

spectra of esters⁴ with α -halo substituents also indicate that the carbonyl stretching frequencies of the halo esters are higher than those of the non-halogenated esters. It was expected that fluorine in the α -position would cause a marked shift, and recent studies of fluorinated esters have substantiated this expectation.⁵ Thus far, no studies have been reported for esters containing several different halogen atoms in the α -position. Such data are furnished in the present investigation (Table I). Since any factor causing a decrease in the ionic character of a carbonyl bond should also cause a shortening of the C-O linkage of the ester, such stretching frequencies also are recorded.

TABLE I

Ester	INFRARED SPECTRA OF HALOGENATED ACETIC ESTERS			
	(C=O), cm. ⁻¹	(C-O), cm. ⁻¹	(C-Cl), ^e cm. ⁻¹	(C-Br), cm. ⁻¹
CH ₃ COOEt	1740	1236, 1245 ^b
CH ₂ BrCOOEt	1740	1281	..	553
CHBr ₂ COOEt	1753, 1739	1268, 1278	..	583, 598 ^f
CH ₂ ClCOOEt	1753	1288, 1311	697	..
CHIFCOOEt	1754	1275
CHBrFCOOEt	1754	1284	..	594 ^f
CHClFCOOEt	1754	1276, 1290	731	..
CHCl ₂ COOEt	1758	1268-1302	719	..
CHBrClCOOEt	1758, 1742	1265-1297	703	582 ^{f,g}
CCl ₃ COOEt	1770 ^e , 1761 ^d	1310 ^e , 1268 ^d
CH ₂ FCOOEt	1778, 1750	1290 ^a
CHF ₂ COOEt	1770	1301
CClF ₂ COOEt	1770	1317 ^a	731	..
CF ₃ COOEt	1789	1319 ^a

^a Due to interference by C-F absorption, this value is estimated. ^b Shoulder. ^c H. M. Randell, R. G. Fowler, N. Fuson and J. R. Dangi, "Infrared Determination of Organic Structure," D. Van Nostrand, Co., Inc., New York, N. Y., 1949. ^d Ref. 6; R. R. Hampton and J. E. Newell, *Anal. Chem.*, 21, 914 (1949). ^e Compare with values for CH₂Cl (712 cm.⁻¹), CH₂Cl₂ (704 cm.⁻¹) and CCl₂F₂ (737 cm.⁻¹). ^f Broad absorption band. ^g Estimated.

In ethyl fluoroacetate, ethyl difluoroacetate, ethyl chlorofluoroacetate, ethyl bromofluoroacetate and ethyl iodofluoroacetate, a series of esters is available in which a hydrogen atom is replaced successively by fluorine, chlorine, bromine and iodine. The expected effect of a second halogen would be a shift of the carbonyl stretching band to higher frequencies, the order of the effect being F > Cl > Br > I. Such an effect, however, was observed only with a second fluorine substituent. The replacement of hydrogen by halogen atoms other than fluorine caused a decrease in the carbonyl band frequency and, surprisingly, chlorine, bromine and iodine all caused a shift of about the same magnitude.

The C-O band at 7.6-8.1 μ , on the other hand, was successively shifted to shorter wave lengths. Ethyl fluoroacetate, ethyl dibromoacetate and ethyl bromochloroacetate showed the presence of two absorption peaks in the carbonyl region.⁶

(4) (a) O. Burkard and L. Kahovec, *Monatsh.*, 71, 333 (1938); (b) L. Kahovec and K. W. F. Kohlrusch, *ibid.*, 74, 115 (1942); (c) H. Cheng, *Z. physik. Chem.*, B24, 293 (1934); (d) R. E. Chernizkaya and J. R. Syrkin, *Compt. rend. acad. sci. URSS*, 55, 513 (1947.) Chernizkaya and Syrkin^{4d} suggest that this α -substitution of halogen decreases the ionic character of the carbonyl bond.

(5) (a) M. Hauptschein, C. S. Stokes and E. A. Nodiff, *THIS JOURNAL*, 74, 4005 (1952); (b) G. Rappaport, M. Hauptschein, J. F. O'Brien and R. Filler, *ibid.*, 75, 2695 (1953); (c) R. Filler, *ibid.*, 76, 1376 (1954).

(6) It has been suggested by the Referee that in an inert solvent at high dilution these split bands may disappear assuming the phenomena is due to dimer formation.

Bender⁷ observed this phenomenon with ethyl fluoroacetate and attributed it to a dimer, which would also explain the high boiling point of the ester.

The shift of the stretching frequency of the C-Cl band in ethyl chloroacetate to longer frequencies in the polyhalogen esters implies a shorter bond in the latter esters. The same observation is made for the C-Br band in ethyl bromoacetate as compared to polyhalogen esters.

Acknowledgment.—Financial support by the Ethyl Corporation is gratefully acknowledged. The authors are indebted to Mrs. L. H. Walsh for determining the infrared spectra.

Experimental

Infrared Spectra.—Infrared spectra were determined by use of a Perkin-Elmer model C-21 double beam recording infrared spectrometer for pure liquids in capillary cells or in sealed cells of 0.0125 or 0.029 mm. thickness. The wave length scale was accurate to within ± 2 cm.⁻¹

Esters.—The esters used in this study were purified by rectification from a standard Todd distilling apparatus. The physical properties of the esters are given in Table II.

TABLE II

PHYSICAL CONSTANTS OF ACETIC ESTERS

Ester	B.p., °C. (mm.)		n _D ²⁰	
	Obsd.	Lit.	Obsd.	Lit.
CH ₃ COOEt	78	78 ^d	1.3718	1.3718 ^d
CH ₂ BrCOOEt	154	56-57 (15) ^e	1.4499	1.4489 ^e
CHCl ₂ COOEt	73 (30)	158.7 ^h	1.4380	1.4386 ^e
CHBr ₂ COOEt	65 (5)	121 (74) ^g	1.4973	1.50187 ^{b,c}
CH ₂ ClCOOEt	142.5	142.8 ^h	1.4211	1.42162 ^f
CHIFCOOEt	70 (14)	103 (30) ⁱ	1.4820
CHBrFCOOEt	68 (34)	154 ^j	1.4275
CHClFCOOEt	130	128-130 ^k	1.3953	1.3927 ^a
CHBrClCOOEt	66 (12)	174 ^l	1.4703
CH ₂ FCOOEt	46 (35)	114 ^d	1.3750	1.3747 ^d
CHF ₂ COOEt	98.5	98.5 ^d	1.3465	1.3463 ^d
CClF ₂ COOEt	95.5	97 ^m	1.3578
CF ₃ COOEt	60.5	60.5 ^d	1.3079	1.3073 ^d

^a At 25°. ^b At 12.5°. ^c W. Perkin, *J. Chem. Soc.*, 65, 423 (1894). ^d From ref. 6. ^e M. S. Kharasch, P. S. Skell and P. Fisher, *THIS JOURNAL*, 70, 1058 (1948). ^f A. Karvonen, *Ann. Acad. Sci. Fennicae*, A10, No. 4, 20 (1916). ^g W. Perkin, *J. Chem. Soc.*, 65, 430 (1894). ^h From ref. 4c. ⁱ F. Swarts, *Chem. Zentr.*, 80, I, 13 (1913). ^j F. Swarts, *Mem. couronnés acad. roy. Belg.*, 61, 1 (1901). ^k J. A. Young and P. Tarrant, *THIS JOURNAL*, 71, 2432 (1949). ^l H. Crompton and P. M. Triffitt, *J. Chem. Soc.*, 119, 1874 (1921). ^m F. Swarts, *Rec. trav. chim.*, 27, 132 (1908).

(7) M. L. Bender, *THIS JOURNAL*, 75, 5986 (1953).

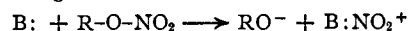
DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

Reactions of Nitrate Esters. III. Evidence for Nitrogen-Oxygen Cleavage in Reductions with Hydrazine and Alkaline Hydrosulfides

BY RAYMOND T. MERROW AND ROBERT W. VAN DOLAH¹

RECEIVED SEPTEMBER 3, 1954

In the reduction of nitrate esters to nitrite ion and the parent alcohols by means of alkaline hydrosulfides² or hydrazine,³ it was suggested that the initial step is a nucleophilic displacement on the nitrate nitrogen atom, *viz.*



(1) Bureau of Mines, Pittsburgh, Pennsylvania.

(2) R. T. Merrow, S. J. Cristol and R. W. Van Dolah, *THIS JOURNAL*, 75, 4259 (1953).

(3) R. T. Merrow and R. W. Van Dolah, *ibid.*, 76, 4522 (1954).

In agreement with this postulate, it has been found that optically active nitrate esters are converted by either hydrazine or ammonium sulfide to optically active alcohols with a high degree of retention of configuration.

Cristol, *et al.*,⁴ demonstrated by hydrogenolysis that (+)-2-octyl nitrate and (+)-2-octanol have the same configuration, and, further, that alkaline hydrolysis of (+)-2-octyl nitrate gave 2-octanol with some retention of configuration, but with considerable racemization. It has been found in this Laboratory that (+)-2-octyl nitrate reacts with hydrazine at room temperature to give (+)-2-octanol having 84% of the activity of the alcohol from which the nitrate was prepared, and that the (-)-nitrate is converted by ammonium polysulfide to (-)-alcohol with 99% of the original activity. The high degree of retention of configuration shows that the nitrogen-oxygen bond is cleaved rather than the alkyl-oxygen bond, although this evidence does not distinguish between the two modes of nucleophilic attack⁵ (*i.e.*, at the alkoxy oxygen or at nitrogen) which would lead to heterolysis of this bond. However, the formal positive charge on the nitrogen atom makes it a more likely site for nucleophilic attack than the oxygen atom.

The reduction of *trans*-1,2-cyclohexanediol dinitrate with hydrazine gave only the *trans*-glycol, while only the *cis*-glycol could be isolated from the ammonium sulfide reduction of the *cis*-dinitrate. These results indicate that, in both types of reduction, O-N cleavage occurs in both nitrate groups.

Experimental

The optically active 2-octanols, resolved by the method of Kenyon,⁵ were converted to the nitrates with mixed acid, according to the procedure of Shriner and Parker.⁶ *cis*- and *trans*-cyclohexanediol dinitrates were prepared by the reaction of the respective glycols in chloroform solution with mixed nitric and sulfuric acids at -5 to -10° .⁷

Optical rotations were measured with a Rudolph high-precision polarimeter, using the pure liquids in 1-dm. tubes, except where noted otherwise. Infrared spectra were run on a Perkin-Elmer model 21 instrument.

Reductions of 2-Octyl Nitrate. A. With Hydrazine.—Two milliliters (1.90 g., 0.011 mole) of (+)-2-octyl nitrate, $[\alpha]_D^{25} +17.51^{\circ}$, prepared from (+)-2-octanol having $[\alpha]_D^{25} +9.63^{\circ}$, was mixed with 5 ml. of 95% hydrazine and just enough ethanol to make the mixture homogeneous. Gas evolution and yellowing of the solution began at once. After standing at room temperature for 6 days, no further gassing was visible. The ethanol was removed by distillation at reduced pressure, and the two layers of the residual liquid were separated. The top layer was dissolved in ether and washed with dilute hydrochloric acid and with water, and the ether solution was dried over sodium sulfate. On evaporation of the ether, there remained 1.20 g. (0.0075 mole) of (+)-2-octanol, $[\alpha]_D^{25} +8.11^{\circ}$. This was characterized by comparison of its infrared absorption spectrum with that of authentic 2-octanol, and with that of the nitrate.

B. With Ammonium Sulfide.—Two grams (0.0114 mole) of (-)-2-octyl nitrate, prepared from (-)-2-octanol having $[\alpha]_D^{25} -8.54^{\circ}$, was treated with 5 ml. of commercial 20% ammonium sulfide solution (containing 5-6% free sulfur) and 10 ml. of ethanol. The mixture became very

red after four hours, and then became lighter as sulfur precipitated out. After 3 days the sulfur was filtered and the pale yellow filtrate extracted with ether and the extract dried with sodium sulfate. The ether and ethanol were distilled off, leaving 1.5 g. of a reddish-yellow oil which smelled strongly of 2-octanol. Distillation yielded 0.4 g. (0.003 mole) of (-)-2-octanol. This was made up to 5 ml. with ethanol and placed in a 4-dm. polarimeter tube. This gave $\alpha_D^{25} -2.70^{\circ}$, $[\alpha]_D^{25} -8.44^{\circ}$. The product obtained from the *dl*-nitrate in similar, larger-scale runs was characterized as 2-octanol by its infrared spectrum.

Reductions of Cyclohexanediol Dinitrates. A. *trans*-Dinitrate with Hydrazine.—Two and one-half grams (0.012 mole) of *trans*-1,2-cyclohexanediol dinitrate and 5 ml. of 95% hydrazine were allowed to stand together at room temperature with occasional shaking. After two days, when the mixture was homogeneous and no more gas evolution was observed, the mixture was distilled until all of the hydrazine was removed. The residual yellow oil was crystallized to an oily solid by freezing with Dry Ice. When sucked dry on a sintered glass disk, it weighed 0.5 g. and melted at $93-94^{\circ}$. A mixed m.p. with authentic *trans*-1,2-cyclohexanediol, m.p. $103-104^{\circ}$, was not depressed but a mixed m.p. with the *cis* isomer showed considerable depression. Recrystallization of the crude product from ethyl acetate gave 0.4 g. (0.0035 mole) of pure *trans*-1,2-cyclohexanediol, m.p. and mixed m.p., $103-104^{\circ}$. No *cis*-glycol was found.

B. *cis*-Dinitrate with Ammonium Sulfide.—Two and one-half grams (0.012 mole) of *cis*-1,2-cyclohexanediol dinitrate, 10 ml. of ammonium sulfide solution and 10 ml. of ethanol were allowed to stand for 24 hours. The precipitated sulfur was filtered, and the ethanol was removed from the filtrate by distillation. The remaining aqueous solution was extracted with five 10-ml. portions of chloroform. On evaporation of the solvent, the extract yielded a mass of yellowish-white crystals from which, by recrystallization from carbon tetrachloride, was obtained 0.6 g. (0.005 mole) of *cis*-1,2-cyclohexanediol, m.p. $93-94^{\circ}$. A mixed m.p. with the authentic *cis*-glycol, m.p. 97° , was $95-96^{\circ}$, and with authentic *trans*-glycol was $76-77^{\circ}$. There was also obtained a trace of solid melting at $84-85^{\circ}$ which was apparently mainly *cis*-glycol, as a mixed m.p. with *trans*-glycol was depressed but a mixed m.p. with pure *cis* was not depressed.

The infrared spectrum of the product melting at $93-94^{\circ}$ was identical with that of the authentic *cis* glycol.

Acknowledgment.—The authors are indebted to Mr. Boris Franzus for the preparation of the *cis*- and *trans*-cyclohexanediol dinitrates, to Mr. Alexander Shadan for a sample of (+)-2-octanol, to Miss Joan Reinhart and Mr. R. H. Pierson for running the infrared spectra, and to Dr. R. H. Boschan for an authentic sample of *cis*-1,2-cyclohexanediol.

ORGANIC CHEMISTRY BRANCH, CHEM. DIV.
RESEARCH DEPT.
U. S. NAVAL ORDNANCE TEST STATION, INYOKERN
CHINA LAKE, CALIFORNIA

Reactions of Vanillin and Its Derived Compounds. XXIV.¹ Some Ethers of Vanillin and Vanillic Acid²

BY IRWIN A. PEARL

RECEIVED AUGUST 30, 1954

In connection with other studies in our laboratories a number of aliphatic ethers of vanillin and vanillic acid were required. A literature search indicated that many of the ethers of vanillin had been prepared, but only the methyl, ethyl and *n*-propyl

(1) For paper XXIII of this series, see *THIS JOURNAL*, **76**, 3635 (1954).

(2) The results reported here are from a research program at this Institute, sponsored by the Sulphite Pulp Manufacturers' Research League; acknowledgment is made for their permission to publish these results.

(4) S. J. Cristol, A. Shadan and B. Franzus, Abstracts of Papers, 125th National Meeting of the American Chemical Society, Kansas City, Mo., Spring, 1954, p. 20N.

(5) J. Kenyon in H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 418.

(6) R. L. Shriner and E. A. Parker, *THIS JOURNAL*, **55**, 766 (1933).

(7) S. J. Cristol, private communication.