quinone isomerized oils exhibited much less after-tack than did the Nickel-Carbon isomerized oils.

Summary

Anthraquinone and its derivatives have been found to be effective catalysts for the isomerization of drying and semi-drying oils to conjugated forms. A possible mechanism to account for the catalytic activity of these materials has been proposed. Possible commercial application of the isomerization of oils with anthraquinone was briefly discussed.

Acknowledgment

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REFERENCES

1. Bradley, T. R., and Richardson, D., Ind. Eng. Chem., *32*, 963 (1940).
2. British Patent 544,482 (April 15, 1942).
3. Falkenburg, L. B., Schwab, A. W., Cowan, J. C., and Teeter, H. M., Ind. Eng. Chem., *38*, 1002 (1946).
4. Kass, J. P., in Mattiello's "Protective and Decorative Coatings," Vol. IV, Chap. 12, New York, John Wiley & Sons, Inc., 1944
5. Kass, J. P., and Skell, P. S., Am. Chem. Soc. Meeting, Detroit, Mich., April 12-16 (1943).
6. Radlove, S. B., and Falkenburg, L. B., J. Am. Oil Chem. Soc., *25*, 1 (1948).
7. Radlove, S. B., Teeter, H. M., Bond, W. H., Cowan, J. C., and Kass, J. P., Ind. Eng. Chem., *38*, 997 (1946).
8. Schwarcman, A., U. S. Patent 2,207,686 (July 9, 1940).
9. Sorensen, S. O., and Konen, J. C., U. S. Patent 2,213,935 (September 3, 1940).
10. Spitzer, W. C., Ruthruff, R. F., and Walton, W. T., Am. Paint J., *26, 18 (1941)*.
11. Terrill, R. I., Oil and Soap, *23*, 339 (1946).
12. Waterman, H. J., and Vlodrop, C. van, J. Soc. Chem. Ind., *55*, 320T (1936).
13. *Ibid., 55*, 333T (1936).
14. Waterman, H. J., Vlodrop, C. van, and Pfauth, M. J., Verfkronick, *13*, 1930 (1946).

Bromination of Methyl Esters of Soybean Fat Acids and Methyl Linoleate With N-Bromosuccinimide[1]

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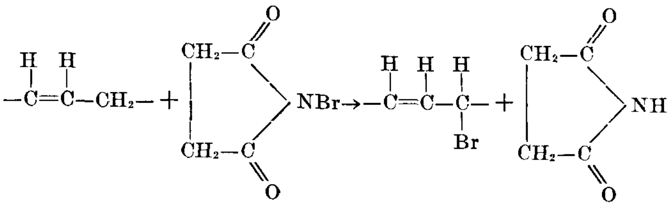
ZIEGLER, *et al.* (5), have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may easily be replaced by bromine by means of N-bromosuccinimide. The reaction may be formulated as follows:



The reaction is of quite general applicability, but in the field of fats and oils apparently the only instance of its use is Ziegler's bromination of methyl oleate. Beyond the statement that the bromine in methyl bromoleate is loosely bound, Ziegler gave no further description of the product and its reactions.

Since the double bonds in unsaturated fatty acids are located near the center of the carbon chain, this reaction is of great interest as a possible means of introducing a reactive center without undesirable side reactions such as polymerization or loss of unsaturation. This reactive center might serve for the preparation of new derivatives of unsaturated fatty acids through replacement of bromine by other groups, such as hydroxyl or cyano groups, or through coupling reactions.

The reaction of methyl esters of soybean fat acids with N-bromosuccinimide was therefore studied, and the reactions of the brominated esters with sodium methoxide, cuprous cyanide, and sodium cyanide were investigated. The reaction was also applied to methyl linoleate.

Although it became necessary to discontinue this investigation before more than preliminary data had been obtained on the replacement of halogen in the brominated methyl esters, the data are, nevertheless, presented because they may be of interest to others.

Discussion of Results

The reaction of methyl esters of soybean fat acids with N-bromosuccinimide proceeded rapidly and almost quantitatively (Tables I and II). The conditions specified by Ziegler (5), i.e., refluxing the reaction mixture which contained a small amount of carbon tetrachloride, were too vigorous and resulted in marked decomposition of the product. Excellent results were obtained, however, at temperatures of 70°C. or lower.

TABLE I

Bromination of Methyl Esters of Soybean Fat Acids and Methyl Linoleate

(40-Minute Reaction Time)

Substance	Halogen transfer	Succinimide recovered
	Per cent	*Per cent*
Methyl esters of soybean fat acids	97	86
	99	91
	92	96
	99	96
Methyl linoleate	76	107
	72	111

A solvent was not necessary to insure complete reaction (Table III) although a small amount facilitated stirring and filtration of the reaction mixture. When the volume of carbon tetrachloride or mixed heptanes was increased, the extent of reaction was substantially decreased (Tables III and IV), but this effect could be overcome by prolonging somewhat the time of reaction (Table II). Other solvents used included benzene and halogenated aliphatic and aromatic hydrocarbons (Table IV). Increasing the volume of these solvents had little effect on the extent of reaction. From the standpoint of color of product, benzene and mixed heptanes were outstanding.

Besides causing bromination, N-bromosuccinimide may also add to the ethylenic bond. The addition product with methyl esters of soybean fat acids would contain approximately 3% nitrogen. Nitrogen analy-

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TABLE II

Effect of Variation of Time of Reaction Upon Bromination of Methyl Esters of Soybean Fat Acids

(3.5 ml. Solvent per 10 g. of Ester)

Solvent	Time of reaction	Halogen transfer
	Minutes	*Per cent*
Carbon tetrachloride	10	41
	20	71
	25	78
	30	97
	40	99
Mixed heptanes	25	72
	35	84
	47	95

TABLE III

Effect of Variation of Volume of Carbon Tetrachloride on Bromination of Methyl Esters of Soybean Fat Acids

(25-Minute Reaction Time)

Volume of solvent	Halogen transfer
Ml.	*Per cent*
0	97
0	96
0	98
3.5	78
10.0	62
20.0	56
35.0	54

TABLE IV

Effect of Various Solvents on Bromination of Methyl Esters of Soybean Fat Acids

(25-Minute Reaction Time)

	Halogen transfer	
	3.5 ml. solvent	35 ml. solvent
	Per cent	*Per cent*
Carbon tetrachloride	78	54
Chloroform	99	99
1,2-Dichloroethane	99	100
1,1,2,2,-Tetrachloroethane	100	100
Chlorobenzene	98	99
1,2-Dibromoethane	99	98
Benzene	98	97
Mixed heptanes	72	32

sis of a typical sample of brominated methyl esters of soybean fat acids indicated the presence of 0.5% of nitrogen but, after the sample was washed once with water, it contained only 0.05% of nitrogen. This observation indicates that the nitrogenous impurity was merely dissolved succinimide. Karasch and Priestley have reported (2) that N-bromosuccinimide did not add to olefins such as propene, 2-methylpropene, vinyl chloride, and styrene.

With methyl linoleate (Table I) bromination proceeded to the extent of 84.5% based upon analysis of the product for halogen. Iodometric titration of recovered succinimide indicated, however, that bromination had proceeded only to the extent of 72-76%. No satisfactory explanation for this discrepancy has been suggested. The somewhat less complete halogen transfer in the case of methyl linoleate as compared to that of the methyl esters of soybean fat acids may be due to loss of hydrogen bromide in side reactions, which could result from enhanced reactivity of methyl bromolinoleate. An enhancement of reactivity might be expected because of activation of the central methylene group by two ethylenic linkages and as a consequence of the absence of relatively large proportions of inert or less reactive diluents, i.e., methyl stearate and methyl oleate, which are present in the methyl esters of soybean fat acids.

The halogen introduced by N-bromosuccinimide should be allylic in nature, and, in fact, the brominated methyl esters produced immediately a precipitate with cold, alcoholic silver nitrate. Attempts were made, therefore, to replace the halogen of these esters with methoxyl and cyano groups. The reagents employed were sodium methoxide, sodium cyanide, and cuprous cyanide. In each case, and particularly in the attempts to introduce the cyano group, it was found that while the reagent removed halogen, replacement with the desired group did not occur to the extent anticipated.

From the reaction with sodium methoxide a neutral and an acidic fraction were isolated. Analyses of the neutral fraction can be explained upon the premise that this material contains 8.5% of unreacted brominated esters and 91.5% of a bromine-free substance having a methoxyl content of 15.3%, a figure which is 79% of the calculated methoxyl content (19.3%) for methyl esters of methoxylated soybean fat acids. These data indicate that the methoxylated esters, if actually present, represent about 50% by weight of the reaction products isolated. The acidic fraction had a neutral equivalent of 466, and it is probable that this material is some type of dimer, or perhaps an estolide, formed by a coupling reaction during removal of halogen by the sodium methoxide. The neutral and acidic fractions taken together account for approximately 82% by weight of the expected yield of debrominated product.

In the reaction with sodium cyanide, halogen content was reduced from 18.6% to 0.12 and 0.47% in the two volatile fractions isolated, whereas the nitrogen content of these products was only 0.26% and 0.18%, respectively, as compared to the calculated value 4.31%. In the second fraction a somewhat high alkoxyl value indicates that some replacement of halogen by ethoxyl occurred through contact with the ethanol in the reaction mixture. Most of the crude reaction product was converted to a pasty solid during the distillation.

The treatment with cuprous cyanide resulted in reduction of bromine to 3.17% and introduction of only 0.28% of nitrogen. A substantial increase in viscosity was noted during the reaction. These observations may be explained if coupling is assumed to be the predominate reaction under the conditions employed.

Because of the complexity of the products of these reactions no attempt was made to determine their exact structure. Other reactions than replacement and coupling may have occurred; for example, dehydrohalogenation, hydrolysis, and cyclization. For these reasons, the explanations given constitute merely one possible interpretation of the experimental data. It may be concluded that the customary conditions for effecting replacement of allylic halogen are not satisfactory for the brominated methyl esters of soybean fat acids.

Experimental

Bromination With N-Bromosuccinimide. A preliminary experiment with methyl esters of soybean fat acids under the conditions used by Ziegler (5) for methyl oleate disclosed that these conditions were too vigorous. Hydrogen bromide was evolved copiously, and the product was almost black. The brominations reported in this paper were conducted therefore according to the following procedure unless otherwise noted.

In a flask equipped with a stirrer and immersed in a constant temperature bath (70°C.) was placed the desired amount of methyl esters of soybean fat acids or methyl linoleate together with any solvent employed. After stirring for a few minutes until temperature equilibrium was reached, the calculated amount of powdered N-bromosuccinimide was added. Stirring was continued for 40 minutes, after which the mixture was filtered to remove succinimide and unreacted N-bromosuccinimide. Carbon tetrachloride was a convenient solvent for rinsing the flask and washing the filtercake. The filtrate was evaporated *in vacuo* at 45°, and the product remained as an orange-colored oil. The material recovered on the filter was titrated iodometrically to determine the amount of unreacted N-bromosuccinimide and the approximate transfer of halogen was calculated. The brominated oils are unstable and evolve hydrogen bromide on standing at room temperature. They may be preserved for some time, however, if stored at 0° to − 40°.

The results of several typical experiments conducted under these conditions in the presence of 3.5 g. of carbon tetrachloride per 10 g. of methyl esters are given in Table I. Analysis of the product of a typical experiment indicated the presence of 18.3% bromine. The calculated value, based upon Mattil's (3) data for the composition of soybean oil, was 18.9%. This corresponds to 96.8% halogen transfer and is in excellent agreement with the value of 97% determined iodometrically. The percentages of succinimide recovered, listed in Table I, are based upon the calculated value for 100% halogen transfer; they are uncorrected for halogen content.

Methyl linoleate was prepared by debromination of tetrabromostearic acid. Spectrophotometric analysis indicated 98.2% purity; 0.32% of conjugated materials were present. The results obtained when methyl linoleate was brominated in accordance with the procedure outlined are summarized in Table I. Analysis of a typical product gave Br, 18.03%; calculated value, 21.4%.

Effect of Variation of Reaction Conditions Upon Bromination. Time of Reaction. A series of experiments was performed in which methyl esters of soybean fat acids were brominated for various lengths of time in the presence of 3.5 ml. of carbon tetrachloride or mixed heptanes per 10 g. of esters. The conditions otherwise were those outlined above. The results are given in Table II.

Solvent Effects. Since bromination is essentially complete in 40 minutes at 70°C. when 3.5 ml. of carbon tetrachloride per 10 g. of esters is present, a reaction time of 25 minutes was selected for a series of experiments to demonstrate the effect of varying the amount of this solvent. The results of these experiments, which otherwise followed the procedure given above, are shown in Table III.

The effect of using other solvents than carbon tetrachloride is shown by the data of Table IV. In these experiments the reaction time was 25 minutes; the temperature, 70°C.; and the volume of solvent employed, either 3.5 ml. or 35 ml. per 10 g. of esters.

Reaction Between Brominated Methyl Esters of Soybean Fat Acids and Sodium Methoxide. In a small flask equipped with a stirrer, condenser, and drying tube was placed 25 ml. of absolute methanol and 0.53 g. (0.023 mole) of sodium. To the resulting solution of sodium methoxide was added 10 g. (0.023 mole of combined bromine) of brominated methyl esters of soybean fat acids. The mixture was stirred for 2 hours at room temperature, but there was no indication of reaction. The mixture was then refluxed. A solid began to separate after 1.5 hours, and refluxing was continued for a total time of 12 hours. After standing for 2 days at 0°C., the mixture was filtered from a solid (sodium bromide) and evaporated, yielding a gelatinous semi-solid residue which appeared to contain soaps. The residue was extracted 10 times with 10-ml. portions of petroleum ether (b.p. 30°-60°), and the extract was filtered and evaporated. An orange-colored oil (4.6 g.) was obtained which had n_D^{30}, 1.4601. Anal.: Found—Br, 1.58; OCH_3, 14.68.

The soaps remaining after extraction with the petroleum ether were dissolved in 50 ml. of water. The solution was neutralized with sulfuric acid, and the free fatty acid was isolated in the customary way. It weighed 2.0 g. and had n_D^{30}, 1.4863. Anal.: Found—Br, 1.86; OCH_3, 8.15; neut. equiv. 466.

Reaction Between Brominated Methyl Esters of Soybean Fat Acids and Sodium Cyanide. Brominated methyl esters of soybean fat acids (21.1 g., containing 0.05 moles of combined bromine) were treated with 3.63 g. (0.05 mole) of sodium cyanide according to a recommended procedure (1) for the conversion of benzyl chloride to benzyl cyanide. Distillation of the crude reaction product gave two fractions: (1) b.p. 110°-145°C. at 3 mm.; wt. 2.13 g.; n_D^{30}, 1.4498; (2) b.p. 145°-150° at 3 mm., wt. 6.03 g.; n_D^{30}, 1.4539. The non-volatile residue was large and consisted of a carbonized pasty solid. Anal.: Fraction 1, Found—N, 0.26; Br, 0.12. Fraction 2, Found—N, 0.18; Br, 0.47; OCH_3, 12.8.

A related experiment in which cuprous cyanide was employed in an attempt to replace bromine with the cyano group (4) gave a product containing 3.17% bromine and 0.28% nitrogen. During this experiment an increase in viscosity from approximately 0.062 poise for the brominated ester to 0.5 poise for the product was noted.

Acknowledgment

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Summary

1. The reaction of N-bromosuccinimide with methyl esters of soybean fat acids and with methyl linoleate has been investigated, and the influence of changes in the conditions of reaction has been studied.

2. The reaction of brominated methyl esters of soybean fat acids with sodium methoxide produced both methoxylated products and a dimer-like substance.

3. The reaction of brominated methyl esters of soybean fat acids with sodium cyanide and cuprous cyanide did not result in significant replacement of bromine with the cyano group.

REFERENCES

1. Adams, R., and Thal, A. F., Organic Syntheses, Collective. Volume I, p. 101, John Wiley and Sons, New York (1932).
2. Kharasch, M. S., and Priestley, H. M., J. Am. Chem. Soc. *61*, 3425-3432 (1939).
3. Mattil, W. H., Oil and Soap *21*, 198-199 (1944).
4. Supniewski, J. V., and Salzburg, P. L., Organic Synthesis, *loc. cit.*, p. 39.
5. Ziegler, K., Spath, A., Schaaf, E., Schumann, W., and Winkelmann, E., Ann. *351*, 80-119 (1942).