Table XI. Electrolysis of Potassium 2,4,4-Trimethylpentanoate

pH	14.0
RCO_2K, *M*	1.0
Amperes	8.0
Volts	13.0
Voltage at anode *vs.* sce	1.2
Temp, °C	55
Time, min	40
mmoles of RCO_2K electrolyzed	19
mmoles of volatile products	6
mfaradays	200
Current yield, %, of volatile products	5

Volatile products	Mole %
2,2-Dimethylpentane 4,4-Dimethyl-1-pentene	40.6[a]
Propene	17.2
2-Methylpropene	13.4
trans-4,4-Dimethyl-2-pentene	12.0
cis-4,4-Dimethyl-2-pentene	Trace
2,3-Dimethyl-1-pentene	16.9
2,3-Dimethyl-2-pentene	0.0
	100.0

[a] Unresolved on the vpc column.

3,3-Dimethyl-1-butyl *p*-Toluenesulfonate. This ester was prepared in 84% yield by allowing 3,3-dimethyl-1-butanol (10.2 g, 0.10 mole) containing 1% 3,3-dimethyl-2-butanol to react with *p*-toluenesulfonyl chloride (21.0 g, 0.15 mole) and pyridine (60 cc). The crude tosylate was taken up in chloroform and then washed successively with dilute HCl, water, dilute K_2CO_3, and water; the chloroform solution was then dried over anhydrous K_2CO_3, and the chloroform was removed at 30° under reduced pressure; nmr: singlet (9.0 H) at 0.86 ppm, triplet (2.1 H) at 1.55 ppm, singlet (3.3 H) at 2.41 ppm with a small shoulder on the downfield side (possibly some *o*-tosylate), triplet (2.0 H) at 4.07 ppm, poorly shaped doublet (2.3 H) centered at 7.31 ppm, poorly shaped doublet (2.3 H) centered at 7.75 ppm. There was a small peak (*ca.* 0.17 H) at 1.18 ppm; this latter peak indicates the possible presence of ~5% 3,3-dimethyl-2-butyl tosylate or ~3% 2,3-dimethyl-2-butyl tosylate.

Solvolyses of 3,3-dimethyl-1-butyl *p*-Toluenesulfonate were carried out by refluxing the ester for 19 hr in acetic or formic acids in the presence of a small excess of sodium acetate or cesium formate, respectively. Esters were isolated in 50–60% yield. After reduction with lithium aluminum hydride, the alcohol component was identified by gas chromatographic retention time as 3,3-dimethyl-1-butanol, not contaminated by any other C_6 alcohol. In another acetolysis the olefinic products were removed by sweeping the reaction vessel with nitrogen during the solvolysis, the last traces being removed by distilling at 10 mm three-quarters of the solvent into the trap. The olefinic products and yields were: 1.4% 3,3-dimethyl-1-butene, 0.9% 2,3-dimethyl-1-butene, and 1.0% 2,3-dimethyl-2-butene; ethylene and isobutylene were not detected.

2,4,4-Trimethylpentanoic Acid. The Grignard reagent from 2-chloro-4,4-dimethylpentane, (bp[54] 64.5° (85 mm), $n^{20}\mathrm{D}$ 1.4180, 99% pure by vpc, 74.8 g, 0.556 mole) and magnesium turnings was carbonated with CO_2, yielding 2,4,4-trimethylpentanoic acid (35%), bp 108–110° (12 mm), $n^{25}\mathrm{D}$ 1.4231; lit.[55] bp 109.8–109.5° (12–14 mm), $n^{20}\mathrm{D}$ 1.4231.

Electrolysis of Potassium 2,4,4-Trimethylpentanoate. The electrolysis cell[51] was modified to separate the cathode and anode by a sintered-glass disk of medium porosity; the cathode compartment contained 12 *M* KOH, the anode compartment the aqueous RCO_2K–KOH electrolyte. In addition to the compounds listed in Table XI, 4,4-dimethyl-2-pentanol and 4,4-dimethyl-2-pentyl 2,4,4-trimethylpentanoate were identified; the remainder, probably rearranged alcohols and esters, were not identified.

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(54) Prepared by W. H. James, The Pennsylvania State College, 1943.

(55) J. W. Heyd, Ph.D. Thesis, The Pennsylvania State College, 1937.

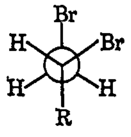
Conformational Stability in Ethyl 2,3-Dibromopropionate

Richard J. Jablonski and Eugene I. Snyder[1]

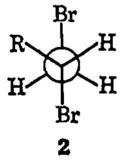
Contribution from the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268. *Received September 28, 1967*

Abstract: Preparation of *threo*-$BrCHDCDBrCO_2C_2H_5$ and comparison of its nmr spectrum with that of undeuterated ester permits unequivocal identification of the most stable conformer as the one with *trans* bromines.

A study of the conformer distribution in two 1-substituted 1,2-dibromoethanes, $BrCH_2CHBrR$, has shown[2] that the more stable conformer with R = *t*-butyl is **1** (bromines *gauche*) whereas that with R = C_6H_5 is **2** (bromines *trans*). It has been assumed[3] that the most stable conformer of $BrCH_2CHBrCO_2H$ (R = CO_2H) corresponds to **2**, but no definitive support is available. Although dipole–dipole repulsions between bromines will undoubtedly favor **2**, the carboxyl (and carboxylate) group is also a polar one. The extent of bromine–carboxyl (or carboxylate) electrostatic interactions will depend sensitively on the precise geometry of the latter with respect to the halogen, but it seems reasonable that these will be repulsive and will tend to favor **1**.



1



2

The conformation of ethyl 2,3-dibromopropionate has been unequivocally determined by examination of

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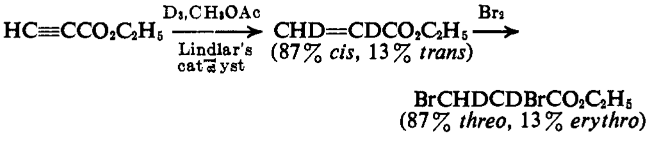
(1) This investigation was supported in part by Public Health Service Research Grant GM-12113 from the National Institute of General Medical Sciences.

(2) M. Buza and E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1161 (1966).

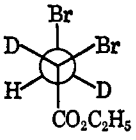
(3) R. Freeman, K. A. McLauchlan, J. I. Musher, and K. G. R. Pachler, *Mol. Phys.*, **5**, 321 (1962).

the nmr spectrum of *threo*-$BrCHDCDBrCO_2C_2H_5$ (*threo*-I-d_2) using a variant of the approach previously described.[2] Synthesis of the dideuterated ester was accomplished using standard reactions according to the sequence

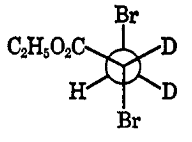


$$HC{\equiv}CCO_2C_2H_5 \xrightarrow[\text{Lindlar's catalyst}]{D_2, CH_3OAc} \underset{(87\%\ cis,\ 13\%\ trans)}{CHD{=}CDCO_2C_2H_5} \xrightarrow{Br_2} \underset{(87\%\ threo,\ 13\%\ erythro)}{BrCHDCDBrCO_2C_2H_5}$$

The conformers of *threo*-I-d_2 corresponding to **1** and **2** are



1′



2′

The chemical shift of the sole acid side-chain proton in *threo*-I-d_2 corresponds to that of one of the magnetically nonequivalent protons of the methylene protons in $BrCH_2CHBrCO_2C_2H_5$ (I). Unless the geometry of the above conformers is grossly distorted from the staggered arrangement, the vicinal HD coupling constant of the proton in conformer **1′** is gauchoid whereas that of **2′** is transoid. Now it is well known that for vicinal proton–proton couplings in ethanes $J_{gauche} < J_{trans}$. Therefore, if the proton in *threo*-I-d_2 corresponds to the proton of I which has the smaller of the two vicinal coupling constants, conformer **1′** is the more stable; if the proton in *threo*-I-d_2 corresponds to that methylene proton of I which has the larger of the two vicinal coupling constants, conformer **2′** is the more stable.

The relevant nmr spectral parameters (for 40% solutions in benzene) are listed in the table. For maximum accuracy all line positions were measured with reference to the highest field line of the ethyl $-CH_2-$ quartet, which was imbedded in the low-field portion of the ABK spectrum of I. The chemical shifts of protons 1–3 are therefore given with respect to this line; spectral parameters of I were determined by computer-based analysis and compare favorably with those previously reported[4] (Table I). The chemical shifts in *threo*- and *erythro*-I-d_2 were measured directly from the deuterium-decoupled spectra.

Table I. Nmr Parameters

$BrCH_2CHBrCO_2C_2H_5$		
ν_1 −21.80		J_{12} = 11.18 cps
ν_2 5.18		J_{13} = 4.40 cps
ν_3 35.14		J_{23} = −9.80 cps
threo-$BrCHDCDBrCO_2C_2H_5$	ν 7.0	
erythro-$BrCHDCDBrCO_2C_2H_5$	ν 35.7	

The lowest field proton, H_1, of chemical shift ν_1, is readily assigned to the proton adjacent to the carbonyl. It is apparent that the proton in *threo*-I-d_2 corresponds to H_2. Since this is the proton which shows the larger of the two vicinal couplings, J_{12} and J_{13}, this unambiguously identifies the most stable conformer as **2**. The same conclusion is reached by inspection of the chemical shift observed in the minor isomer, *erythro*-I-d_2. Since the conformational energy difference in the ester and in the acid is virtually identical,[5] the dominant conformer of the acid must also correspond to **2**.

From these and other recent results[5] we see that the conformational energy difference, $E_2 - E_1$, becomes increasingly negative (*i.e.*, **2** becomes more stable relative to **1**) in the series R = $(CH_3)_3C$, C_6H_5, $CO_2C_2H_5$. Since this order is precisely what would be expected on the basis of the "size" of these groups as measured by their A values,[6] one interpretation of our results is that in this molecule steric effects are predominant in determining its conformation. (It must be realized that this qualitative relation between "size" in acyclics and A values probably is not valid for acyclics in general.[7]) A corollary is that repulsive electrostatic interactions involving halogens and carboxylic ester groupings are energetically unimportant in determining conformer distribution in acyclics. However, our results could also be interpreted on the basis of an attractive interaction between the aforementioned groups.

That the resonance position of the acid side-chain proton in either *erythro*- or *threo*-I-d_2 does not correspond exactly to the resonance frequency of the corresponding protons in I is an example of the well-documented isotope effect on chemical shift.[8] What is more interesting is the observation that there is a differential isotope shift in the two diasteromers.[9] Precise measurements give $|\nu_{erythro} - \nu_{threo}| = 28.7$ cps, whereas $|\nu_3 - \nu_2| = 30.0$ cps.

Experimental Section

Nmr spectra were obtained with an A-60 spectrometer system utilizing an NMR Specialties HD-60A spin decoupler. Sweep widths were calibrated by the audio side-band method. Propiolic acid and ethyl propiolate were prepared according to previous descriptions.[10]

Ethyl Acrylate-α,β-d_2. A solution of ethyl propiolate (6.27 g, 0.064 mol) in 30 ml of methyl acetate (freed of acid by washing with sodium bicarbonate) containing Lindlar's catalyst[11] (0.230 g, 3.8% by weight) was shaken in a deuterium atmosphere at an initial pressure of 22 psig. After cessation of deuterium uptake (*ca.* 1 hr) catalyst was removed by filtration and the solution was concentrated by distillation. In addition to the ethyl resonances, the nmr spectrum showed triplets at 6.31 and 5.80 ppm (from internal TMS) in the ratio 87:13, which collapsed to singlets upon irradiation at the deuterium frequency. From the published[12] spectral parameters of ethyl acrylate these can be unequivocally assigned to the *cis*- and *trans*-$CHD{=}CDCO_2C_2H_5$, respectively. Previous workers[13] have reported catalytic reduction of methyl acrylate by D_2 leads to a *cis:trans* ratio of about 3.

Ethyl 2,3-Dibromopropionate-2,3-d_2. The concentrated solution of $CHD{=}CDCO_2C_2H_5$ prepared above was maintained at 0°, and a solution of bromine in methyl acetate was added until the bromine color persisted. Several portions of CCl_4 were added and distilled to remove excess bromine. Fractionation afforded

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(4) E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1155 (1966).

(5) E. I. Snyder, *ibid.*, **88**, 1165 (1966).

(6) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 44.

(7) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Am. Chem. Soc.*, **89**, 1135 (1967).

(8) O. S. Lee and J. Warkentin, *Can. J. Chem.*, **43**, 2424 (1965).

(9) We have observed such differential isotope shifts in other compounds, but that reported here is the largest by far.

(10) E. H. Ingold, *J. Chem. Soc.*, **127**, 1203 (1925); B. F. Strauss and W. Voss, *Ber.*, **69**, 168 (1926).

(11) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(12) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

(13) J. Yoshino, J. Koniyama, and M. Shinomiya *J. Am. Chem. Soc.*, **88**, 4482 (1966).

7.48 g of material, bp 69.5–71.5° (5–6 mm), $n^{20}\mathrm{D}$ 1.4994 (lit.[14] $n^{20}\mathrm{D}$ 1.5007 for undeuterated ester), whose infrared spectrum was indicative of the title compound. Its nmr spectrum showed the ethyl group and two broad lines which upon deuterium decoupling gave two sharp resonances at 3.97 and 3.49 ppm in the ratio of 87:13, respectively. *Anal.*[15] Calcd for $BrCHDCDBrCO_2C_2H_5$: 25.00 atom % excess D. Found: 24.55%, or 1.96 deuteriums per molecule.

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(14) H. C. Murfitt and J. C. Roberts, *J. Chem. Soc.*, **146**, 371 (1944).

(15) Performed by the falling-drop method by Mr. Josef Németh, Urbana, Ill.

Structure of Electron Impact Fragments. The C_4H_4O Radical Cation from 2-Pyrone

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Contribution from the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801. *Received October 25, 1967*

Abstract: Prominent in the mass spectrum of 2-pyrone is an M − CO radical cation of controversial structure. The electron impact fragmentations of the four monodeuterio-2-pyrones have been studied and the distribution of deuterium among the various daughter cations has been measured. The observed deuterium distributions allow confident exclusion of a furan-like structure for the 2-pyrone M − CO radical cation. Other structural implications of the observed isotope distributions are considered.

Owing to the difficulty in obtaining evidence pertaining to the structures of fragments resulting from electron impact induced decompositions, many workers have attempted to infer fragment structures and decomposition pathways from the precepts of ground-state solution chemistry. More recently, photochemical reactions have been used as models for gas-phase electron impact induced decompositions.[2] While the correlations thus suggested have proven to be of considerable empirical value, only rarely are those mechanistic and structural conjectures supported experimentally. Because of the importance of mass spectrometry as a tool for structural determination, the validity of these proposed structures and fragmentation schemes is of vital concern. Even so, there are few definitive studies of fragment ion structure, for the present experimental methods for investigating the structures of fragments formed within a mass spectrometer are not always applicable, and, when applicable, always yield negative evidence, thereby allowing only the exclusion of certain postulates from further consideration.

The current 2-pyrone literature is illustrative of the problems encountered in assigning structures of electron impact induced ions. Nakata, *et al.*,[3] studying the mass spectra of variously substituted 2-pyrones, noted that the principal mode of fragmentation involves initial loss of carbon monoxide[4] to produce ions which they term "electron deficient furans." Although there is no evidence that these M − CO ions are furanlike, this assignment is no less reasonable than most of the literature assignments of electron impact fragment structures. There is precedent for the recombination of the entities on either side of a carbonyl upon its expulsion as carbon monoxide,[5] and a number of satisfying canonical structures may be written for a furanlike radical cation.

In the case of 2-pyrone (**1**) Pirkle pointed out that even though the subsequent fragmentation of the C_4H_4O radical cation (the M − CO ion) produces an array of ions whose masses and abundances are apparently quite similar to those produced upon the fragmentation of the furan molecular ion, the assumption that the two isomeric C_4H_4O radical cations are both furanlike would be in error.[6] Experimentally, Pirkle found that the *m/e* 39 peak arising from loss of a formyl radical (or from consecutive loss of carbon monoxide and a hydrogen atom) from the C_4H_4O radical cation was shifted to *m/e* 40 in the case of 2-pyrone-3-*d* but remained principally at *m/e* 39 in the spectrum of 2-pyrone-6-*d*. Observing that the symmetry of a furanlike C_4H_4O radical cation would necessitate the equivalence of hydrogens 3 and 6 (eq 1) Pirkle concluded that the C_4H_4O radical cation from 2-pyrone cannot have cyclic furanlike structure **2** since the M − CO ions derived from 2-pyrone-3-*d* and 2-pyrone-6-*d* do not fragment identically. Noting that reasoning of the type commonly used in assigning structures to electron

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[1] Archer Daniels Midland Fellow, 1966–1967; Union Carbide Fellow, 1967–1968.

[2] For examples, see M. M. Bursey and L. R. Dusold, *Tetrahedron Letters*, 2649 (1967); S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966); N. J. Turro, D. S. Weiss, W. F. Haddon, and F. W. McLafferty, *ibid.*, **89**, 3370 (1967).

[3] H. Nakata, Y. Hirata, and A. Tatematsu, *Tetrahedron Letters*, 123 (1965).

[4] Although it is unnecessary to consider the source of the expelled carbon monoxide to interpret the isotope distributions to be presented, it should be pointed out that there is considerable analogy for carbonyl groups being expelled as carbon monoxide. For examples, see J. H. Beynon, G. K. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); J. P. McCollum and S. Meyerson. *J. Am. Chem. Soc.*, **85**, 1739 (1963); J. M. Wilson, M. Ohashi, H. Budzikiewicz, C. Djerassi, S. Ito, and T. Nozoe, *Tetrahedron*, **19**, 2247 (1963); P. Beak, T. H. Kinstle, and G. A. Carls, *J. Am. Chem. Soc.*, **86**, 3833 (1964). Of even greater relevance, it has been shown by ^{13}C labeling that a substituted 2-pyrone loses its carbonyl carbon with the initial carbon monoxide expulsion [R. A. W. Johnstone, B. J. Millard, F. M. Dean, and A. W. Hill, *J. Chem. Soc.*, 1712 (1966)].

[5] See J. H. Beynon, "Mass Spectroscopy and Its Application to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p 259.

[6] W. H. Pirkle, *J. Am. Chem. Soc.*, **87**, 3022 (1965).