m, 6 H, aromatic) and 2.58 (s, 5 H, CH_2D and CH_3).

Formation and Subsequent Deuteration of *m*-Xylene Dianion 7.—The green *m*-xylene dianion **7** was prepared by treating 5.30 g (0.05 mol) of *m*-xylene with *n*-amylsodium, prepared from 16.05 g (0.15 mol) of *n*-amyl chloride and 6.90 g (0.30 mol) of sodium, and 12.76 g (0.11 mol) of TMEDA under the conditions used for the formation of 1,3-dimethylnaphthalene dianion **1**. Subsequent quenching of the reaction mixture with 15 ml of deuterium oxide afforded *m*-xylene-d_2, as established by nmr analysis: nmr (hexane) δ 6.92 (m, 4 H, aromatic) and 2.20 (m, 4 H, CH_2D). Vpc analysis of the crude reaction mixture showed no impurities.

Alkylation of *m*-Xylene Dianion 7 with Excess Methyl Iodide.—Dianion **7** (0.05 mol) was prepared as outlined above and subsequently treated with 21.3 g (0.15 mol) of methyl iodide under the conditions used for the alkylation of 1,3-dimethylnaphthalene dianion **1**. Vpc analysis of the crude reaction mixture showed the presence of two peaks in the ratio of 15:1. The major component was shown by vpc and nmr analysis to be 1,3-diethylbenzene, while the minor component was identified as 1-ethyl-3-methylbenzene.

Metalation and Subsequent Alkylation of *m*-Xylene by Means of *n*-Amylsodium in the Presence of DABCO.—To a slurry of *n*-amylsodium prepared from 6.90 g (0.30 mol) of sodium and 16.05 g (0.15 mol) of *n*-amyl chloride was added 12.32 g (0.11 mol) of DABCO followed by 5.30 g (0.05 mol) of *m*-xylene. The reaction mixture was stirred for 2 hr at room temperature; it was then cooled to 5°; and 21.3 g (0.15 mol) of methyl iodide was added dropwise. The cold bath was removed and the reaction mixture was stirred for an additional 2 hr at room temperature and then processed in the usual manner. Vpc analysis of the crude reaction mixture showed the presence of *m*-xylene, 1-ethyl-3-methylbenzene, and 1,3-diethylbenzene in a ratio of 2.8:1.0:1.1.

Metalation and Subsequent Alkylation of *m*-Xylene by Means of *n*-Amylsodium in the Presence of Sodium *tert*-Butoxide.—*m*-Xylene (5.30 g, 0.05 mol) was treated with *n*-amylsodium prepared from 6.90 g (0.30 mol) of sodium and 16.05 g (0.15 mol) of *n*-amyl chloride, in the presence of 13.64 g (9.142 mol) of sodium *tert*-butoxide under the usual conditions. Methyl iodide (21.3 g, 0.15 mol) was then added as described above, and the reaction mixture was stirred for 2 hr at room temperature and then processed in the usual manner. Vpc analysis of the crude reaction mixture showed the presence of *m*-xylene, 1-ethyl-3-methylbenzene, and 1,3-diethylbenzene in a ratio of 1.0:1.1:4.6.

Metalation and Subsequent Alkylation of *m*-Xylene by Means of *n*-Amylsodium in the Absence of a Catalyst.—To a slurry of *n*-amylsodium prepared from 6.90 g (0.30 mol) of sodium and 16.05 g (0.15 mol) of *n*-amyl chloride in hexane was added 5.3 g (0.05 mol) of *m*-xylene and the reaction was allowed to stir at room temperature for 2 hr. Addition of 21.3 g (0.15 mol) of methyl iodide followed by the usual work-up and vpc analysis of the crude reaction mixture showed the presence of *m*-xylene with only trace amounts of 1-ethyl-3-methylbenzene. No 1,3-diethylbenzene could be detected.

Formation and Subsequent Deuteration of *o*-Xylene Dianion 8.—Treatment of 5.3 g (0.05 mol) of *o*-xylene with *n*-amylsodium prepared from 11.50 g (0.50 mol) of sodium and 26.75 g (0.25 mol) of *n*-amyl chloride in the presence of 20.30 g (0.175 mol) of TMEDA under the conditions described earlier afforded the green-brown *o*-xylene dianion **8**. Neutralization of the reaction mixture with 20 ml of deuterium oxide afforded *o*-xylene-d_2, as shown by vpc and nmr analysis: nmr (hexane) δ 6.95 (s, 4 H, aromatic) and 2.12 (m, 4 H, CH_2D).

When 5.3 g (0.05 mol) of *o*-xylene was treated with *n*-amylsodium prepared from 6.9 g (0.30 mol) of sodium and 16.05 g (0.15 mol) of *n*-amyl chloride in the presence of 12.76 g (0.11 mol) of TMEDA followed by deuteration with deuterium oxide, only 1.64 deuterium atoms were incorporated in each molecule of *o*-xylene, as shown by quantitative nmr analysis.

Attempted Dimetalation of *p*-Xylene.—*p*-Xylene (5.3 g, 0.05 mol) was treated with *n*-amylsodium prepared from 11.50 g (0.50 mol) of sodium and 26.75 g (0.25 mol) of *n*-amyl chloride in the presence of 20.30 g (9.175 mol) of TMEDA. The reaction mixture was stirred for 2 hr and was then neutralized with 20 ml of deuterium oxide. Nmr analysis of the crude product showed the incorporation of only one deuterium atom per molecule of *p*-xylene: nmr (hexane) δ 7.91 (s, 4 H, aromatic) and 2.21 (s, 5 H, CH_3 and CH_2D).

Registry No.—**1**, 36374-74-0; **2a**, 38645-27-1; **2b**, 38645-28-2; **2c**, 36374-75-1; **2d**, 36262-46-1; **3**, 38645-31-7; **4**, 38645-32-8; **5**, 38645-33-9; **6a**, 38677-69-9; **6b**, 38645-34-0; **7**, 36295-90-6; **8**, 38645-36-2; 1,8-dimethyl naphthalate, 81-84-5; 1,8-bishydroxymethylnaphthalene, 2026-08-6; 1,8-dimethylnaphthalene, 569-41-5; *n*-amylsodium, 1822-71-5; TMEDA, 110-18-9; benzophenone, 119-61-9; 1,3-dimethylnaphthalene, 575-41-7; 1,3-dimethylnaphthalene-d_2, 38669-44-2; 1,2-dimethylnaphthalene, 573-98-8; 1,6-dimethylnaphthalene 575-43-9; 1,2-dimethylnaphthalene-d_2, 38645-39-5; 1,6-dimethylnaphthalene-d_2, 38645-40-8; 1,8-dimethylnaphthalene-d_2, 38645-41-9; *m*-xylene, 108-38-3; *m*-xylene-d_2, 38645-42-0; *o*-xylene, 95-47-6; *o*-xylene-d_2, 38644-46-1.

Acknowledgment.—Support of this research by a Faculty Research Grant, Western Michigan University, and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.