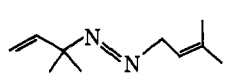
to vpc, it was synthesized independently.[10] The decomposition of **1** and **2** was shown by nmr and vpc to be remarkably clean. As in other delocalized radicals,[6] disproportionation is of minor importance; in fact, our value of less than 2% disproportionation relative to recombination appears to be the lowest yet reported.

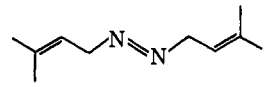
It should be noted that **2** is a potentially dangerous compound. Early in the course of our work a 75-mg neat sample of **2** was sealed into a 30-cm^3 evacuated tube. When the tube was lowered into an oil bath at 116°, the sample suddenly decomposed with a flash of yellow light. Although the tube did not break, further work with **2** was confined to solutions, where no such problems were encountered.

Three factors which may affect the distribution of C_{10} products are: (1) relative spin density at the radical termini, (2) steric effects, and (3) product stability. On account of the exothermicity of radical recombination, little importance is attached to the latter. The esr results of Kochi and Krusic[11,12] show negligible dependence of spin density at allylic carbon on alkyl substitution. Thus, the product distribution from **1** reflects only the greater steric hindrance to recombination of a tertiary site compared with a primary site. Propargylic carbon atoms, on the other hand, show substantially greater spin density than allenic ones.[12] In opposition to the steric effect, this favors head-to-head recombination. The optimum occurs in the recombination of an allenyl with a propargyl radical.[13]

The product composition from **1** is approximately the same as that from thermolysis of **3**[14] and **4**.[15] Using 0.00153 *M* Koelsch radical[16] and 0.0344 *M* 2,2,6,6-



3



4

tetramethylpiperidine-1-oxyl[17] as scavengers, we have found that the cage effect in thermolysis of **1** at 53° in benzene is 0.50 and 0.45, respectively. If the cage effect for **3** and **4** is comparable, rotation of radicals within the solvent cage must be faster than recombination;[3] otherwise, one would expect a different product distribution from each azo compound. The similar behavior of **1**, **3**, and **4** also mitigates against an eight-membered cyclic decomposition mechanism which would produce exclusively the tail-to-tail product. Further evidence that these radicals randomize within the solvent cage before recombining can be adduced from product studies in the presence of excess 2,2,6,6-tetramethylpiperidine-1-oxyl. The C_{10} recombination products, which were isolated by column chromatography of thermally decomposed mixtures in pentane, were shown by vpc to occur in essentially the same ratio as in unscavenged runs.

(10) L. Skattebol and S. Solomon, *J. Amer. Chem. Soc.*, 87, 4506 (1965).
(11) J. K. Kochi and P. J. Krusic, *ibid.*, 90, 7157 (1968)
(12) J. K. Kochi and P. J. Krusic, *ibid.*, 92, 4110 (1970).
(13) Head-to-head and head-to-tail dimers have been isolated previously from the Grignard reagent of 3-bromo-3-methyl-1-butyne; see G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, 31, 970 (1966).
(14) J. E. Baldwin, J. E. Brown, and G. Höfle, *J. Amer. Chem. Soc.*, 93, 788 (1971).
(15) Unpublished results of R. J. Crawford.
(16) C. F. Koelsch, *J. Amer. Chem. Soc.*, 79, 4439 (1957).
(17) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 65, 3273 (1965).

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(18) NDEA Graduate Fellow, 1971–present.

Paul S. Engel,* David J. Bishop[18]
Department of Chemistry, Rice University
Houston, Texas 77001
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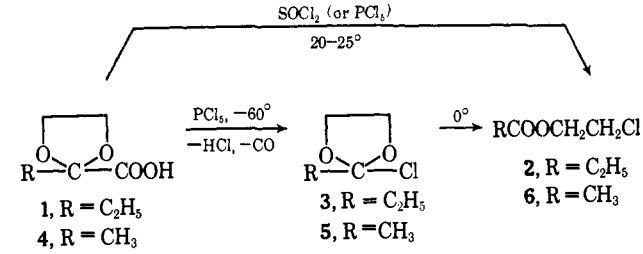
Stereospecific Formation of Epoxides and Halohydrin Esters from Diols

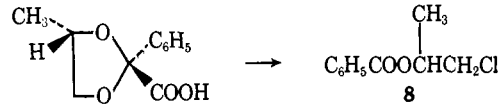
Sir:

Treatment of 2-carboxy-2-ethyl-1,3-dioxolane (**1**) with thionyl chloride at room temperature yields 2-chloroethyl propionate (**2**)[1,2] and not 2-chloro-2-ethyl-1,3-dioxolane (**3**)[3] as originally claimed.[4] Actually,



we have shown that treatment of 2-carboxy-2-methyl-1,3-dioxolane (**4**) with phosphorus pentachloride in methylene chloride at −60° yields 2-chloro-2-methyl-1,3-dioxolane (**5**)[5] which rearranges to 2-chloroethyl acetate (**6**) rapidly on warming to 0°.

Although this type of chemistry has been noted by several authors, the synthetic possibilities and advantages have not been explored. In this communication we point out the high regiospecificity and stereospecificity involved in the conversions of ketals of α-keto acids to esters of halohydrins. For example, treatment of 2-carboxy-4-methyl-2-phenyl-1,3-dioxolane (**7**)[6] (trans/cis about 3/2—made from 1,2-propanediol) with phosphorus pentachloride in methylene chloride affords 85–92% yields of 1-chloro-2-propyl benzoate (**8**).[6] No



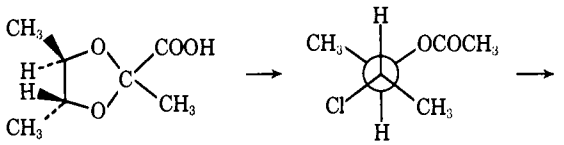
7 (trans shown)

trace of isomer was seen in the nmr analysis.

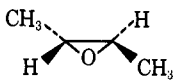
Similar treatment of D(−)-2-carboxy-2,4,5-trimethyl-1,3-dioxolane (**9**),[6] $\alpha^{22}D$ −14° (neat, 1 dm), yields L(+)-*erythro*-3-chloro-2-butyl acetate (**10**),[7] $\alpha^{22}D$ 12.7 (neat, 1 dm), which on treatment with strong base yields D(+)-2,3-epoxybutane (**11**),[8] $[\alpha]^{21}D$ 70° (*c* 0.0149,

(1) S. M. McElvain and A. N. Bolstad, *J. Amer. Chem. Soc.*, 73, 1988 (1951).
(2) R. P. A. Sneeden, *J. Chem. Soc.*, 477 (1959).
(3) For the formation and reactions of such ortho ester chlorides, see (a) A. Gross, J. Freiberg, and B. Costisella, *Chem. Ber.*, 101, 1250 (1968), and (b) S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 3, 548 (1964), for other examples.
(4) E. Vogel and H. Schinz, *Helv. Chim. Acta*, 33, 116 (1950).
(5) For a similar chlorinated ortho ester chloride see ref 3a.
(6) All new compounds prepared in this work gave analyses, nmr, ir, and mass spectral data consistent with the assigned structures.
(7) For (±)-*erythro*-3-chloro-2-butyl acetate, see R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 87, 5172 (1965).

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



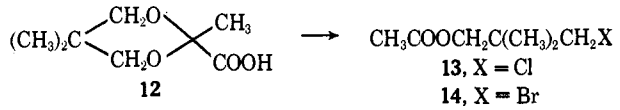
10



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[9]) 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-



12

$CH_3COOCH_2C(CH_3)_2CH_2X$

13, X = Cl

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° (neat, 1 dm), was obtained from the Norse Laboratories, Inc.

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

Melvin S. Newman,* Chin H. Chen[10]

Chemistry Department, The Ohio State University
Columbus, Ohio 43210

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Factors Involved in Photoinduced n,π* Singlet Isomerizations of Cyclic β,γ-Unsaturated Ketones

Sir:

Studies on cyclic β,γ-enones[1] indicate that 1,3- and 1,2-acyl migrations result, respectively, from singlet[1a,b] and triplet reactions.[1c-f] Recently a spin polarization mechanism has been proposed to rationalize such 1,2- and 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 **3**[5] (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 **1α–1β**[6] obtained upon deuteriomethylation of the corresponding 1-methyl-1-en-2-one. Irradiation[4] of **1α–1β** yielded **2α–2β** and **3α–3β**. The R_α 1.68-ppm peak was too weak to be detected in the deuterated mixture **2α–2β** (submerged in methylene signals), and thus shows that conversion of **1α–1β** to **2α–2β** had occurred in a stereospecific manner. In aldehydes **3α–3β**, nmr analysis indicated a 9:1 mixture, and therefore they had also been formed stereospecifically.

Similar irradiation[4] 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] Irradiation[4] of the 3:7 mixture of **4α–4β**[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**

(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) 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 ($CDCl_3$) 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) ϵ_{285} 8900; ir (film) 1725 cm^{-1}; nmr ($CDCl_3$) 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_α and 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.