786

Addition of Formic Acid to Olefinic Compounds. I. Monoölefinic Compounds[2]

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Formic acid at its boiling point at atmospheric pressure adds readily to the double bonds of oleic, elaidic and 10-hendecenoic (undecylenic) acids, methyl oleate, oleyl alcohol, cyclohexene, 1-hexene and the unreacted olefinic material separated from the hydrolyzed reaction product of oleic acid with formic acid, to yield the corresponding formate esters which are readily hydrolyzed. Oleic and elaidic acids and methyl oleate are readily converted in good yields to monohydroxystearic acids; oleyl alcohol yields dihydroxyoctadecanes; 1-hexene yields a mixture of 2-hexanol ($^2/_3$) and 3-hexanol ($^1/_3$); and 10-hendecenoic acid yields monohydroxyhendecanoic acids (isolated as methyl esters). Castor oil, methyl ricinoleate and crotyl alcohol do not add formic acid to the double bond. In the absence of catalysts, approximately 24 hours are required for 80% addition of anhydrous formic acid; perchloric acid in small amounts (0.5–2% by weight of olefinic compound) reduces the reaction time to 5 to 15 minutes. Sulfuric acid is a slightly less efficient catalyst when anhydrous formic acid is used but the efficiency of these catalysts is reversed with 90% formic acid. Boron fluoride–acetic acid complex (1:2) is also an efficient catalyst. Acetic acid, catalyzed by perchloric acid, also adds to the double bond but at a lower rate and less completely than formic acid.

This paper describes the uncatalyzed and catalyzed addition of 90–100% formic acid to certain monoölefinic compounds, namely, oleic, elaidic and 10-hendecenoic (undecylenic) acids, methyl oleate, oleyl alcohol, cyclohexene, 1-hexene, and the unreacted olefinic material (approximately 20%) separated from the hydrolyzed reaction product of oleic acid with formic acid. The attempted addition of formic acid to methyl ricinoleate (methyl 12-hydroxy-*cis*-9-octadecenoate), castor oil (which consists predominantly of glycerides of ricinoleic acid) and crotyl alcohol is also reported.

The addition of formic acid to olefinic compounds is, generally, a homogeneous and easily controlled reaction, excess formic acid is readily recovered by vacuum distillation, and hydrolysis of the intermediate formate esters is not difficult. Furthermore, in the hydration of oleic acid, the melting point of the once crystallized monohydroxystearic acid is relatively high and sharp (*ca.* 75°), suggesting that a complicated mixture of isomeric hydroxy acids is not obtained and that the 9- and 10-isomers predominate. Pure 10-hydroxystearic acid, m.p. 81°, readily can be isolated from the crude monohydroxystearic acids obtained from oleic acid by formic acid addition and hydrolysis, whereas its isolation from the monohydroxystearic acid mixture obtained from oleic acid by sulfation and hydrolysis is tedious and poor yields are obtained.

In most of the work reported in this paper, the 99–100% grade of formic acid was employed because the reaction mixtures were usually homogeneous and the reactions were complete almost instantaneously regardless of the size of the experiment. As shown in the experimental part under the hydration of oleic acid, however, the readily available and inexpensive 90% commercial grade of formic acid worked almost as well, with minor modifications in the reaction procedure. In this case the reaction mixture was heterogeneous throughout the entire reaction period and in reactions about ten times the size reported, reaction times had to be increased significantly. It is noteworthy that even when the anhydrous grade of formic acid was employed in the addition reactions, the acid recovered was about 90% presumably because of the accumulation of water during the decomposition of formic acid to carbon monoxide and water.[3,4] The rate of decomposition of formic acid at its boiling point in the presence or absence of strong acids is high when its water content is 3% or less, but its decomposition is negligible at an initial water content of about 10% during the relatively short reaction periods required.

The addition of acetic acid to the double bond of oleic acid in the absence of catalysts is negligible at its boiling point. With perchloric acid as catalyst, maximum addition to the double bond is only about 40% in a reaction time of 15 min. or one hour, whereas with formic acid 80% addition is usually obtained. Maximum yields of once crystallized monohydroxystearic acids from the hydrolyzed acetic acid–oleic acid product are only 30%. When sulfuric acid is employed as the catalyst instead of perchloric acid, only poor yields of monohydroxystearic acids can be obtained after hydrolysis even though the crude reaction products have low iodine numbers. Undesirable side re-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Service, United States Department of Agriculture.

(2) Presented at the Fall Meeting of the American Chemical Society, Atlantic City, New Jersey, September 16, 1952.

(3) H. N. Barham and L. W. Clark, This Journal, 73, 4638 (1951).

(4) E. R. Schierz, *ibid.*, 45, 447 (1923).

actions are obviously occurring. In the addition of formic acid to oleic acid, however, side reactions are negligible as shown by the fact that the original oleic acid can be entirely accounted for either as unconverted olefinic material or monohydroxystearic acids, and this unconverted olefinic material can also be converted in fair yield to monohydroxystearic acids.

Formic acid also adds readily to the double bond of elaidic acid, *trans*-9-octadecenoic acid, giving a 75% conversion to monohydroxystearic acids and a 65% yield after crystallization. Similar results are obtained with methyl oleate and oleyl alcohol, the hydrolyzed products consisting of monohydroxystearic acids and dihydroxyoctadecanes, respectively.

The filtrates obtained in the recrystallization of the crude monohydroxystearic acids prepared from oleic or elaidic acid have iodine numbers of about 60. The unsaturated components of these filtrates consist of about $^2/_3$ *trans*-olefinic acids and $^1/_3$ *cis*. These add formic acid to the extent of about 75% and a 50% yield of once crystallized monohydroxystearic acids can be obtained. The over-all yield, therefore, of purified monohydroxystearic acids from either oleic or elaidic acid is about 85% in two passes; the over-all conversion is over 95%.

Formic acid adds readily to cyclohexene and 1-hexene yielding cyclohexyl formate (70%) and secondary hexyl formates (55%), respectively. The composition of the latter was determined by mild alkaline hydrolysis followed by fractional distillation of the resulting hexanols through an efficient column (over one hundred theoretical plates). The distillate consisted of about $^2/_3$ 2-hexanol and $^1/_3$ 3-hexanol; no 1-hexanol could be detected. Anhydrous formic acid also adds to 10-hendecenoic acid yielding monohydroxyhendecanoic acids, which could be isolated only as the methyl esters.

The addition of formic acid to olefinic compounds clearly proceeds by way of intermediate carbonium ion formation. Thus: (a) the reaction is catalyzed by strong acids (perchloric, sulfuric); (b) formic acid, a relatively strong organic acid, adds to the double bond at a significant rate at its boiling point, whereas acetic acid (uncatalyzed) does not; (c) the formate ester group does not show up exclusively at the original double bond position (1-hexene yields a mixture of 2- and 3-hexyl formates); (d) no 1-hexyl formate is apparently formed from 1-hexene, a result consistent with the known greater stability of secondary carbonium ions compared with that of primary; (e) in the addition of formic acid to oleic acid in the presence of strong acid catalysts, marked increase in reaction time results in a more complex mixture of products; (f) the unsaturated components of the filtrates (iodine number about 60), isolated from the crystallization of the crude monohydroxystearic acids from oleic acid (100% *cis*), are about $^2/_3$ *trans;* (g) the filtrates from the crystallization of the crude monohydroxystearic acids obtained from either oleic or elaidic acid (100% *trans*) have the same *trans*-acid content, suggesting a common intermediate; and (h) treatment of pure 10-hydroxystearic acid, m.p. 81°, with formic acid and perchloric acid, under the same reaction conditions used in the addition of formic acid to oleic acid, yields formoxystearic acids, iodine number 15, and, after hydrolysis, the equilibrium mixture of monohydroxystearic acids, iodine number 18, is obtained. Crystallization from commercial hexane to remove unsaturates yields the expected mixture of monohydroxystearic acids, m.p. 75°.

The most reasonable explanation for the failure of formic acid to add to β-hydroxy olefinic compounds, such as castor oil, methyl ricinoleate and crotyl alcohol, is the reduction of the electron density of the double bond by the strongly electron-attracting hydroxyl group thereby lessening the possibility of reaction between the olefinic compound and the electrophilic dihydroxycarbonium ion (conjugate acid) from formic acid, $\left[H-C\begin{matrix}OH\\OH\end{matrix}\right]^+$.

The failure of formic acid to add to the double bonds present in castor oil was attributed, at first, to insolubility of the oil in the reaction medium. When it was found, however, that oleyl alcohol which was also insoluble, added formic acid readily, and that methyl ricinoleate which was readily soluble, did not, it was obvious that another explanation was required. Since the product isolated from the interaction of methyl ricinoleate and formic acid was methyl formoxyoctadecenoate, it was thought that the water liberated during esterification was interfering. This explanation was also unlikely because of the ease of addition to the double bond of oleyl alcohol, in which water is also liberated as a result of esterification. To be certain that water was not interfering, however, preformed methyl formoxyoctadecenoate was retreated with formic acid under the usual anhydrous conditions and again no loss of unsaturation was observed.

The possibility that steric hindrance was a factor was also given consideration in view of the close proximity of the hydroxyl or formoxy group to the double bond. Therefore, crotyl alcohol (CH_3-$CH{=}CHCH_2OH$), whose double bond–hydroxyl group relationship is similar to that in castor oil and methyl ricinoleate but in which steric effects should be absent, was selected for study. The only reaction observed between crotyl alcohol and formic acid was esterification to yield crotyl formate.

Experimental

Starting Materials.—Oleic acid, iodine number 88, and methyl oleate, iodine number 82, were prepared from olive oil.[5] Their compositions were 96–98% oleic, 2–4% saturates and < 0.2% polyunsaturates. Oleyl alcohol, iodine number 93.5 (composition: 98% oleyl, 2% saturated and <0.2% polyunsaturated alcohols), was prepared from a commercial grade.[6] *trans*-Unsaturated components were absent in these three materials.[7] Elaidic acid, m.p. 43°, was prepared from oleic acid by elaidinization with 0.3% powdered selenium at 220°.[7a] Cyclohexene was prepared by the dehydration of cyclohexanol over 85% phosphoric acid,

(5) H. B. Knight, E. F. Jordan, Jr., E. T. Roe and D. Swern, *Biochem. Preparations*, **2**, 100 (1952).

(6) D. Swern, H. B. Knight and T. W. Findley, *Oil and Soap*, **21**, 133 (1944).

(7) (a) D. Swern, H. B. Knight, O. D. Shreve and M. R. Heether, *J. Am. Oil Chemists' Soc.*, **27**, 17 (1950); (b) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **22**, 1261 (1950).

followed by efficient fractional distillation.[8] 1-Hexene, b.p. 62.8–63.0° (753 mm.), $n^{20}D$ 1.3881, was obtained by efficient fractional distillation of a good commercial grade. The preparation of 10-hendecenoic acid has already been reported.[9] Castor oil was the U. S. P. grade. Methyl ricinoleate, iodine number 83, was prepared from castor oil by methanolysis and fractional distillation.[10] Crotyl alcohol was obtained by efficient fractional distillation of the purest commercial grade. The anhydrous formic acid was the Eastman Kodak white label grade[11]; it assayed 100%. The 90% formic acid was the best commercial grade. Boron fluoride–acetic acid complex (1:2) was the commercial grade.

Preparation of Monohydroxystearic Acid. (a) Addition of Formic Acid to Oleic Acid.—A mixture of 100 g. (0.35 mole) of oleic acid, 200 ml. of anhydrous formic acid and 1 ml. of 70% aqueous perchloric acid (1% of the oleic acid) was refluxed for 5–15 min. in an atmosphere of nitrogen. The mixture became homogeneous between 90 and 100°. The excess formic acid, b.p. 43–49° (100 mm.), was recovered by distillation under reduced pressure and the residue in the flask (crude formoxystearic acid, 112 g.; iodine number 13.5; saponification number 301; acid number 174) was saponified by boiling for 15 min. with a 100% excess of 6 *N* sodium hydroxide. The hot soap solution was slowly poured into an excess of 6 *N* hydrochloric acid with stirring, and the oily upper layer was allowed to solidify. The solid product was air-dried; it consisted of crude monohydroxystearic acids; 108 g., m.p. 73–74°, iodine number 15.5, acid number 186, hydroxyl oxygen 4.16%. Its composition, therefore, was about 78% monohydroxystearic acids, 17% olefinic material and 5% saturates originally present plus unaccounted material. Recrystallization at room temperature from petroleum naphtha, hexane fraction (5 ml. per gram of solute) yielded 76 g. (70%) of colorless monohydroxystearic acids; m.p. 73–74°, iodine number 2, acid number 187, hydroxyl oxygen 5.21% (calculated for monohydroxystearic acid: iodine number 0; acid number 187; hydroxyl oxygen 5.33%). Melting points as high as 80° have been obtained on the once crystallized products. The filtrate from this crystallization had an iodine number in the range of 59–68. Infrared analysis[7] showed that 65–75% of the olefinic substances in these filtrates had the *trans* configuration.

In replicate experiments, identical results were obtained when the reaction mixture was poured into a large volume of cold water and the formoxystearic acids were extracted with ether. As little as 0.5% (based on oleic acid) of 70% perchloric acid has been used with equal success. Also, no difference in results was noted when the catalyst was omitted and the reaction time was 24 hr.

When 5 ml. of 85% sulfuric acid per 100 g. of oleic acid was the catalyst, a 15-min. reflux period was required (5 min. was insufficient). A 75% conversion and a 60% yield of once-crystallized monohydroxystearic acids, m.p. 74–77°, were obtained. The once-crystallized product was yellow. Identical results were obtained when 5 ml. of boron fluoride–acetic acid complex (1:2) was substituted for the sulfuric acid, except that the once-crystallized product was colorless, m.p. 76–78°. When the reflux time was increased in the presence of sulfuric acid, the iodine number of the resulting crude formoxystearic acids increased, rather than decreased, as shown in Table I.

The anhydrous formic acid could be replaced by the 90% grade. In a reaction consisting of 20 g. of oleic acid, 40 ml. of 90% formic acid and 2 g. of 100% sulfuric acid, a one-hour reflux period (reaction mixture heterogeneous) reduced the iodine number to 27–28 (conversion 69%). Up to 4 hr. of reflux gave no further decrease (or increase) in iodine number. Hydrolysis of the reaction product and recrystallization from petroleum naphtha yielded 14 g. (65%) of monohydroxystearic acids, m.p. 74.5–76.2°, hydroxyl oxygen 5.38%. With 1% perchloric acid as the catalyst a 16-hr. reflux period was required for 60–65% conversion, whereas with 5% boron fluoride–acetic acid complex (1:2) approximately 2 hr. was required for 55% conversion. In the absence of strong acid catalysts 90% formic acid added at a negligible rate at its boiling point.

TABLE I

EFFECT OF REACTION TIME ON THE ADDITION OF FORMIC ACID TO OLEIC ACID WITH 85% SULFURIC ACID AS CATALYST

Reflux time, min.	Iodine no. of crude formoxystearic acids	Reflux time, min.	Iodine no. of crude formoxystearic acids
0[a]	88	60	18.5
5	78.5	120	24.5
15	16.1	240	26.1
30	17.4	480	24.2

[a] The iodine number of the oleic acid used as the starting material was 88. The reaction mixture contained 100 g. of oleic acid, 200 ml. of anhydrous formic acid and 5 ml. of 85% sulfuric acid.

The lack of solubility of oleic acid in the reaction medium undoubtedly accounts for the fact that large scale laboratory experiments with 90% formic acid require much longer reaction times.

(b) Addition of Formic Acid to Elaidic Acid.—Elaidic acid was treated with anhydrous formic acid as described in the first paragraph of (a) above, giving a 65% yield (75% conversion) of monohydroxystearic acids, m.p. 77–78°.

(c) Addition of Formic Acid to Filtrates Obtained by Recrystallization of Crude Monohydroxystearic Acids from Oleic Acid.—These filtrates had iodine numbers ranging from 59–68. Sixty-five to 75% of the unsaturated components of these filtrates had the *trans* configuration, whereas the oleic acid from which they were obtained was 100% *cis*.

Thirty-eight grams of filtrate (pale yellow liquid, iodine number 64), 76 ml. of anhydrous formic acid and 0.38 ml. of 70% perchloric acid were refluxed for 15 min. The formoxystearic acids obtained (41 g.) had the following characteristics: iodine number 17; acid number 166; saponification number 279. Saponification and acidification yielded 39 g. of crude monohydroxystearic acids, hydroxyl oxygen, 3.87%, from which 18 g. of purified monohydroxystearic acids was obtained by crystallization from petroleum naphtha.

Dihydroxyoctadecanes by Addition of Formic Acid to Oleyl Alcohol.—Fifteen grams (0.055 mole) of oleyl alcohol, 30 ml. of anhydrous formic acid and 0.15 ml. of 70% perchloric acid were refluxed for 1 hr. (The usual 15 min. reaction time found to be adequate for oleic acid and other soluble olefinic compounds was insufficient here since the mixture was heterogeneous during the entire reaction period. Oleyl alcohol must have a small, but significant, solubility in the reaction medium.) The reaction mixture was poured into water and the reaction product was dissolved in ether and washed with water until acid-free. The crude formoxyoctadecyl formates (15 g.) was a pale yellow liquid; iodine number 22.6 and saponification number 284 (conversion 76%). It was dissolved in 450 ml. of 0.2 *N* alcoholic potassium hydroxide and the bulk of the alcohol was boiled off on the steam-bath. Hot water was added to precipitate the crude dihydroxyoctadecanes as an oil, which solidified on cooling. The lower aqueous layer was discarded and the solid was remelted with hot water and allowed to resolidify. The hard solid thus obtained weighed 13.4 g. Crystallization from 67 ml. of petroleum naphtha (hexane fraction) yielded 9.6 g. (60%) of purified dihydroxyoctadecanes, m.p. 62.5–63.5°, hydroxyl oxygen 10.6% (calcd. 11.2%).

Cyclohexyl Formate.—Fifty grams (0.61 mole) of cyclohexene, 100 ml. of anhydrous formic acid and 0.5 ml. of 70% perchloric acid were mixed. The temperature rose spontaneously to 40°. The mixture was then refluxed for 15 min. at its highest reflux temperature (105°). The catalyst was neutralized by the addition of sodium bicarbonate and the reaction mixture was fractionally distilled. Seventy-three grams of formic acid, b.p. 43–49° (98–100 mm.) was obtained as a forerun, and 54 g. (69%) of cyclohexyl formate, b.p. 94.5–95.0° (97–98 mm.) and $n^{25}D$ 1.4392, was then obtained as a colorless liquid with a pleasant odor; saponification number, calcd. 438, found 430.

Hexyl Formates.—One hundred grams (1.19 moles) of 1-hexene, 200 ml. of anhydrous formic acid and 1 ml. of 70%

(8) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 152.

(9) E. F. Jordan, Jr., and D. Swern, THIS JOURNAL, 71, 2377 (1949).

(10) D. Swern and E. F. Jordan, Jr., *Biochem. Preparations*, 2, 104 (1952).

(11) Reference to a company name is intended to be descriptive only and does not constitute a recommendation of the product of the company mentioned.

perchloric acid were mixed and treated as described under the preparation of cyclohexyl formate above. After the recovery of 160 g. of unreacted formic acid, b.p. 51–57° (125 mm.), 94 g. (55%) of mixed hexyl formates, b.p. 85.5–95° (125 mm.) and $n^{20}D$ 1.4012, was obtained. The esters were dissolved in a 100% excess of 5 *N* alcoholic KOH with *cautious* warming and were allowed to remain overnight at room temperature. The solution was diluted with several volumes of saturated sodium chloride solution and then extracted three times with ether. The ether solution was washed free of alkali with saturated sodium chloride solution and once with a small volume of water to remove salt. The ether was separated by distillation and the residual hexanols were distilled through a column with over one hundred theoretical plates. Only two fractions were obtained consisting of 3-hexanol,[12] b.p. 82.2–83.8° (124–125 mm.) and $n^{25}D$ 1.4135, and 2-hexanol,[12] b.p. 86–87.6° (124–125 mm.) and $n^{25}D$ 1.4121, in the proportion of 1:2, respectively. No 1-hexanol was obtained.

Monohydroxyhendecanoic Acids.—A mixture of 100 g. of 10-hendecenoic acid (0.54 mole; iodine number, 132), 200 ml. of anhydrous formic acid and 1 ml. of 70% perchloric acid was refluxed for 15 min. The reaction mixture was poured into water and the upper oily layer was dissolved in ether and washed with water until free of acid. Evaporation of the ether yielded 115 g. of crude formoxyhendecanoic acids (amber liquid): iodine number 11; acid number 233; saponification number 404. These were refluxed for 4 hr. with 230 ml. of anhydrous methanol containing 2.3 g. of naphthalene-2-sulfonic acid as catalyst. The catalyst was neutralized with sodium bicarbonate, and the excess methanol was recovered by distillation. The residue (120 g.) was then distilled from an alembic flask and, after removal of a small amount of forerun (8 g., b.p. 81–106° (0.3 mm.)), 52 g. (48% yield) of methyl monohydroxyhendecanoates, b.p. 106–113° (0.3–0.6 mm.), saponification number 258 and hydroxyl oxygen 7.1%, was obtained (calcd.: saponification number 255; hydroxyl oxygen 7.4%).

Isolation of 10-Hydroxystearic Acid.—One hundred grams of monohydroxystearic acids, m.p. 73–74°, and hydroxyl oxygen 5.21%, prepared as described above under section (a), Preparation of Monohydroxystearic Acids, was dissolved in 500 ml. of 95% ethanol. The solution was cooled to 0° overnight and the white granular precipitate was separated and air-dried; yield 73 g., m.p. 78–79° (P-1). The filtrate was evaporated to dryness at room temperature yielding a white amorphous solid; 26 g., m.p. 65–70° (F-1). The P-1 fraction was recrystallized five additional times and each of the filtrates evaporated to dryness. Small samples of the P fractions were reserved for melting point determinations. Table II summarizes the results of the fractional crystallizations. It is clear that recrystallization to a constant melting point is an insufficient criterion of purity. We prefer to crystallize monohydroxystearic acids until the melting point of the precipitate and filtrate are substantially the same. A mixed melting point of P-6 with authentic 10-hydroxystearic acid, obtained from *cis*-9,10-epoxystearic acid by catalytic hydrogenation and fractional crystallization, showed no depression.

(12) F. Hovorka, H. P. Lankelma and S. C. Stanford, This Journal, 60, 820 (1938); F. A. Karnatz, Ph.D. Thesis, Pennsylvania State College (1937).

Table II

Isolation of 10-Hydroxystearic Acid by Fractional Crystallization of Monohydroxystearic Acids, M.p. 73–74[a]

Fraction	Weight, g.	M.p., °C.	Fraction	Weight, g.	M.p., °C.
Original	100	73–74	...	..	...
P-1	73	78–79	F-1	26	65–70
P-2	65	79.5–80.5	F-2	7	64–66
P-3[b]	55	80.5–81.5	F-3	10	65–75
P-4	52	81–82	F-4	3	74–77
P-5	50	81.5–82.5	F-5	2	78–80
P-6	48	81.5–82.5[c]	F-6	2	80–81

[a] The solvent was 5 ml. of 95% ethanol per gram of monohydroxystearic acids; crystallization temperature, 0°. [b] Fractions P-3 through P-6 consisted of glistening needles and plates. All of the F-fractions were amorphous. [c] C. G. Tomecko and R. Adams, This Journal, 49, 522 (1927), report 81–82°.

Substantially identical results were obtained in fractionally crystallizing the monohydroxystearic acids obtained from the uncatalyzed addition of formic acid to oleic acid.

Conversion of 10-Hydroxystearic Acid to the Equilibrium Mixture.—A mixture consisting of 15 g. (0.05 mole) of 10-hydroxystearic acid, m.p. 81–82°, 30 ml. of anhydrous formic acid and 0.075 ml. of 70% perchloric acid was refluxed for 1 hr. Homogeneity occurred at 70°. The reaction mixture was poured into water, extracted with ether, and the ether solution was washed with water to remove unreacted formic acid. Evaporation of the ether yielded 16 g. of colorless, odorless formoxystearic acids, iodine number 15. (The iodine numbers of formoxystearic acids obtained directly from oleic acid by the above reaction are in the range of 13–17.) Saponification and acidification yielded 14 g. of crude monohydroxystearic acids, from which 11 g., m.p. 75.5–77°, was isolated by crystallization from petroleum naphtha.

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