xylene). Thus, inversion must have taken place in the transformation of 9 to 10 because inversion is known⁸ 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-butanediol⁹) 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-

$(CH_3)_2C \stackrel{CH_2O}{\longrightarrow} CH_3$	\rightarrow	CH ₃ COOCH ₂ C(CH ₃) ₂ CH ₂ X
CH ₂ O COOH		13, X = Cl
12		14. X = Br

phorus tribromide) in high yields.6

In a typical experiment a solution of 1.00 g (5.75 mmol) of 12 in 5 ml of dry CH_2Cl_2 was added dropwise during 1 hr to a solution of 1.20 g (5.75 mmol) of PCl_5 in 15 ml of CH_2Cl_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 CH_2Cl_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.⁶

(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, $\alpha^{25}D - 12.9^{\circ}$ (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,π^* Singlet Isomerizations of Cyclic β,γ -Unsaturated Ketones

Sir:

Studies on cyclic β , γ -enones¹ indicate that 1,3- and 1,2-acyl migrations result, respectively, from singlet^{1a,b}

(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)

Journal of the American Chemical Society | 94:6 | March 22, 1972

and triplet reactions.^{1c-f} Recently a spin polarization mechanism has been proposed to rationalize such 1,2and 1,3-acyl migrations.² 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_{α} and R_{β} groups.

Irradiation^{3,4} 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 3⁵ (2%). The 1.68-ppm methyl peak in ketone 2 was assigned to R_{α} 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 $1\alpha-1\beta^6$ obtained upon deuteriomethylation of the corresponding 1-methyl-1en-2-one. Irradiation⁴ of $1\alpha-1\beta$ yielded $2\alpha-2\beta$ and $3\alpha-3\beta$. The R_{α} 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 irradiation⁴ of 4 yielded 42% enone 4, 12% bridged ketone 5 (see also ref 3), and 5% aldehyde 6.7 The assignments of nmr signals in 5 are based on NOE.⁸ Irradiation⁴ of the 3:7 mixture of 4α - $4\beta^{6}$ (prepared from the corresponding 1-methyl-1-en-2-one) yielded a *ca.* 3:7 mixture of 5α - 5β , but the ratio of the aldehydes 6a-6b was 1:1 (from nmr).⁹ 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, π^* 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) ϵ_{227} 3400 (plateau); ir (film) 1725 cm⁻¹; nmr (CDCl₈) 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) ϵ_{235} 8900; ir (film) 1725 cm⁻¹; nmr (CDCl₃) 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 \mathbf{R}_{α} and \mathbf{R}_{β} in 5 independently due to close δ 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^{10} in order to preserve stereospecificity. The overlap of orbitals depicted in 7 is also in agreement with the spin



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



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polarization mechanism.² 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 photostationary 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 β -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 4α -4 β (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 α , α -disubstituted enones (see also ref 1f), irradiations⁴ of cholest-5-en-3-one (uv (C₆H₁₂) ϵ_{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.^{1c}

The conjugative effect was also realized by a phenyl group. Namely, irradiation⁴ of hydrophenanthrone **10**, ¹² uv (MeOH) ϵ_{224} 15,400, ϵ_{262} 11,700, ϵ_{267} 11,400, ϵ_{292} 1200, for 5 hr resulted in¹³ (tlc separation yields given in per cent): ketone **10** (63%), cyclobutanone **11** (17%), and decarbonylation product **12** (4%). Irradiation⁴ 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. 246

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

(13) Compound 11: oil; M⁺ 198.1042 (calcd for $C_{14}H_{14}O$, 198.1045); uv (MeOH) ϵ_{257} 900, ϵ_{275} 900; ir (CHCl₃) 1780, 1650 cm⁻¹; nmr (CDCl₃) 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 $C_{13}H_{14}O$, 170.1095); ir (CHCl₃) no C=O; nmr (CDCl₃) 1.23 (A₂B₂, 3,4-H's), 2.4-3.1 (A₂B₃, 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 $(13a)^{14}$ was irradiated⁴ 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 interaction¹⁶ 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 $(\epsilon_{295}$ 153) due to its chair conformation shifts the equilibrium toward enone 1 (ϵ_{290} 33) and the ratio of 1/2is 15/1 (from glc). In enone 4 (ϵ_{295} 100) and ketone 5 $(\epsilon_{295}$ 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 irradiation¹⁷ 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 $\sigma-\pi$ 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;^{18,19} in this case the aldehydes could be formed from vibrationally different excited states.

(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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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*-amylsodium³ 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-TMEDA⁵ in hexane and the reaction mixture was allowed to warm slowly to room temperature. Reaction occurred quite rapidly to give the insoluble brickred 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

(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-butoxide¹ 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.

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

^{(15) 14}a: mp 115°; M⁺ 412; uv (EtOH) ϵ_{298} 58; CD (EtOH) ϵ_{298} +1.16; ir (KBr) 1711 cm⁻¹; nmr (CDCl₈) 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.

^{(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).

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(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
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