[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

ADDITION OF IODINE (I) 3,5-DINITROBENZOATE TO SIMPLE OLEFINS

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Various investigators have studied the reactions of halogen carboxylates of the type $\mathrm{HalO}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R}$ with a small number of olefins.[1] By the reaction of equimolecular quantities of iodine and the silver salts of the proper carboxylic acids with a solution of cyclohexene in an organic solvent, Birckenbach and co-workers (1) succeeded in isolating the acetate, the benzoate, and the phthalate of 2-iodo-1-cyclohexanol. By the same type of reaction, Bockemüller and Hoffmann (2) claimed preparation of the acetate of 2,3-dichloro-1-propanol from allyl chloride, chlorine, and silver acetate, and Uschakow and Tchistow (3) obtained the benzoates of 2-chloro-1-cyclohexanol and 2-bromo-1-cyclohexanol from cyclohexene and the appropriate halogen and silver salt.

Prévost (4) has shown that when equivalent quantities of iodine and silver salt react with an olefin in benzene, the product obtained is the dicarboxylate rather than the iodinated ester. He postulated (5, 6) that the iodinated ester was formed as an intermediate which reacted immediately with excess silver salt to form the diester. He reported (5, 7), however, that when the reaction was carried out in carbon tetrachloride, the second step took place only slowly and the halogen ester could be isolated.

None of the above investigators made a systematic study of the general applicability of these reactions to the simple aliphatic olefins, nor were they concerned with the possible use of the products as derivatives for the identification of olefins. Because of the fact that no completely satisfactory derivative method for olefin identification existed at the time this work was begun,[2] we undertook a study of the reaction of equimolecular quantities of iodine and the silver salt of 3,5-dinitrobenzoic acid with olefins in the hope of obtaining crystalline derivatives.

We have found that the reaction of different olefins, containing from two to seven carbon atoms, with iodine and the silver salt of 3,5-dinitrobenzoic acid in ether proceeds according to the general equation,

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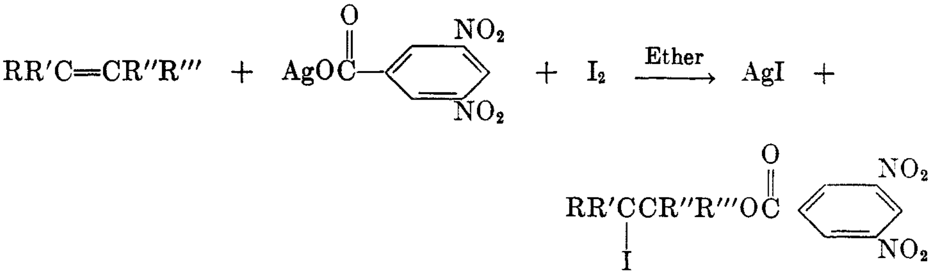
[1] For a summary of the reactions of the halogens with silver salts of carboxylic acids, see Kleinberg, *Chem. Revs.*, **40**, 381 (1947).

[2] Lester, Rodgers, and Reid, *J. Am. Chem. Soc.*, **66**, 1674 (1944), prepared solid sulfide derivatives by the addition of 4-mercaptobiphenyl to 1-olefins from 1-hexene through 1-heptadecene, but the close proximity of melting points of the derivatives rendered this series of little value for the identification of olefins. After our work was in progress, Kharasch and Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949), reported the preparation of solid derivatives which in general afford a ready means for the identification of olefins, by the addition of 2,4-dinitrobenzenesulfenyl chloride to olefins.



and gives white, nicely crystalline iodoalkyl esters of 3,5-dinitrobenzoic acid. The melting points which are recorded in Table I are, with few exceptions, sufficiently different to permit the use of these solids in the identification of the common low-molecular weight olefins. In all cases where unsymmetrical olefins were used there was no evidence of isomer formation which would result if the iodine (I) 3,5-dinitrobenzoate added to the unsymmetrical double bond in both of the two possible directions. Two or three recrystallizations were required to bring the melting points to the values indicated, but in every case until the maximum melting point was reached, analysis revealed the presence of a non-isomeric impurity.

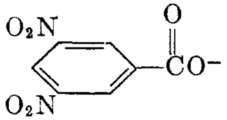
TABLE I[a]

SOLID DERIVATIVES OF SIMPLE OLEFINS

IODOALKYL ESTERS OF 3,5-DINITROBENZOIC ACID

OLEFIN	M.P., °C., OF DERIVATIVE	IODINE	
		Calc'd	Found
Ethylene	91.2–92.0	34.7	34.5
Propylene	82.2–83.0	33.4	33.3
1-Butene	69.0–70.4	32.2	32.1
cis-2-Butene	96.4–97.6	32.2	31.9
trans-2-Butene	91.8–92.8	32.2	32.1
Isobutylene	108.4–109.2	32.2	32.1
1-Pentene	76.2–77.0	31.1	31.1
2-Pentene	124.5–125.5	31.1	31.0
1-Hexene	49.4–50.4	30.1	30.1
1-Heptene	52.0–53.0	29.1	29.2
Cyclopentene	111.0–111.8	31.3	31.0
Cyclohexene	158.4–159.0	30.3	30.1

[a] All melting points are corrected.

The direction of the addition to unsymmetrical double bonds is a question of considerable theoretical interest. If the reagent does indeed add as I^+ and  ions, then it would be expected that the initial attack would be by I^+ ion to form a cyclic iodonium ion. The reaction would be consummated by attack of the 3,5-dinitrobenzoate ion at either of the original olefinic carbons, the nature of the final product being determined by the point of attack. It is significant in this connection that no change in product could be effected by carrying out the reaction in the presence of peroxides.

In a study of the nature of the products formed in the case of unsymmetrical olefins, the addition product of iodine (I) 3,5-dinitrobenzoate to 1-butene was chosen as a representative compound of the group. Elucidation of its structure was greatly complicated by the facts that (a) any reaction in which the halogen is substituted is subject to the possibility of the neighboring group effect; (b) hydrolysis of the iodoesters is unsuccessful because of the extreme lability of the iodine in the corresponding iodohydrins in either acid or basic solution; (c) the corresponding iodohydrins, and in fact the analogous chloro- and bromo-hydrins, are not reliably characterized in the literature; and (d) the iodohydrins are extremely unstable, a fact which renders the separation of a mixture of the isomers by fractional distillation and structural proof by oxidation difficult.

TABLE II[a]

HALOHYDRINS OF 1-BUTENE

HALOHYDRIN	n_D^{20}	B.P., °C.	MM.	% YIELD BASED ON EPOXIDE	M.P., °C. OF 3,5-DINITROBENZOATE	3,5-DINITROBENZOATE HALOGEN	
						Calc'd	Found
1-Chloro-2-butanol	1.4425[b]	50–51	19	35	99.8–100.2	11.7	11.6
2-Chloro-1-butanol	1.4438	52–53	19	29	76.2–77.0[c]	11.7	11.6
1-Bromo-2-butanol	1.4765	61–63	15	38	90.0–90.8	23.0	22.8
2-Bromo-1-butanol	1.4802	65–66	15	21	68.2–69.4	23.0	23.0
1-Iodo-2-butanol	1.5361	29–30	0.6	46	69.0–70.4	32.2	32.1
2-Iodo-1-butanol	1.5396	30–31	0.6	11	74.6–76.8	32.2	31.7

[a] All melting points are corrected.

[b] Helferich and Speidel, *Ber.*, **54**, 2634 (1921) reported n_D^{20} 1.4353.

[c] Cristol and Eilar, *J. Am. Chem. Soc.*, **72**, 4353 (1950), reported 74–76°.

After considerable investigation it became apparent that the problem could best be approached by a study of the three isomeric pairs of chloro-, bromo-, and iodo-hydrins. These compounds were obtained by reaction of 1,2-epoxybutane with the appropriate hydrohalic acid, and separation of the resulting pair of isomers was in each case effected by fractional distillation. Data on these six halobutanols are shown in Table II.

The lower-boiling of the two isomeric chlorobutanols obtained from 1,2-epoxybutane by treatment with hydrochloric acid was assigned the structure 1-chloro-2-butanol on the basis of the following: (a) it was oxidized by acid dichromate to 1-chloro-2-butanone; (b) it was identical with the aluminum isopropoxide reduction product of an authentic sample of 1-chloro-2-butanone; (c) it reacted less rapidly than did its isomer with 3,5-dinitrobenzoyl chloride (8). The high-boiling isomer (a) was oxidized to α-chloro-*n*-butyric acid with nitric acid and (b) was proved to be identical with the chlorohydrin produced by reduction of α-chloro-

n-butyryl chloride with lithium aluminum hydride. It was therefore assigned the structure 2-chloro-1-butanol.

The lower-boiling of the two bromohydrins was also characterized as the secondary alcohol, 1-bromo-2-butanol, by dichromate oxidation to 1-bromo-2-butanone and by the fact it was the slower reacting of the two isomers toward 3,5-dinitrobenzoyl chloride. The higher-boiling bromohydrin was assigned the structure 2-bromo-1-butanol on the basis of its oxidation to α-bromo-*n*-butyric acid with nitric acid. It is of interest to note that in attempted proof of structure by dehalogenation by catalytic hydrogenation in basic solution according to the method of Levene, Walti, and Haller (9), both isomers gave 2-butanol as the only product isolated. The fact that this reaction probably proceeds through an epoxide intermediate vitiates its use for structural proof.

Because of the extreme instability of 1-iodo-2-butanol and 2-iodo-1-butanol, a mixture of the two could not be subjected to long fractional distillation without extensive decomposition. The mixture was separated into two relatively pure fractions which gave different pure 3,5-dinitrobenzoates with 3,5-dinitrobenzoyl chloride. The predominant compound in the lower-boiling fraction was assigned the structure 1-iodo-2-butanol on the basis of its oxidation to 1-iodo-2-butanone, as well as its less rapid rate of reaction with 3,5-dinitrobenzoyl chloride. The halohydrin in the higher-boiling fraction was accordingly assigned the structure 2-iodo-1-butanol. Thus, in each of the three pairs of halohydrins, the primary alcohol is the higher-boiling isomer.

It is also noteworthy that the percentage of primary alcohol in the total mixture of isomers obtained in the reaction with 1,2-epoxybutane decreased in the order of increasing strength of the acid, HCl (45%) > HBr (36%) > HI (20%). This would be the order expected if the point of attack of the halide ion on the oxonium ion formed by the addition of a proton to the epoxide is influenced by steric factors.

The Lucas test (10) as applied on the various pairs of halohydrins was inconclusive. The chlorohydrins did not form a second layer, whereas each of the bromohydrins slowly formed a cloudy solution, and each of the iodohydrins gave an almost instantaneous positive test. The similarity of the behavior of the two halohydrins in each isomeric pair may be attributed to the operation of the neighboring group effect, which, for these particular reactions, is now under investigation in our laboratories.

Pure 3,5-dinitrobenzoates were prepared for all six halohydrins and the melting point of each was found to be significantly different from that of its isomer (see Table II). Moreover, the 3,5-dinitrobenzoate prepared from each of the secondary halohydrins was identical with that prepared by the reaction of the corresponding halogen and silver 3,5-dinitrobenzoate on 1-butene. This would be expected if the addition involved cationic halogen and 3,5-dinitrobenzoate anion. By anology it may be assumed that the structures of all the iodo-3,5-dinitrobenzoates formed from unsymmetrical olefins listed in Table I are those in which the halogen appears on the less highly substituted carbon atom.

EXPERIMENTAL

Preparation of olefins. Anesthetic grade *ethylene*, purchased from the Puritan Compressed Gas Corporation, was passed through a calcium chloride drying-tube before use. *Propylene* and *isobutylene* were prepared by the action of sulfuric acid on isopropyl and *tert*-butyl alcohol, respectively, and were dried by passage through a calcium chloride tower.

1-Hexene and *cyclopentene* were prepared by dehydration of 1-hexanol and cyclopentanol, respectively, over activated alumina at 350°. The crude products were fractionated, the 1-hexene fraction boiling at 61.5–62° at 734 mm. and the cyclopentene at 44.6–45° at 734 mm. being used.

The *1-butene*, *cis-* and *trans-2-butene*, and *1-pentene* were research grade products of the Phillips Petroleum Company. The *2-pentene* was the technical grade product of the Phillips Petroleum Company which consists of a mixture of the *cis-* and *trans*-isomers.

Eastman's *cyclohexene* was purified by distillation, the fraction boiling at 82.5–83.0° at 733 mm. being used. The *1-heptene*, purchased from the Connecticut Rubber Company, was used without further purification.

Silver salt of 3,5-dinitrobenzoic acid. Exactly 53.03 g. (0.25 mole) of 3,5-dinitrobenzoic acid was added portionwise to a hot solution of 16.7 ml. of concentrated ammonium hydroxide (15 *M*) in 400 ml. of water until all the solid had dissolved and the solution tested acid to litmus. The solution containing the ammonium salt was filtered hot and then permitted to cool to 50°. To this 42.4 g. (0.25 mole) of silver nitrate in 250 ml. of water was added and the entire solution was diluted to approximately 2 liters. The precipitated salt was filtered, washed several times with water, and dried at 45°. To facilitate drying, the salt may be washed with 95% alcohol, but when this is done the dry silver salt appears to take on a darker color, which, however, has no apparent effect on subsequent reactions. The average yield was 74 g. or 92.6%.

Preparation of β-iodoalkyl 3,5-dinitrobenzoates from olefins. In a 50-ml. Erlenmeyer flask 2.6 g. (0.008 mole) of silver 3,5-dinitrobenzoate was shaken with 24 ml. of absolute ether. About 0.6 g. of olefin was mixed with the slurry and 2 g. of solid iodine was added in small amounts. After each addition, the mixture was shaken until the color of the iodine was discharged; addition was continued until a faint color of iodine persisted after several minutes of shaking.

The reaction mixture was filtered from the precipitated silver iodide, which was then extracted several times with small portions of ether. The combined ethereal solution was washed with 10% sodium carbonate solution to which a small amount of sodium thiosulfate had been added for removal of free iodine. The solution was then washed, first with water and then with saturated sodium chloride solution, and finally dried over sodium sulfate in the dark. The ether was then removed under reduced pressure at ice temperature and the residue purified by immediate recrystallization from high-boiling Skellysolve.

The derivative obtained by reaction of 1-butene with iodine and silver 3,5-dinitrobenzoate proved identical with the 3,5-dinitrobenzoate formed by reaction of 3,5-dinitrobenzoyl chloride with the lower-boiling of the two isomeric iodobutanols resulting from the treatment of 1,2-epoxybutane with hydriodic acid (see Tables I and II). This lower-boiling iodobutanol was later shown to be 1-iodo-2-butanol.

Preparation of the 3,5-dinitrobenzoates of the chloro- and bromo-butanols from 1-butene. To a mixture of 75 ml. of dry chloroform and 9.5 g. (0.03 mole) of silver 3,5-dinitrobenzoate cooled in an ice-salt mixture, a solution of 0.03 mole of the appropriate halogen dissolved in 20 ml. of dry chloroform was added over a 10–15 minute period with shaking. 1-Butene was then passed into the solution for 15 minutes with continuous shaking. The solid silver halide which precipitated was removed and the filtrate washed with six 25-ml. portions of 5% sodium carbonate solution. The chloroform solution was then dried over Drierite, the chloroform removed by distillation, and boiling petroleum ether added to dissolve the ester. The solution was then cooled and the chloro- and bromo-butyl 3,5-dinitrobenzoates removed and purified by recrystallization from petroleum ether.

Each of the two 3,5-dinitrobenzoates did not depress the melting point of the corresponding derivative obtained from the lower-boiling haloalcohol resulting from the reaction of 1,2-epoxybutane with the appropriate hydrohalic acid. These lower-boiling haloalcohols were later proved to be 1-chloro-2-butanol and 1-bromo-2-butanol, respectively (see Table II).

Preparation of halohydrins from 1,2-epoxybutane. To 0.5 mole of the appropriate concentrated hydrohalic acid, cooled to 0°, 36.0 g. (0.5 mole) of 1,2-epoxybutane was added dropwise over the course of 1½–2 hours with continual stirring. Two layers were formed, an upper aqueous layer and a lower layer containing the isomeric halohydrins. The layers were separated, and the upper layer saturated with sodium chloride and extracted with six 20-ml. portions of ether. The ether extracts were combined with the water-insoluble layer and the resulting solution was washed with small portions of 5% sodium carbonate solution until all the acid was removed. The ether solution was dried over Drierite, the ether removed by distillation, and the residue fractionated through a Todd column packed with glass helices. The purity of the various fractions was followed by refractive index measurements taken on each 2 ml. of distillates. The yields and physical constants of the halohydrins are shown in Table II.

Oxidation of 2-halo-1-butanols. Oxidation of the higher-boiling chlorobutanol and bromobutanol with nitric acid by the procedure of Cristol and Eilar (10) gave as the only isolable products α-chloro-n-butyric and α-bromo-n-butyric acid, respectively. The corresponding amides, after purification by vacuum sublimation, melted at 76.2–77.0° [reported 78.4–78.9° (11)] and 106.2–108.2° [reported 108° (12)], with no depression upon admixture with authentic samples.

Attempted oxidation of the same compounds with acid dichromate led to very poor yields of acids, with considerable ester formation; no ketones could be isolated.

Oxidation of 1-halo-2-butanols. Oxidation of the lower-boiling chlorobutanol, bromobutanol, and iodobutanol with acid dichromate by the procedure of Sherrill (13) gave, as the only isolable products, the corresponding ketones in over 50% yield. The melting points of the semicarbazones of 1-chloro-2-butanone, 119.0–120.6°, [reported, 121° (14)], and of 1-bromo-2-butanone, 112.8–114°, were not depressed upon admixture with authentic samples. The authentic sample of 1-bromo-2-butanone was obtained by bromination of 2-butanone according to Favorsky and Issatschenko (15).

1-Iodo-2-butanone, b.p. 42–43°/3 mm., decomposed readily.

Anal. Calc'd for C_4H_8IO: C, 24.3; H, 3.6; I, 64.1.

Found: C, 24.1; H, 3.8; I, 64.0.

Attempted nitric acid oxidation of the lower-boiling chlorobutanone led to products formed by cleavage of the carbon chain; no ketone could be isolated from the reaction mixture.

Preparation of the 3,5-dinitrobenzoates of the halobutanols. A mixture of stoichiometric amounts of the halobutanol and 3,5-dinitrobenzoyl chloride was heated on a steam-bath for 1 hour (ten minutes in the case of the iodobutanols). Ether was then added to dissolve the ester formed and the solution was washed with 5% sodium carbonate solution until removal of 3,5-dinitrobenzoic acid was complete. The ether was removed by distillation and boiling petroleum ether (b.p. 80–90°) was added in a quantity sufficient to dissolve the ester. The hot solution was filtered, then cooled, and crystals of the ester removed. In all the derivatives thus obtained, two or three recrystallizations were required to raise the melting points to the values recorded in Table II.

In every case, the primary alcohol when heated with 3,5-dinitrobenzoyl chloride gave almost instantaneous and copious evolution of hydrogen chloride. The secondary alcohols reacted with noticeably less vigor.

The m.p. of the 3,5-dinitrobenzoate of the lower-boiling chlorobutanol was not depressed by the corresponding derivative of an authentic sample of 1-chloro-2-butanol, prepared by aluminum isopropoxide reduction of 1-chloro-2-butanone by the general method of Winstein, *et al.* (16). On the other hand, the 3,5-dinitrobenzoate of the higher-boiling chlorobutanol proved identical with that of an authentic sample of 2-chloro-1-butanol prepared by reduction of α-chloro-*n*-butyric acid with lithium aluminum hydride (17).

Catalytic hydrogenation of the bromobutanols. Catalytic hydrogenation of 1-bromo-2-butanol and of 2-bromo-1-butanol in a 10% solution of sodium hydroxide with 5% palladium on charcoal (9) in each case gave 2-butanol as the only product. The 3,5-dinitrobenzoate, m.p., 74.8–75.4°, did not depress the m.p. of an authentic sample.

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SUMMARY

1. A series of solid iodoalkylesters of 3,5-dinitrobenzoic acid has been prepared and the melting points of the compounds are reported. The melting points of these compounds prepared from the common lower molecular weight olefins are, with few exceptions, sufficiently different to permit the use of these solids as derivatives.

2. Three pairs of isomeric 1-halo-2-butanols and 2-halo-1-butanols have been prepared by the reaction of hydrochloric, hydrobromic, and hydriodic acids respectively, on 1,2-epoxybutane. These isomers were separated by fractional distillation and assigned structures on the basis of oxidation to known ketones or acids, relative rates of reaction with 3,5-dinitrobenzoyl chloride, and in some cases comparison with known samples.

3. Reaction of chlorine, bromine, and iodine, respectively, and silver 3,5-dinitrobenzoate on 1-butene gave a halogenated butyl 3,5-dinitrobenzoate identical, in every case, with the ester obtained by treatment of the appropriate 1-halo-2-butanol with 3,5-dinitrobenzoyl chloride.

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