Monohydroxylation of Unsaturated Oils: III. Use of Halogen Intermediates[1]

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Abstract

Hydroxylation of safflower and linseed oils by routes involving halogen compounds is described. A product containing 20.5% Br was obtained by treatment of safflower oil in CCl_4 solution with N-bromosuccinimide (NBS) in presence of benzoyl peroxide and UV illumination. Bromine was totally removed using Ag_2O in 50% dioxan; the resulting hydroxyl value (HV) was only 100, against an expected HV of 180, perhaps because of dehydration and ether formation. Using other silver salts, bromine replacement with hydroxyl was always incomplete. Such residual bromine was totally replaced by hydrogen, without altering other characteristics, by treatment of the product with zinc amalgam in acetic acid. Linseed oil by similar NBS bromination (Br 22.2%) and Ag_2O treatment gave a product with Br 2.9%, HV 74, conj. diene 15% and conj. triene 4%. Halogen-replacement difficulties also attended the hydrobromination of these oils at the double bonds, followed by hydroxylation. Addition of hypochlorous or hypobromous acid to safflower oil, followed by total replacement of halogen with hydrogen using zinc amalgam, yielded products of HV 75 and 83 respectively. The degree of hydroxylation was only half of that expected from the loss of unsaturation.

Introduction

We have previously studied various means of introducing hydroxyl functions at or near the unsaturated centers of safflower and linseed oils. Three more routes involving halogen intermediates are now described. In the first of these, the oils were brominated using N-bromosuccinimide (NBS), and attempts made to replace the bromine with hydroxyl particularly by the use of silver salts. Several workers have dealt with the first of these reactions, notably Nanavati et al. (1), who were interested in creating conjugation by subsequent dehydrobromination, perhaps accompanied by debromination. Dulog et al. (2) showed that in the reaction of NBS with methyl linoleate, the allylic bromination product easily lost HBr to form triene. The liberated HBr reacted with NBS forming elemental bromine which easily added to double bonds forming dibromides. Such reactions are suppressed but never fully eliminated by using excess NBS, carrying out the reaction at low temperatures and activating it with peroxides or ultraviolet illumination (3–5).

Replacement of bromine with hydroxyl following NBS treatment has been effected by several means. Silver salts have been widely used. Silver acetate in acetic acid (6–8), silver oxide (9) and silver nitrate in methanol-nitric acid (2) are some of these. For other hydroxylations, silver nitrate (10,11) and silver nitrate in wet and dry acetonitrile (12,13) have been employed. Autoclaving with sodium bicarbonate was used by Naudet et al. (14) to obtain hydroxy acids from brominated esters.

The second route involves addition of HBr to double bonds (15) and subsequent replacement of halogen with hydroxyl. In the third route, a hypohalous acid adds to the double bond (16–18). The hydroxy group that enters is left alone, and hydrogen must replace the halogen. Several procedures for such replacement involve zinc (19,20) or zinc amalgam (21). These reactions were examined for their application to commercial refined safflower and linseed oils.

NBS Treatment and Hydroxylation

Bromination of Oils With NBS

In 300 ml of carbon tetrachloride, 30 g of safflower oil, 0.8 g of benzoyl peroxide and 25 g of NBS were dissolved, and the solution refluxed for 1 hr. Succinimide was removed by filtration. The recovered fatty product contained Br 17.8%. Illumination of the reaction vessel with UV light gave a product with Br 20.5% (calculated for methyl linoleate monobromide, 21.4%). Similar treatment of 20 g of linseed oil with 30 g of NBS under UV illumination yielded a product with Br 22.2%.

Replacement of Bromine With Hydroxyl

A large number of procedures were examined for the replacement of Br with hydroxyl in both these brominated oils. Results are summarized in Table I.

Conclusions

Ultraviolet illumination raised the extent of benzoyl peroxide-catalyzed bromination of fatty oils using NBS. Though primarily a free radical reaction (22), simultaneous ionic mechanisms are not ruled out, and side reactions in particular are of this nature (2). Hence the higher degrees of bromination under combined UV illumination and benzoyl peroxide catalysis are probably a result of nonallylic bromination.

The difficulty of bromine replacement with hydroxyl shown in the results in Table I confirms nonallylic bromination. Indeed Dulog et al. (2) have used the replacement reaction with silver nitrate to determine the extent of allylic bromination. Treatment of 5 g of brominated safflower oil in 15 g of dioxan-water (1:1) with 6.5 g of well-washed, freshly-precipitated silver oxide (23) yielded a product free from halogen, low in free acidity, but with a HV of 100 against an expected value of ca. 180 (Expt. 11). The IR spectrum showed a distinct peak at 1100 cm^{-1} attributed to dialkyl ether (2). A separate experiment in which the product was examined at intervals showed that such ether formation occurred from the very start of the replacement reaction.

Other silver reagents give only partial replacement. Frequently the products have 5–8% of residual Br and HV 80–95 (Expts. 1,2,4–8). In products of HV 80 and 82 and residual Br content 8.0%, obtained following treatment with silver acetate in acetic acid

TABLE I
Replacement of Bromine With Hydroxyl in Oils Brominated With NBS

Expt. No.	Reagent	Medium and conditions	Product characteristics				
			Residual Br %	HV	AV	Conj. diene %	Conj. triene %
Brominated safflower oil (% Br 20.5)							
1.	Silver acetate	Acetic acid, 5 hr, RT	8.0	80	18	17.5	2.0
2.	–do–	–do– , 2 hr, 60 C	8.0	82	20	16.0	3.0
3.	–do–	Acetic acid-water (120:20), 8 hr, reflux	1.2	89	24	19.0	1.5
4.	Silver nitrate	Chloroform, 3 hr, RT	7.0	80	10	17.8	3.5
5.	–do–	92% ethanol, 5 hr, 60 C	5.0	95	19	18.5	2.0
6.	–do–	–do–, 5 hr, RT	6.5	90	10	18.0	2.0
7.	–do–	–do–, 10 hr, RT	5.0	89	9.8	17.5	2.5
8.	–do–	Methanol + HNO_3, 5 hr, 60 C	4.0	89	15	17.0	2.0
8a.	–do–	–do–, 1 hr, 90 C	1.0	88	10	18.2	2.4
9.	Silver oxide	Water, 4 hr, reflux	Formed a film				
10.	–do–	Ether-water (100:10), 5 hr, RT	7.0	43	10	17.0	4.0
11.	–do–	Dioxan-water (50:50), 5 hr, RT	Nil	100	8	18.0	Nil
12.	–do–	Acetonitrile, 3 hr, 60 C	16	46	10	18.0	Nil
13.	–do–	NaI-acetone, then as in No. 10	3.2[a]	20	9	32	45
14.	Silver nitrate	92% ethanol, 5 hr, RT	2.8	98	15	19.9	2.8
14a.	–do–	Above product treated with Zn-amalgam, acetic acid	Nil	95	28	19.0	2.0
15.	–do–	92% ethanol, 6 hr, 60 C	2.5	96	16	Not determined	
16.	Mercuric chloride	Acetone, 5 hr, reflux	19.5	Nil	Nil	17.0	Nil
17.	Sodium bicarbonate	Some water, tetrahydrofuran, 3 hr, 130 C, autoclave	8.7	61	29	28.2	11.2
18.	–do–	–do–, 4 hr, reflux	17.0	27	20	18.0	4.8
19.	–do–	–do–, 100 C, autoclave at 55 atm. pressure for 1 hr	7.8	63	38	26.2	14.5[b]
19a.	–do–	Part of the above product stirred with silver oxide, 50% dioxan, 5 hr, RT	Nil	94	30	23.0	6.2
19b.	–do–	Remainder of the product refluxed with Zn-amalgam-acetic acid, 6 hr	Nil	64	38	27.2	7.2
Brominated linseed oil (% Br 22.2)							
20.	Silver nitrate	Methanol-nitric acid, 45 mins, 80 C	8.7	60.5	3.9	14.8	3.8
21.	–do–	92% ethanol, 5 hr, RT	9.0	62.5	5.2	13.9	4.0
22.	Silver oxide	50% aqueous dioxan, 5 hr, RT	2.9	74.4	6.2	14.6	4.0
23.	Silver acetate	Acetic acid-water (75:10), 5 hr, RT	11.4	67.9	19.9	13.0	3.2

[a] % Iodine.
[b] Also 5.4% conj. tetraene.

(Expts. 1 and 2), lost halogen has been replaced almost quantitatively by hydroxyl.

In Experiment 13, 5 g of the brominated product was treated with 7.5 g of sodium iodide in 75 ml of acetone and refluxed for 0.5 hr on a water bath to replace bromine with iodine. The precipitated sodium bromide was removed by filtration and the fatty product freed of solvent (24). The product was treated in ether medium with Ag_2O to yield a product free from halogen with a HV of 20, and 32% diene and 45% triene conjugation calculated from the UV absorptions at 232 μ and 268 μ. Dehydrohalogenation reactions predominate when the iodine-containing product is treated with Ag_2O.

Treatment of 5 g of the brominated oil with 1.3 g of sodium bicarbonate dissolved in 3.9 g water and 25 ml of tetrahydrofuran in an autoclave, as described by Naudet et al. (14), gave incomplete halogen replacement and a rather high acid value. The low HV and high degree of diene conjugation (26.2–28.2%) developed pointed to dehydration (Expts. 17 and 19). When simple refluxing with bicarbonate was tried, there was little halogen replacement (Expt. 18).

Similar results were obtained when brominated linseed oil was treated with silver reagents. Silver oxide treatment gave the best product (Expt. 22), with residual Br 2.9%, HV 74 and diene and triene conjugation of 14.6% and 4.0%.

Hydrohalogenation and Halogen Replacement

Hydrobromination

Safflower oil (5 g) was dissolved in 200 ml of dry benzene and illuminated with a mercury arc lamp. Dry hydrogen bromide gas, prepared by adding bromine to tetralin (25), was bubbled into the solution for 2 hr (15) using external cooling to keep the system at ambient temperature. The solution was washed with water until the washings were neutral to litmus, dried and solvent removed to give a product with an iodine value of 35.0 and Br 17.5%.

Bromine Replacement With Hydroxyl

Three silver reagents were employed for replacement. Analysis of the products gave the following results: silver acetate in acetic acid at room temperature, Br 8–9%, HV 48–54; silver nitrate in methanol containing nitric acid, Br 4.8%, HV 45; and silver oxide in 50% aqueous dioxan, Br 2.5%, HV 40.

Conclusions

Replacement of halogen with hydroxyl using three silver salts is incomplete, as was also generally noted in the NBS route.

Halohydrin Formation and Halogen Replacement

Halohydrin From Safflower Oil

To 10 g of safflower oil dissolved in 10 g of ether, 50 ml of 1.08 M hypobromous acid solution (16) was added at 0 C with stirring for 2 hr. The crude bromohydrin was isolated with ether (% Br 17.3, IV 52.0, HV 83, AV 2.9). Similar addition of 110 ml of 1.84 M hypochlorous acid (26) to 10 g of safflower oil furnished the crude chlorohydrin (% Cl 10.8, IV 58.5, HV 75, AV 2.5).

Replacement of Halogen With Hydrogen

The halohydrins (4 g) were treated with 7 g of zinc amalgam in 75 ml of refluxing glacial acetic acid for 5 hr, and the products isolated by ether extraction. Both halohydrins yielded products free of halogen. The product derived from the bromohydrin had AV 9, HV 82 and that from the chlorohydrin had AV 10, HV 74.

Conclusions

While the replacement of halogen with hydrogen is complete, the initial addition of hypohalous acid to the unsaturated oils is unsatisfactory. A loss of one unit of IV should theoretically lead to an increase of 2 HV units on formation of a halohydrin. Only half this HV for the IV lost has been attained even in the chlorohydrin, and this is the better of the two halohydrins in this respect. Further, these reactions expend unsaturation in creating hydroxyl, in contrast to other routes such as autoxidation (27), in which the occurrence of allylic reactions lead to retention of most of the total unsaturation while introducing hydroxyl groups.

ACKNOWLEDGMENT

Financed in part by PL-480 funds under grant FG-In-153 of the ARS U.S.D.A.

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[Received January 31, 1969]