4-en-7-one (**13a**)[14] was irradiated[4] for 2 hr to afford a *ca.* 1:7 photoequilibrium mixture of **13a** and the ketone **14a**.[15] As these reactions were neither sensitized with acetophenone nor quenched with *trans*-piperylene, they proceed *via* the n,π* triplet states.

Conformation Aspects. The fact that the equilibrium between **13a** and **14a** is highly in favor of **14a** is noteworthy, because models indicate severe steric interaction between 6β- and 10-methyl groups. In addition to the conjugative effect mentioned, it was found that relative ϵ values of enones, a reflection of their conformations,[16] are involved in governing the state of equilibria. Namely, in contrast to the ϵ of enone **13a** (ϵ_{295} 105), that of **14a** is small (ϵ_{298} 58) due to poor carbonyl–double bond interaction[16] resulting from its fixed boat conformation, and this difference in ϵ values shifts the equilibrium toward ketone **14a**. This factor is involved in the equilibrium of other photostationary mixtures. Thus, the high ϵ value of bridged ketone **2** (ϵ_{295} 153) due to its chair conformation shifts the equilibrium toward enone **1** (ϵ_{290} 33) and the ratio of **1**/**2** is 15/1 (from glc). In enone **4** (ϵ_{295} 100) and ketone **5** (ϵ_{295} 167), the smaller difference in ϵ values shifts the **4**/**5** ratio to 5/1 (from glc).

Irradiation of the 7-keto steroid **13b** resulted in a *ca.* 1:1 photoequilibrium mixture of **13b** and **14b** although **13b** is unsubstituted in the α position.[1a] This behavior again is in line with the fact that in enone **13b** the carbonyl and the double bond are coupled to an exceptional extent, ϵ_{290} 240 (EtOH), as opposed to the bridged ketone **14b**, ϵ_{297} 48 (EtOH).

The mentioned relation of ϵ values to equilibria was supported by equilibrium studies between **13b** and **14b** in various solvents upon monochromic irradiation[17] at 290 nm; the ratio of **13b**/**14b** was 0.67 in *tert*-BuOH (ϵ_{13b} 190/ϵ_{14b} 41), 0.96 in dioxane (ϵ_{13b} 151/ϵ_{14b} 40), and 1.00 in cyclohexane (ϵ_{13b} 140/ϵ_{14b} 43).

Aldehyde Formation. Contrary to the behaviors of **1** and **2**, enone **13a** yielded no aldehyde. This can be interpreted as follows. Formation of a free radical is unfavored because of limited freedom of movement enforced by the rigid ring structure. Even if they were formed, in order for the free acyl radical (sp configuration) to abstract a methyl hydrogen, it should approach the allyl radical perpendicularly so that a maximum σ–π orbital overlap is ensured as in **15**; however, this is sterically impossible for the 7-one **13a**. When the carbonyl group is in a terminal ring, as in **1** and **4**, this overlap can be achieved (**15**).

Formation of 1,3-acyl migration products can also be explained by photochemically allowed $({}_{\sigma}2_a + {}_{\pi}2_a)$ or $({}_{\sigma}2_s + {}_{\pi}2_s)$ cycloadditions;[18,19] in this case the aldehydes could be formed from vibrationally different excited states.

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[14] F. Lederer and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1078 (1962).

[15] **14a**: mp 115°; M$^+$ 412; uv (EtOH) ϵ_{298} 58; CD (EtOH) ϵ_{298} +1.16; ir (KBr) 1711 cm^{-1}; nmr (CDCl$_3$) 1.68 (s, 6-Me), 1.93 (s, 6-Me), 3.22 ppm (t, J = 3 Hz, 4-H). The assignments of 1.68- and 1.93-ppm peaks (see **14a**) are based on NOE; irradiation at 1.68 ppm caused a 14% increase in the area of the 3.22-ppm 4-H signal, whereas irradiation at 1.93 ppm resulted in no increase.

[16] *Cf.* M. Gorodetsky, A. Yogev, and Y. Mazur, *J. Org. Chem.*, **31**, 699 (1966).

[17] A JASCO CRM Model FA was employed.

[18] E. Baggiolini, K. Schaffner, and O. Jeger, *J. Chem. Soc. D*, 1103 (1969).

[19] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

Metalations of Dimethylarenes with Organosodium Reagents. The Catalytic Effect of Certain Tertiary Amines

Sir:

We wish to report a mild and efficient method for the α,α' dimetalation and subsequent functionalization of certain dimethylarenes. Initial attempts to obtain such dianions by means of organosodium reagents, alone or in the presence of alkoxides,[1] resulted only in monometalations and/or low-yield dimetalations. It is now found that *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) exerts a marked catalytic influence upon such dimetalations, similar to that reported for metalations with organolithium reagents.[2]

Addition of an equimolar amount of TMEDA to a suspension of *n*-amylsodium[3] 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 resulting mixture was found to be an exceedingly powerful metalating agent capable of quantitatively converting dimethylarenes to their α,α' dianions at room temperature within 2 hr.[4] In a typical experiment 1,3-dimethylnaphthalene was added at −15° to slightly over 2 equiv of a freshly prepared mixture of *n*-amylsodium–TMEDA[5] in hexane and the reaction mixture was allowed to warm slowly to room temperature. Reaction occurred quite rapidly to give the insoluble brick-red 1,3-dimethylnaphthalene dianion **1**, in quantitative yield, as evidenced by quenching the reaction mixture with deuterium oxide followed by nmr analysis of the deuterated product. 1,3-Dimethylnaphthalene dianion **1** reacts quite readily at room temperature with electrophilic reagents to give α,α'-dicondensation products in high yield. Thus, treatment of **1** with excess methyl iodide afforded 1,3-diethylnaphthalene (**2a**), picrate

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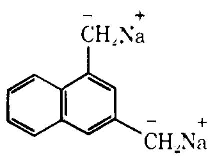
[1] (a) A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, 20, 428 (1955); (b) A. A. Morton and A. E. Brachman, *J. Amer. Chem. Soc.*, 73, 4363 (1951); (c) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950); (d) R. A. Benkeser, T. F. Crimmins, and Wen-houg Tong, *J. Amer. Chem. Soc.*,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

[2] (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).

[3] *n*-Amylsodium was prepared in the usual manner by slow addition of *n*-amyl chloride to a sodium dispersion at low temperature and high-speed stirring.

[4] Under these conditions *n*-amylsodium in the presence of sodium *tert*-butoxide[1] effected only partial dimetalation of dimethylarenes, while *n*-amylsodium alone effected no dimetalation at all.

[5] *n*-Amylsodium–TMEDA solutions are not stable over long periods of time and best metalation results are obtained when the carbon acid is added immediately following the addition of TMEDA.



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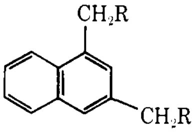

2a, R = CH_3
b, R = $COH(C_6H_5)_2$
c, R = COOH

mp 99-100° (lit.[6] mp 100.5°), in nearly quantitative yield. Similarly, reaction of **1** with 2 equiv of benzophenone gave diol[7] **2b**, mp 192-193°, in 50% yield, while carbonation with excess solid carbon dioxide produced dicarboxylic acid[7] **2c**, mp 224-225°, in 74% yield. Next, the dimetalation of *m*-xylene, with *n*-amylsodium-TMEDA, was investigated. This compound had previously been dimetalated[8] in low yield by heating with *n*-amylsodium in octane for 3 hr. Reaction of *m*-xylene with slightly over 2 equiv of *n*-amylsodium-TMEDA in hexane at room temperature for 2 hr produced the insoluble α,α'-disodio *m*-xylene in quantitative yield, as determined by subsequent quenching with deuterium oxide and quantitative nmr analysis. Treatment of the *m*-xylene dianion with an excess of methyl iodide afforded 1,3-diethylbenzene in excess of 90% yield. Vpc analysis of the crude reaction mixture showed only traces of the monocondensation product 1-ethyl-3-methylbenzene (**3**).

It is particularly interesting to note that 1,4-diazabicyclo[2.2.2]octane[9] (DABCO) was found to have no catalytic effect on metalations with *n*-amylsodium in hexane. Thus, treatment of *m*-xylene with slightly over 2 equiv of *n*-amylsodium-DABCO followed by excess methyl iodide afforded a mixture of products consisting mainly of *m*-xylene and **3**.

In contrast to organolithium compounds whose complexes with a variety of chelating agents have been studied quite extensively,[2,10] little is known about complexes involving organometallic compounds of the heavier alkali metals.[11] The catalytic effect of TMEDA in metalations with *n*-amylsodium may be attributed to complex formation between the amine and the organosodium reagent similar in nature to that occurring between alkyllithium reagents and tertiary aliphatic amines.[2,10] Such complex formation would help disperse the large *n*-amylsodium aggregates[12] thereby providing a larger surface area for the metalation reaction to occur.

The present method, which involves the use of amines as catalysts in metalations with *n*-amylsodium (and presumably with other alkylsodium reagents) presents a significant advance over similar metalations with *n*-amylsodium alone or in the presence of certain other catalysts,[1] since it allows such reactions to proceed at very high yields, mild conditions, and short reaction time.

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

[7] Satisfactory elemental analysis, ir, and nmr spectra were obtained for this new compound.

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

[9] DABCO was found to be almost as effective in catalyzing metalations with alkyllithium reagents[2a] as TMEDA.

[10] (a) J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, **85**, 2171 (1963); (b) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963); (c) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964); (d) T. L. Brown, R. L. Geteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2134 (1964).

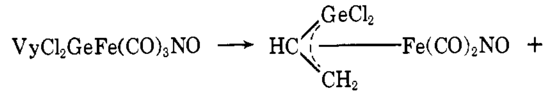
[11] C. J. Pedersen (private communication) has found that certain polyethers [C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967)] can form complexes with stabilized organosodium and organopotassium reagents, such as benzylsodium and benzylpotassium, but that the polyether ring is gradually decomposed by the organometallic compounds. It has also been recently reported [report appearing in *Chem. Eng. News*, **49** (24), 31 (1971)] that tetramethyl-1,2-cyclohexanediamine has a chelating effect on α-cumylsodium in cumene.

[12] A. A. Morton, "Solid Organoalkali Metal Reagents," Gordon and Breach, New York, N. Y., 1964, pp 5-6.

Halogen-Bridged Germanium-Metal Bonds and Germanium-Bridged Metal-Metal Bonds

Sir:

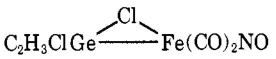
We recently attempted to prepare (vinyldichlorogermyl)tricarbonylnitrosyliron, $(C_2H_3)Cl_2Ge{-}Fe(CO)_3NO$, hoping to cause a rearrangement to the π-germaallyl analog[1]



$$VyCl_2GeFe(CO)_3NO \longrightarrow HC\langle^{GeCl_2}_{CH_2}\rangle{-}Fe(CO)_2NO + CO \qquad (1)$$

Instead of the expected product, a compound which we formulate as μ-chloro-(vinylchlorogermyl)dicarbonylnitrosyliron(*Fe-Ge*) (I, orange crystals, mp 47-48°) was formed in the reaction between $NaFe(CO)_3NO$ and vinyltrichlorogermane.

$C_2H_3GeCl_3 + NaFe(CO)_3NO \longrightarrow$



$$C_2H_3ClGe\overset{Cl}{\diagup\!\diagdown}Fe(CO)_2NO + CO + NaCl \qquad (2)$$

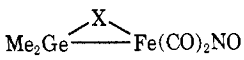
I

To our knowledge this is the first compound of this type, although Graham and coworkers have observed an interaction between a chlorine bound to molybdenum and the tin atom of a similarly bound $SnCl_3$ group.[2]

The elemental analyses and mass spectrum support the empirical formula of I. *Anal.* Calcd for $C_5H_3GeFeO_4NCl$: C, 17.6; H, 0.89; Ge, 21.3; Fe, 16.4. Found: C, 17.8; H, 0.94; Ge, 21.6; Fe, 16.8. The mass spectrum has isotope patterns characteristic of Ge_1Fe_1 at *m/e* 313, 285, 257, and 227 representing the ions $C_2H_3Cl_2GeFe(CO)_nNO^+$ ($n = 2, 1, 0$) and $C_2H_3Cl_2GeFe^+$, respectively.

Compounds which we formulate with bridging halogen atoms are also formed in high yield when dimethyldibromogermane and dimethyldichlorogermane are treated with sodium tricarbonylnitrosylferrate (II, X = Cl, yellow needles, mp 55-62° dec; III, X = Br, orange crystals, mp 80-82°).

$Me_2GeX_2 + NaFe(CO)_3NO \longrightarrow$



$$Me_2Ge\overset{X}{\diagup\!\diagdown}Fe(CO)_2NO + CO + NaX \qquad (3)$$

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[1] R. C. Job and M. D. Curtis, submitted for publication.

[2] M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.*, **90**, 2189 (1968).