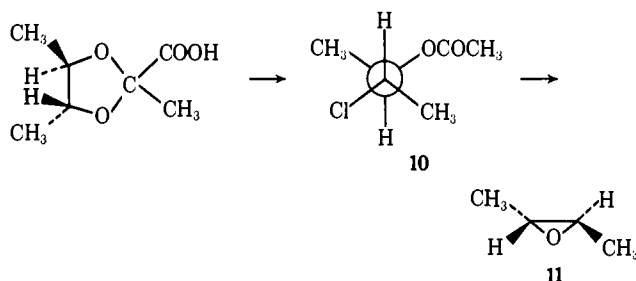
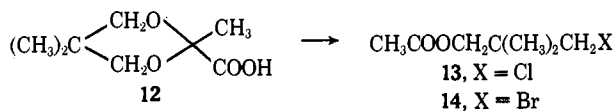


xylene). Thus, inversion must have taken place in the transformation of **9** to **10** because inversion is known<sup>8</sup> to occur on conversion of **10** to **11**.



The smooth stereospecific transformation of **9** to **11** represents an excellent way of preparing optically active epoxides. Since the conversion of an optically active diol (in the present case *D*(-)-2,3-butanediol<sup>9</sup>) to the ketal **9** does not involve a change in configuration at either carbon and the subsequent steps involve two inversions at one carbon (it may be either carbon), the resulting epoxide must have the same configuration at each carbon as did the original diol. This is true even if a mixture of halo esters is obtained. This mixture need not be separated because each component must give the same epoxide.

That this reaction is not confined to ketals prepared from 1,2-glycols nor to chloro compounds is shown by the conversion of 2-carboxy-2,5,5-trimethyl-1,3-dioxane (**12**) to 3-chloro-2,2-dimethylpropyl acetate (**13**), and to 3-bromo-2,2-dimethylpropyl acetate (**14**) (with phos-



phorus tribromide) in high yields.<sup>6</sup>

In a typical experiment a solution of 1.00 g (5.75 mmol) of **12** in 5 ml of dry  $\text{CH}_2\text{Cl}_2$  was added dropwise during 1 hr to a solution of 1.20 g (5.75 mmol) of  $\text{PCl}_5$  in 15 ml of  $\text{CH}_2\text{Cl}_2$  at room temperature. Immediate evolution of gas occurred. The reaction was essentially over after this addition had been completed. The nmr spectrum of the crude product remaining after removal of  $\text{CH}_2\text{Cl}_2$  under vacuum showed that the only organic compound present was **13**. After a conventional work-up, 0.80 g (84%) of **13**, bp 70–71° (8.5 mm), was obtained.<sup>6</sup>

(8) H. L. Lucas and H. K. Garner, *J. Amer. Chem. Soc.*, **70**, 990 (1948). See also C. C. Price and P. F. Kirk, *ibid.*, **75**, 2396 (1953).

(9) *D*(-)-2,3-Butanediol,  $\alpha^{25D} -12.9^\circ$  (neat, 1 dm), was obtained from the Norse Laboratories, Inc.

(10) Postdoctoral Fellow supported by Grant No. GP-12445X of the National Science Foundation.

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## Factors Involved in Photoinduced $n, \pi^*$ Singlet Isomerizations of Cyclic $\beta, \gamma$ -Unsaturated Ketones

Sir:

Studies on cyclic  $\beta, \gamma$ -enones<sup>1</sup> indicate that 1,3- and 1,2-acyl migrations result, respectively, from singlet<sup>1a, b</sup>

(1) (a) N. Furutachi, Y. Nakadaira, and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 1028 (1969); (b) R. G. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971); (c)

and triplet reactions.<sup>1c-f</sup> Recently a spin polarization mechanism has been proposed to rationalize such 1,2- and 1,3-acyl migrations.<sup>2</sup> In the following we discuss the steric, conjugative, and conformational aspects of 1,3-acyl migrations.

**Steric Aspects.** As shown below, conversions of **1** to **2-3** and of **4** to **5** proceed stereospecifically, but formation of aldehyde **6** involves scrambling of  $R_\alpha$  and  $R_\beta$  groups.

Irradiation<sup>3, 4</sup> of **1** in *tert*-BuOH (or *n*-pentane, cyclohexane, or benzene) (450-W high-pressure Hg lamp, Pyrex tube for 8 hr) gave, after tlc separation, ketone **1** (70%), bridged ketone **2** (3%), and, in addition, aldehyde **3**<sup>5</sup> (2%). The 1.68-ppm methyl peak in ketone **2** was assigned to  $R_\alpha$  from the 19% NOE on 9-H at 3.48 ppm; in contrast no NOE was observed upon irradiation at 1.92 ppm.

The steric course of this reaction was next investigated using the 9:1 mixture of  $1\alpha-1\beta$ <sup>6</sup> obtained upon deuteriomethylation of the corresponding 1-methyl-1-en-2-one. Irradiation<sup>4</sup> of  $1\alpha-1\beta$  yielded  $2\alpha-2\beta$  and  $3\alpha-3\beta$ . The  $R_\alpha$  1.68-ppm peak was too weak to be detected in the deuterated mixture  $2\alpha-2\beta$  (submerged in methylene signals), and thus shows that conversion of  $1\alpha-1\beta$  to  $2\alpha-2\beta$  had occurred in a stereospecific manner. In aldehydes  $3\alpha-3\beta$ , nmr analysis indicated a 9:1 mixture, and therefore they had also been formed stereospecifically.

Similar irradiation<sup>4</sup> of **4** yielded 42% enone **4**, 12% bridged ketone **5** (see also ref 3), and 5% aldehyde **6**.<sup>7</sup> The assignments of nmr signals in **5** are based on NOE.<sup>8</sup> Irradiation<sup>4</sup> of the 3:7 mixture of  $4\alpha-4\beta$ <sup>6</sup> (prepared from the corresponding 1-methyl-1-en-2-one) yielded a ca. 3:7 mixture of  $5\alpha-5\beta$ , but the ratio of the aldehydes **6a-6b** was 1:1 (from nmr).<sup>9</sup> It was also found that irradiation of bridged ketone **2** led to **3** in addition to a photostationary mixture of **1-2**; irradiation of **5** also led to a photostationary mixture of **4-5** and **6**. Finally, these reactions were neither sensitized with acetophenone nor quenched with *trans*-piperylene and hence can be regarded as  $n, \pi^*$  singlet reactions.

The results can be rationalized as follows. Firstly, it can be assumed that transformations **1** to **2** and **4** to **5**

J. R. Williams and H. Ziffer, *Tetrahedron*, **24**, 6725 (1968); (d) H. Hart and R. K. Murray, *Tetrahedron Lett.*, 379 (1969); (e) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3963 (1971); (f) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 1925, 3399 (1969).

(2) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4305 (1971).

(3) Irradiations of **1** and **4** in *n*-pentane with Vycor optics have been reported. Thus, **1** affords a 10:1 mixture of **1-2**, and **4** affords a 4:1 mixture of **4-5**; however, no aldehyde formation was reported: L. A. Paquette and G. V. Meehan, *J. Org. Chem.*, **34**, 450 (1969).

(4) All irradiations were carried out under identical conditions excepting the irradiation period.

(5) Aldehyde **3**: oil;  $M^+$  192; uv (EtOH)  $\epsilon_{227}$  3400 (plateau); ir (film) 1725  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ ) 1.15 (s, 5-Me), 1.75 (s, 1-Me), 4.71 and 4.83 (AB q, 2.4, 11-H's), 5.55 (t, 4, 9-H), 9.75 ppm (t,  $J = 1.8$  Hz, 2-H).

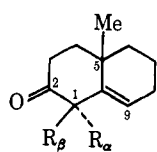
(6) Y. Nakadaira, J. Hayashi, H. Sato, and K. Nakanishi, *J. Chem. Soc. D*, in press.

(7) Aldehyde **6**: oil;  $M^+$  178; uv (EtOH)  $\epsilon_{285}$  8900; ir (film) 1725  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ ) 1.85 (br s, 1-Me), 4.91 (br s, 11-H), 4.87 (br s, 11-H), 5.83 (t, 3, 9-H), 9.75 ppm (t,  $J = 2$  Hz, 2-H).

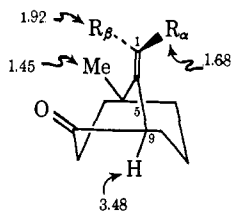
(8) It was not possible to irradiate  $R_\alpha$  and  $R_\beta$  in **5** independently due to close  $\delta$  values. A slightly off-centered irradiation was carried out at 1.71 ppm, upon which the 3.09-ppm intensity increased 18%; in contrast, the 3.41-ppm intensity increased only 8%. An off-centered irradiation at 1.60 ppm resulted in a 13% increase in the 3.41-ppm signal but only a 5% increase in the 3.09-ppm signal.

(9) The 1:1 ratio is the net result of isotope effects, rotation of the allyl radical, and nmr measurement errors; however, the occurrence of free rotation is clear.

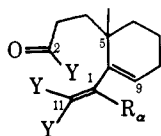
go through the solvated intimate radical pair **7**<sup>10</sup> in order to preserve stereospecificity. The overlap of orbitals depicted in **7** is also in agreement with the spin



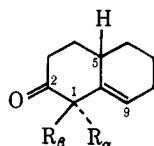
**1**,  $R_\alpha = R_\beta = \text{CH}_3$   
**1 $\alpha$** ,  $R_\alpha = \text{CD}_3$ ;  $R_\beta = \text{CH}_3$   
**1 $\beta$** ,  $R_\alpha = \text{CH}_3$ ;  $R_\beta = \text{CD}_3$



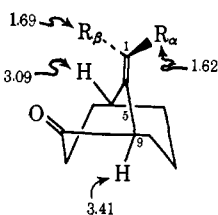
**2**,  $R_\alpha = R_\beta = \text{CH}_3$   
**2 $\alpha$** ,  $R_\alpha = \text{CD}_3$ ;  $R_\beta = \text{CH}_3$   
**2 $\beta$** ,  $R_\alpha = \text{CH}_3$ ;  $R_\beta = \text{CD}_3$



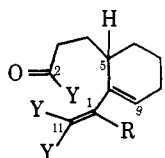
**3**,  $R_\alpha = \text{CH}_3$ ;  $Y = \text{H}$   
**3 $\alpha$** ,  $R_\alpha = \text{CD}_3$ ;  $Y = \text{H}$   
**3 $\beta$** ,  $R_\alpha = \text{CH}_3$ ;  $Y = \text{D}$



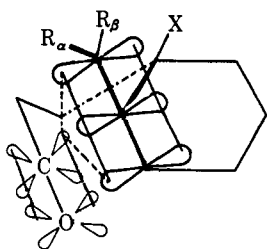
**4**,  $R_\alpha = R_\beta = \text{CH}_3$   
**4 $\alpha$** ,  $R_\alpha = \text{CD}_3$ ;  $R_\beta = \text{CH}_3$   
**4 $\beta$** ,  $R_\alpha = \text{CH}_3$ ;  $R_\beta = \text{CD}_3$



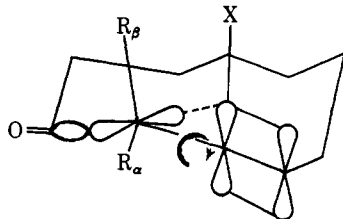
**5**,  $R_\alpha = R_\beta = \text{CH}_3$   
**5 $\alpha$** ,  $R_\alpha = \text{CD}_3$ ;  $R_\beta = \text{CH}_3$   
**5 $\beta$** ,  $R_\alpha = \text{CH}_3$ ;  $R_\beta = \text{CD}_3$



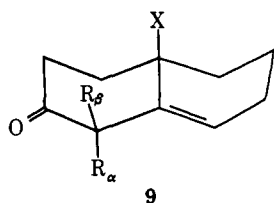
**6**,  $R = \text{CH}_3$ ;  $Y = \text{H}$   
**6 $\alpha$** ,  $R = \text{CD}_3$ ;  $Y = \text{H}$   
**6 $\beta$** ,  $R = \text{CH}_3$ ;  $Y = \text{D}$



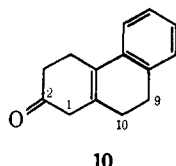
**7a**,  $X = \text{CH}_3$   
**7b**,  $X = \text{H}$



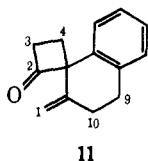
**8**



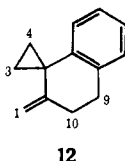
**9**



**10**

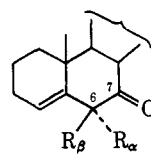


**11**

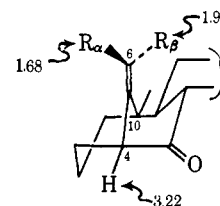


**12**

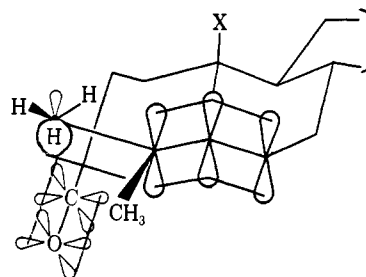
(10) Cf. N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3675 (1966); a similar mechanism has been proposed for  $\beta,\gamma$ -enals: E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Amer. Chem. Soc.*, **92**, 4906 (1970).



**13a**,  $R_\alpha = R_\beta = \text{CH}_3$   
**13b**,  $R_\alpha = R_\beta = \text{H}$



**14a**,  $R_\alpha = R_\beta = \text{CH}_3$   
**14b**,  $R_\alpha = R_\beta = \text{H}$



**15**

polarization mechanism.<sup>2</sup> Now, for steric reasons, the *immediate* precursor of intimate radical pair **7** should be the chair-like conformer **8** but not the boat-like conformer **9**. These intimate radical pairs lead to the photo-stationary mixtures of **1-2** and **4-5**; simultaneously, a portion is liberated from the solvent cage to form free biradicals which afford aldehydes **3** and **6**. Although the allyl radical from **7a** is subject to hindered rotation due to the angular methyl group and thus affords aldehydes **3** *via* specific abstraction of  $\beta$ -methyl hydrogens by the acyl radical, the allyl radical from **7b** is free to rotate and gives the 1:1 mixture of **6a-6b**. Furthermore, retention of the original deuterium ratio in recovered **4 $\alpha$ -4 $\beta$**  (from nmr) leads to the conclusion that this free-radical intermediate reverts neither to **4** nor **5** but instead proceeds to aldehyde **6**.

**Conjugative Aspects.** The incipient allyl radicals **7** are stabilized by conjugation. This assumption was borne out by the fact that in contrast to the mentioned conversions of  $\alpha,\alpha$ -disubstituted enones (see also ref 1f), irradiations<sup>4</sup> of cholest-5-en-3-one (uv ( $\text{C}_6\text{H}_{12}$ )  $\epsilon_{296}$  56) for 24 hr resulted in recovery of the starting material (see also ref 11). Likewise, direct irradiation of a 19-nor-3-keto-5(10)-ene steroid afforded no singlet reaction product.<sup>1c</sup>

The conjugative effect was also realized by a phenyl group. Namely, irradiation<sup>4</sup> of hydrophenanthrone **10**,<sup>12</sup> uv (MeOH)  $\epsilon_{224}$  15,400,  $\epsilon_{262}$  11,700,  $\epsilon_{267}$  11,400,  $\epsilon_{292}$  1200, for 5 hr resulted in<sup>13</sup> (tlc separation yields given in per cent): ketone **10** (63%), cyclobutanone **11** (17%), and decarbonylation product **12** (4%). Irradiation<sup>4</sup> for 4 hr of **11** also gave a mixture of **10**, **11**, and **12**, in which **10** was again the major product.

A 7-keto steroid was next studied as a model of a more rigid structure. Namely, 6,6-dimethyl-cholest-

(11) S. Kuwata and K. Schaffner, *Helv. Chim. Acta*, **52**, 173 (1969).

(12) M. Mousseron, H. Christol, and R. Salle, *C. R. Acad. Sci.*, **245**, 366 (1957).

(13) Compound **11**: oil;  $M^+$  198.1042 (calcd for  $\text{C}_{13}\text{H}_{14}\text{O}$ , 198.1045); uv (MeOH)  $\epsilon_{257}$  900,  $\epsilon_{275}$  900; ir ( $\text{CHCl}_3$ ) 1780, 1650  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ ) 2-3.4 (m, 3,4,9,10-H's), 4.93 (s, 1-H), 4.97 (s, 1-H), 7.13 ppm (s, aromatic H's). **12**: unstable oil;  $M^+$  170.1085 (calcd for  $\text{C}_{13}\text{H}_{14}\text{O}$ , 170.1095); ir ( $\text{CHCl}_3$ ) no C=O; nmr ( $\text{CDCl}_3$ ) 1.23 ( $\text{A}_2\text{B}_2$ , 3,4-H's), 2.4-3.1 ( $\text{A}_2\text{B}_2$ , 9,10-H's), 4.10 (br s, 1-H), 4.67 (br s, 1-H), 7.0-7.2 ppm (m, aromatic H's).

4-en-7-one (**13a**)<sup>14</sup> was irradiated<sup>4</sup> for 2 hr to afford a *ca.* 1:7 photoequilibrium mixture of **13a** and the ketone **14a**.<sup>15</sup> As these reactions were neither sensitized with acetophenone nor quenched with *trans*-piperylene, they proceed *via* the  $n, \pi^*$  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 6 $\beta$ - and 10-methyl groups. In addition to the conjugative effect mentioned, it was found that relative  $\epsilon$  values of enones, a reflection of their conformations,<sup>16</sup> are involved in governing the state of equilibria. Namely, in contrast to the  $\epsilon$  of enone **13a** ( $\epsilon_{295}$  105), that of **14a** is small ( $\epsilon_{295}$  58) due to poor carbonyl–double bond interaction<sup>16</sup> resulting from its fixed boat conformation, and this difference in  $\epsilon$  values shifts the equilibrium toward ketone **14a**. This factor is involved in the equilibrium of other photostationary mixtures. Thus, the high  $\epsilon$  value of bridged ketone **2** ( $\epsilon_{295}$  153) due to its chair conformation shifts the equilibrium toward enone **1** ( $\epsilon_{290}$  33) and the ratio of **1/2** is 15/1 (from glc). In enone **4** ( $\epsilon_{295}$  100) and ketone **5** ( $\epsilon_{295}$  167), the smaller difference in  $\epsilon$  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  $\alpha$  position.<sup>18</sup> 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,  $\epsilon_{290}$  240 (EtOH), as opposed to the bridged ketone **14b**,  $\epsilon_{297}$  48 (EtOH).

The mentioned relation of  $\epsilon$  values to equilibria was supported by equilibrium studies between **13b** and **14b** in various solvents upon monochromatic irradiation<sup>17</sup> at 290 nm; the ratio of **13b/14b** was 0.67 in *tert*-BuOH ( $\epsilon_{13b}$  190/ $\epsilon_{14b}$  41), 0.96 in dioxane ( $\epsilon_{13b}$  151/ $\epsilon_{14b}$  40), and 1.00 in cyclohexane ( $\epsilon_{13b}$  140/ $\epsilon_{14b}$  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 disfavored 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  $\sigma$ – $\pi$  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;<sup>18,19</sup> in this case the aldehydes could be formed from vibrationally different excited states.

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

(15) **14a**: mp 115°;  $M^+$  412; uv (EtOH)  $\epsilon_{298}$  58; CD (EtOH)  $\epsilon_{298}$  +1.16; ir (KBr) 1711  $\text{cm}^{-1}$ ; nmr (CDCl<sub>3</sub>) 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).

**Acknowledgments.** We acknowledge Professor N. J. Turro for discussions, and Dr. George van Lear, Lederle Laboratories, for measurements of mass spectra. This work was supported by Public Health Service Grant No. CA 11572.

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Received November 29, 1971

## 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  $\alpha, \alpha'$  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,<sup>1</sup> 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.<sup>2</sup>

Addition of an equimolar amount of TMEDA to a suspension of *n*-amylsodium<sup>3</sup> in hexane at  $-15^\circ$  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  $\alpha, \alpha'$  dianions at room temperature within 2 hr.<sup>4</sup> In a typical experiment 1,3-dimethylnaphthalene was added at  $-15^\circ$  to slightly over 2 equiv of a freshly prepared mixture of *n*-amylsodium–TMEDA<sup>5</sup> 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  $\alpha, \alpha'$ -dicondensation products in high yield. Thus, treatment of **1** with excess methyl iodide afforded 1,3-diethylnaphthalene (**2a**), picrate

(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-houng 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<sup>1</sup> 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.