# The Reaction of Acrylonitrile and Fumaronitrile with Alpha- And Beta-Eleostearates. Plasticizer Properties of The n-Butyl Esters of the Adducts

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In connection with research on the utilization of tung oil we have previously reported the Diels-Alder reaction of *beta*-propiolactone with *alpha*- and *beta*-eleostearates (8). The resulting acrylic acid adducts contain a free carboxyl group on the cyclohexene nucleus. These materials were converted to plasticizers by esterification of the carboxyl group with appropriate alcohols for the formation of diesters.

It appeared of interest to investigate the diene reaction of the eleostearates with *alpha, beta*-unsaturated nitriles, and to determine what effect the cyano group might have on the plasticizer properties of the adducts. These derivatives would require no further modification, such as esterification, for the preparation of potential plasticizing materials.

Acrylonitrile has been extensively employed in the diene synthesis with a wide variety of conjugated olefins. Bruson and Niederhauser (5) have investigated the reaction of acrylonitrile with eleostearic acid and its methyl ester. Although claims have been made for the use of the adducts as plasticizers, no data were presented to indicate their effectiveness.

Fumaronitrile has received limited attention as a dienophile. Mowry (10) and Blomquist and Winslow (4) reported its reaction with 2-methyl-pentadiene, anthracene, and similar compounds. However we were unable to find any reference to the reaction of fumaronitrile with the eleostearates.

This paper describes the reaction of acrylonitrile and fumaronitrile with the *n*-butyl esters of *alpha*- and *beta*-eleostearic acids and also reports infrared, ultraviolet, and plasticizer data for the adducts.

## Experimental

*Acrylonitrile and Fumaronitrile.* The acrylonitrile employed was Eastman's Practical Grade[2] and was used without further purification. Fumaronitrile was synthesized according to directions given in Organic Syntheses (11). A technical grade of fumaronitrile may be obtained from Monsanto Chemical Company.[2]

*n-Butyl Esters of alpha- and beta-Tung Oil Fatty Acids.* These esters were prepared by alcoholysis with *n*-butanol, followed by high vacuum distillation, as described in a previous publication (8). The esters derived from *alpha* tung oil contained 65% butyl *alpha*-eleostearate and 7% butyl *beta*-eleostearate. The esters derived from *beta* tung oil contained 17% butyl *alpha*-eleostearate and 55% butyl *beta*-eleostearate.

*Reaction of Acrylonitrile with Butyl alpha-Eleostearate.* Butyl esters of *alpha* tung oil fatty acids (406.7 g., containing 0.87 mole butyl eleostearate), 97.8 g. of acrylonitrile (1.84 mole), and 1 g. of hydroquinone were refluxed 120 hrs. At the end of this time spectral analysis indicated that the reaction was about 87% complete, based upon the disappearance of eleostearate.

The unreacted acrylonitrile was removed by vacuum-stripping with carbon dioxide on the steam bath. The product was fractionally distilled, using a short-path column, and a total of nine fractions was collected. The heart cut, fractions 6, 7, and 8 (200 g.), had a boiling range of 183–188°C./60–70 microns. $n_D^{26.2°} = 1.4784$. Spectral analysis indicated that this distilled product contained approximately 1.0% butyl eleostearate.

Anal. Calculated for $C_{25}H_{41}O_2N$: C, 77.47%; H, 10.66%; N, 3.61%. Found: C, 77.50%; H, 10.68%; N, 3.48%.

*Reaction of Acrylonitrile with Butyl beta-Eleostearate.* Butyl esters of *beta* tung oil fatty acids (416.7 g., containing 0.90 mole butyl eleostearate), 95.8 g. of acrylonitrile (1.80 mole), and 1 g. of hydroquinone were refluxed 48 hrs. At the end of this time spectral analysis indicated the reaction to be about 91% complete, based upon the disappearance of eleostearate.

The unreacted acrylonitrile was removed by vacuum-stripping with carbon dioxide on the steam bath. The product was fractionally distilled through a short-path column, and a total of eight fractions was collected. The heart cut, fractions 5, 6, and 7 (240 g.), had a boiling range of 184–190°C./70–75 microns. $n_D^{26.0°} = 1.4775$. Spectral analysis indicated that this distilled product contained approximately 1.5% butyl eleostearate.

Anal. Calculated for $C_{25}H_{41}O_2N$: C, 77.47%; H, 10.66%; N, 3.61%. Found: C, 77.52%; H, 10.77%; N, 3.40%.

*Reaction of Fumaronitrile with Butyl alpha-Eleostearate.* Butyl esters of *alpha* tung oil fatty acids (267.6 g., containing 0.57 mole butyl eleostearate) and 46.8 g. of fumaronitrile (0.60 mole) were dissolved in toluene and made up to a volume of one liter. This solution was refluxed for 30 hrs. At the end of this time spectral analysis showed that 0.48 mole of eleostearate and 0.47 mole of fumaronitrile had reacted and, further, that the 0.1 mole of eleostearate remaining was of the *alpha* form. These data indicate that the reaction was about 84% complete.

The toluene and unreacted fumaronitrile were removed by vacuum-stripping with dry nitrogen on the steam bath. The product was fractionally distilled through a short-path column, and a total of seven fractions was collected. The heart cut, fractions 4, 5, and 6 (125 g.), had a boiling range of 217–226°C./90–230 microns. $n_D^{27.0°} = 1.4842$. Spectral analysis indicated that this distilled product contained approximately 0.5% butyl eleostearate.

Anal. Calculated for $C_{26}H_{40}O_2N_2$: C, 75.68%; H, 9.97%; N, 6.79%. Found: C, 75.69%; H, 9.80%; N, 6.58%.

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[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

[2] The mention of this and other commercial products does not imply endorsement or recommendation by the Department of Agriculture over others having similar properties.

*Reaction of Fumaronitrile with Butyl beta-Eleostearate.* This reaction was carried out identically as described above for the *alpha* adduct. Spectral analysis showed that 0.50 mole of eleostearate and 0.50 mole of fumaronitrile had reacted. These data indicate that the reaction was about 88% complete. The remaining eleostearate (0.07 mole) was entirely the *alpha* form. This product was worked up in a manner analogous to that described for the *alpha*-eleostearate adduct. A total of seven fractions was collected upon fractional distillation. The heart cut, fractions 4, 5, and 6 (143 g.), had a boiling range of 224–234°C./200–450 microns, $n_D^{27.0°} = 1.4862$.

Anal. Calculated for $C_{26}H_{40}O_2N_2$: C, 75.68%; H, 9.97%; N, 6.79%. Found: C, 76.24%; H, 9.90%; N, 5.98%.

*Infrared Spectra.* The infrared spectra of fumaronitrile and acrylonitrile and of their butyl *alpha*-eleostearate and butyl *beta*-eleostearate adducts were measured in chloroform solution against pure dry chloroform with a Model 21 Perkin-Elmer Double Beam Automatically Recording Infrared Spectrophotometer.[2] Concentrations of all the solutions were about 40 g. per liter (exact concentrations are indicated on the figures). The absorption cell length was 0.5156 mm. for all measurements. The following slit and gain programming was used in obtaining all curves: Resolution Dial 915, Response 2, Gain 7, Speed 4, and Suppression 2.

*Ultraviolet Spectra.* Ultraviolet spectra of fumaronitrile and acrylonitrile and of their butyl *alpha*-eleostearate and butyl-*beta*-eleostearate adducts were obtained with an Automatic Recording Cary Spectrophotometer Model 11M.[2] Fumaronitrile and acrylonitrile adducts were measured in absolute ethanol solution containing about 1 g. per liter. Dilutions of these solutions were used as required to obtain optimum absorbancies through the 2-cm. cell employed for all measurements. The fumaronitrile adducts were measured from similar solutions in cyclohexane. The slit control of the spectrophotometer was maintained at 10 for all measurements.

*Plasticizer Screening.* The ester adducts were screened for their plasticizing characteristics with polyvinyl chloride—polyvinyl acetate copolymer. The following formulation was used:

| | |
|---|---|
| Resin (Vinylite VYDR) | 63.5% |
| Plasticizer | 35.0% |
| Stearic acid | 0.5% |
| Basic lead carbonate | 1.0% |

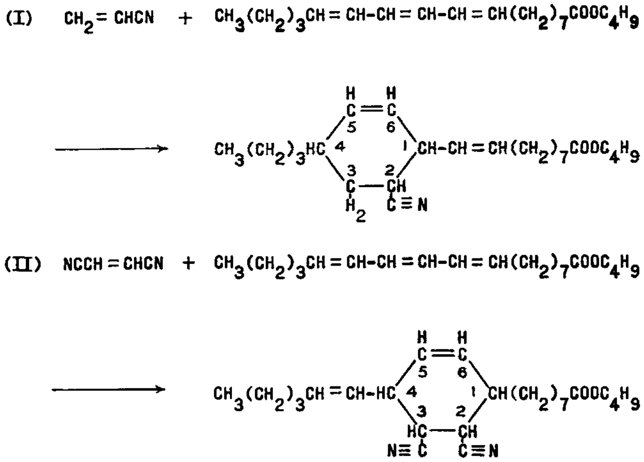
These formulations were milled and molded at 310° F. The detailed procedures followed in these operations as well as the preparation of the test specimen and the various tests have been previously described (9).

## Results and Discussion

The structure of *alpha*-eleostearic acid has been shown to be 9-*cis*, 11-*trans*, 13-*trans*, octadecatrienoic acid (3). The isomeric *beta*-eleostearic acid contains three conjugated *trans* ethylenic bonds (3). In our investigations on eleostearic acids it has been found that dienophiles add only across a *trans*, *trans* pair of ethylenic bonds. It is also known that the Diels-Alder reaction proceeds through *cis* addition. Therefore only one adduct is formed between *alpha*-eleostearic acid and fumaronitrile. However two isomers are possible from the addition of acrylonitrile because the cyano group may be on either the second or third carbon atom of the cyclohexene nucleus. Since there are two positions open in *beta*-eleostearic acid for dienophilic attack, there would result only two isomers from the addition of fumaronitrile, and four isomers from the addition of acrylonitrile.

Equation I illustrates a typical reaction between butyl *alpha*-eleostearate and acrylonitrile. Equation II indicates a similar reaction between butyl *beta*-eleostearate and fumaronitrile.

Equations I and II



*Infrared Spectra.* The spectra of the *alpha*- and *beta*-eleostearates (3) are characterized by four particularly intense bands with maximum absorption at 3.33 microns (C—H stretching vibration), 5.75 microns (C=O stretching of the ester group), 8.55 microns (C—O stretching of the ester group), and 10.04 microns (C—H deformation about a *trans-trans* conjugated C=C—C=C group). The stretching vibrations remain essentially unchanged on adduct formation. Reaction is clearly indicated however by the disappearance of the 10.04 micron band in the spectra of the adducts (Figures 1B, 1C, 1E, and 1F). This is evidence for the consumption of the reactants, *i.e.*, the eleostearates, containing the *trans-trans* conjugated unsaturated groups. The spectra of the *beta*-eleostearate adducts (Figures 1C and 1F) reveal a sharp band with maxima at 10.3 microns, indicating the presence of the isolated C=C (trans) group in these adducts. This is consistent with a Diels-Alder reaction involving a compound like a *beta*- eleostearate containing three C=C (trans) bonds. The two adducts from the *alpha*-eleostearate (Figures 1B and 1E) reveal this 10.3 micron band considerably weaker

TABLE I

Characteristic Absorption Bands in the Infrared Spectra of Fumaronitrile and Acrylonitrile

| Absorption (in microns) | | Assignment |
|---|---|---|
| Acrylonitrile | Fumaronitrile | |
| 3.24 & 3.32 | 3.28 | C—H stretching |
| 4.46 | 4.45 | C≡N stretching (conjugated) |
| 6.19 | 6.19 | C=C stretching |
| 7.07 | ...... | $CH_2$ deformation of $C=CH_2$ terminal group (6) |
| 7.78 | 7.94 | C—H rocking of C—CH=C group (6) |
| 9.14 | ...... | $CH_2$ rocking of $C=CH_2$ group (6) |
| 10.30 | 10.49 | C—H wagging of C—CH=C group (6) |
| 10.42 | ...... | $CH_2$ wagging of terminal $C—CH=CH_2$ group (6) |

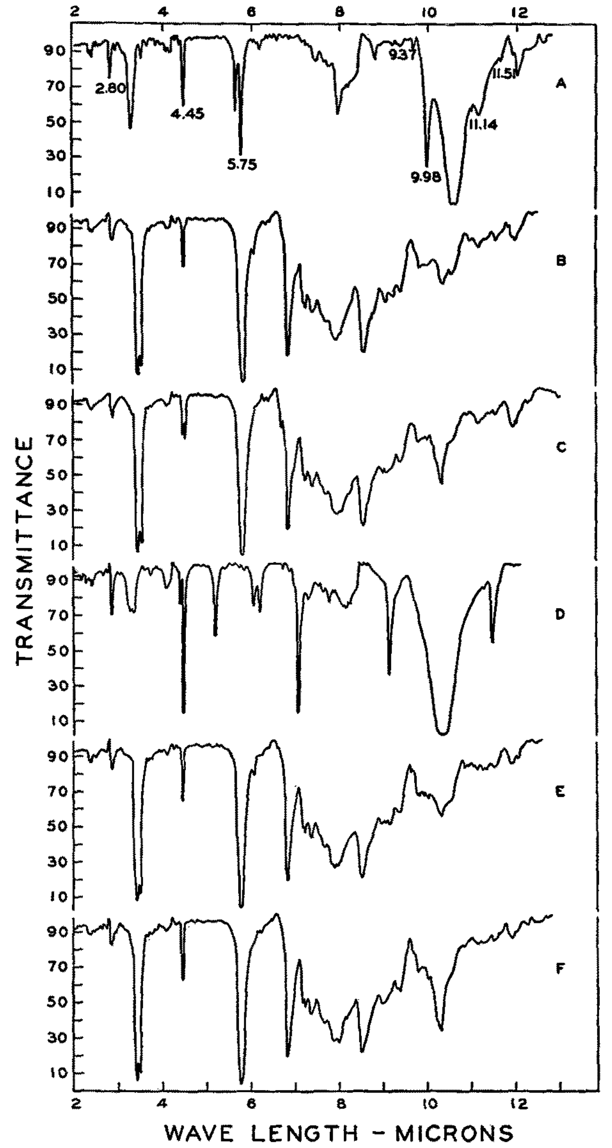


FIG. 1. Infrared Absorption of Chloroform Solutions of:
A. Fumaronitrile. 40.01 g./l.
B. Distilled adduct of fumaronitrile and butyl *alpha*-eleostearate. 44.60 g./l.
C. Distilled adduct of fumaronitrile and butyl *beta*-eleostearate. 40.04 g./l.
D. Acrylonitrile. 41.46 g./l.
E. Distilled adduct of acrylonitrile and butyl *alpha*-eleostearate. 41.60 g./l.
F. Distilled adduct of acrylonitrile and butyl *beta*-eleostearate. 41.13 g./l.

in intensity, indicating the presence of some *beta* isomer.

Fumaronitrile and acrylonitrile exhibit infrared spectra (Figures 1A and 1D) characterized by some six to eight intense bands, presented in Table I. The spectrum of acrylonitrile has been measured and analyzed by several workers (1, 2, 6, 12). It is included in Figure 1 for completeness and to permit comparisons with the spectra of the adducts. The spectrum of fumaronitrile has not, as far as has been ascertained, been previously published.

Adduct formation is indicated by several changes in the characteristic bands of the nitriles. The C—H stretching vibration bands become more intense, shift to slightly longer wavelengths, and show definite resolution, indicating the formation of an increased number of $CH_3$ or $CH_2$ groups. The strong bands with maxima at 6.8 microns, found in the spectra of the adducts and not in those of either fumaronitrile or acrylonitrile, undoubtedly arise from C—H bendings of the saturated $CH_3$ and numerous $CH_2$ groups. The $C{\equiv}N$ and $C{=}C$ stretchings, at 4.4 and 6.2 microns, respectively, become weaker in the larger molecules. The latter almost vanish in the spectra of the adducts, where they occur only as internal $C{=}C$ groups, characterized by weak intensities. It should be noted that the $C{=}C$ stretchings of the adducts with *alpha* eleostearates are somewhat more intense than those of the adducts with the *beta* eleostearates. This result is to be expected as the 6.2 micron stretching of the $C{=}C$ group in the middle of a long chain compound is more intense if *cis* (as in the case of the adducts with *alpha*-eleostearates) than if *trans* (as in the case of the adducts with *beta*-eleostearates). Bands with maxima at about 11.1 and 11.9 microns, found in the spectra of the four adducts, may arise from breathing vibrations of the highly substituted cyclohexene ring in these compounds, but not enough model compounds of such heavily substituted cyclohexene rings are available to make these assignments certain. In the reaction with acrylonitrile, adduct formation is also clearly indicated by complete disappearance of the intense bands at 7.07, 9.14, and 10.42 microns, arising from various $CH_2$ deformations of the $C{=}CH_2$ terminal group.

*Ultraviolet Absorption.* The ultraviolet spectra of fumaronitrile and acrylonitrile and of the four adducts are shown in Figure 2. The spectrum of fumaronitrile exhibits the characteristic band of diene conjugation at 220 millimicrons, and evidence for reaction may be found, and a quantitative measurement of its rate may be made, by measurements of the disappearance of this band. As far as can be ascertained, the spectrum of fumaronitrile has not been previously published. Acrylonitrile would be expected to exhibit, in its spectrum, a similar band with maximum at about 210 millimicrons, beyond the limits of the instrument used in making these measurements. The spectrum of this compound published by Davis and Wiedeman (7) also fails to reach the required wavelength to permit observation and measurement of the expected absorption maximum.

Further evidence for adduct formation, as well as opportunity to follow quantitatively the rate of adduct formation, can be had from measurement of the triene conjugated bands of the eleostearates between 262 and 282 millimicrons. All of the curves show traces of the triene-conjugated eleostearates, representing approximately 1% unreacted ester.

*Plasticizer Tests.* All of the adducts were compatible at the time of milling and molding; however those stocks plasticized with the adducts of acrylonitrile developed a tacky, lacquer-like surface within 26 days. At 60 days the stock plasticized with the adduct of butyl *beta*-eleostearate was bleeding, showing definite incompatibility. Both the butyl *alpha*- and butyl *beta*-eleostearate-acrylonitrile adducts were satisfactory secondary plasticizers when incorporated with either DOP or tricresyl phosphate. There was no evidence of incompatibility during the period of observation. The fumaronitrile adducts have shown no signs of incompatibility during the 111-day period of observation.

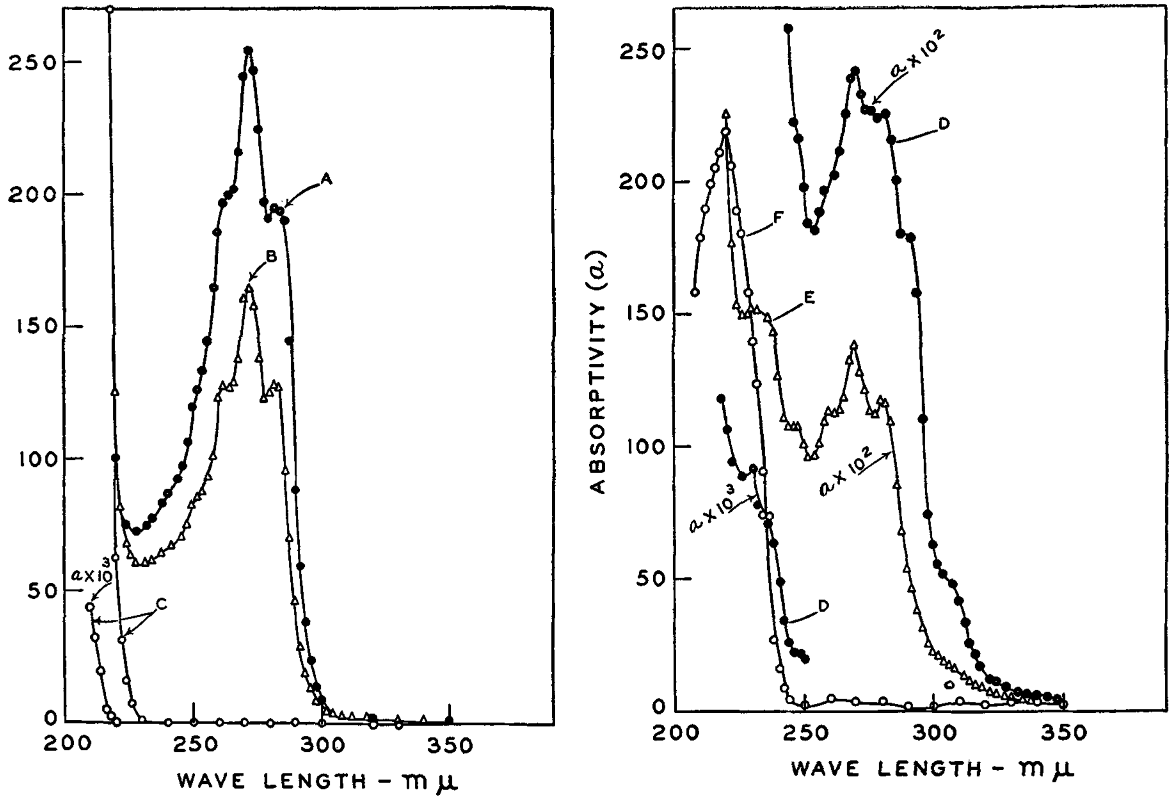


FIG. 2. Ultraviolet Absorption

A. Acrylonitrile—butyl *beta*-eleostearate adduct (in cyclohexane).
B. Acrylonitrile—butyl *alpha*-eleostearate adduct (in cyclohexane).
C. Acrylonitrile (in ethanol).
D. Fumaronitrile—butyl *beta*-eleostearate adduct (in ethanol).
E. Fumaronitrile—butyl *alpha*-eleostearate adduct (in ethanol).
F. Fumaronitrile (in ethanol).

The results of the screening tests (Table II) show that the stocks plasticized by the fumaronitrile adducts are somewhat better in tensile strength, compatibility, and volatility than those plasticized by the acrylonitrile adducts although the latter excel the former in modulus and brittle point.

It is apparent from these results that the presence of two cyano groups on the cyclohexene nucleus leads to greater permanence and an enhanced degree of compatibility between the plasticizer and the resin.

The plasticizing superiority of the *beta*-eleostearate adducts over the *alpha* observed previously (8) is not evident in the acrylonitrile adducts. The cause of this unexpected behavior is not known.

When compared to DOP (di-2-ethylhexyl phthalate), the most serious limitations of these adducts as primary plasticizers, eliminating the economics involved, are questionable compatibility in the acrylonitrile adducts and poorer low-temperature properties in the fumaronitrile adducts. By incorporating the acrylonitrile adducts with DOP or TCP it is possible to achieve either a reduction in volatility of DOP plasticized stocks or an improvement in the modulus and low-temperature performance of TCP plasticized stocks. This does not entail any sacrifice in the desirable plasticizing characteristics of DOP or TCP.

Preliminary experiments have shown that the

TABLE II

Plasticizing Characteristics of the Adducts

| Plasticizer | Tensile Strength P.S.I. | 100% Modulus P.S.I. | Elongation % | Brittle Point °C. | Torsion Test[a] °C. | Compatibility (days)[b] | Volatilities[c] % Loss |
|---|---|---|---|---|---|---|---|
| Acrylonitrile adduct of butyl *alpha*-eleostearate | [d] | 1310 | [d] | —31 | —27 | 108+ | 0.26 |
| *Acrylonitrile adduct + tricresyl* phosphate (50–50) | 3120 | 1630 | 290 | —15 | | 40+ | 0.16 |
| Acrylonitrile adduct of butyl *beta*-eleostearate | 2720 | 1320 | 320 | —33 | —26 | 60 | |
| Acrylonitrile adduct + DOP (50–50) | 2880 | 1460 | 300 | —31 | —28 | 40+ | 0.21 |
| Acrylonitrile adduct + tricresyl phosphate (50–50) | 3080 | 1600 | 300 | —15 | —15 | 40+ | 0.08 |
| Fumaronitrile adduct of butyl *alpha*-eleostearate | 3010 | 1780 | 310 | —9 | —9 | 111+ | 0.06 |
| Fumaronitrile adduct of butyl *beta*-eleostearate | 3070 | 1660 | 320 | —17 | —14 | 111+ | 0.09 |
| Control (DOP) | 2950 | 1600 | 310 | —33 | —24 | | 0.35 |
| Tricresyl phosphate | 3600 | 2430 | 275 | 0 | 0 | | 0.14 |

[a] Clash-Berg method (Ind. Eng. Chem., *34*, 1218 [1942]).
[b] + indicates no bleeding during time specified.
[c] Activated carbon method ASTM D 1203-52T.
[d] Sample did not rupture at maximum extension obtainable (380%) on IP-4 with a 1-in. test length at load of 2770 P.S.I.

acrylonitrile adduct of raw tung oil is also a satisfactory plasticizer. A detailed account of its properties will appear in a subsequent publication.

## Summary

Acrylonitrile and fumaronitrile have been employed as dienophiles in the Diels-Alder reaction with butyl *alpha-* and *beta-*eleostearates, and infrared and ultraviolet spectra determined for the addition product as well as for the dienophiles.

The adducts have been tested as primary plasticizers for vinyl resins and compared with dioctyl phthalate. The fumaronitrile adducts were found superior to the acrylonitrile adducts with regard to compatibility; however the latter are satisfactory as secondary plasticizers. By incorporating the acrylonitrile adducts with DOP or TCP, it is possible to achieve either a reduction in volatility of DOP plasticized stocks or an improvement in the modulus and low-temperature performance of TCP plasticized stocks. This does not entail any sacrifice in the desirable plasticizing characteristics of DOP or TCP.

## Acknowledgment

The authors express their appreciation to Elsie F. DuPré and Donald Mitcham for infrared and ultraviolet determinations; to L. E. Brown for elemental analyses, and R. R. Mod for assistance in the plasticizer screening tests.

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[Received March 19, 1956]

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# Some Derivatives of Hydroxyhydroquinone as Antioxidants

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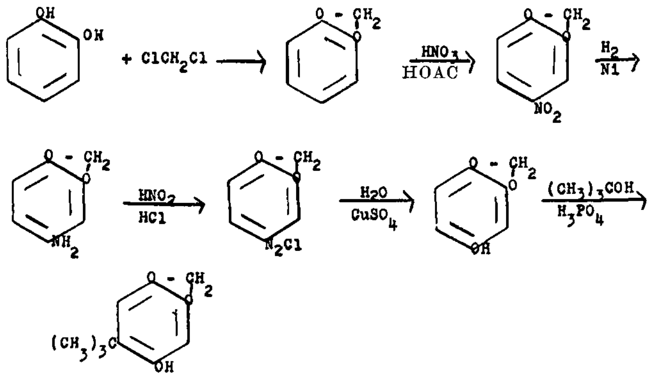
The improvement of inhibiting potency of phenolic antioxidants by the introduction of certain substituents into the proper position of the aromatic nucleus has been observed for several compounds. For example, Rosenwald, Hoatson, and Chenicek (9) showed that addition of certain alkyl groups to the nucleus greatly enhanced potency; the addition of a tert-butyl group in the ortho position was especially favorable.

This enhancement also takes place with certain substituted hydroquinones. Thus the potency of 4-hydroxyanisole (8) is greatly increased by the introduction of a tert-butyl group in the nucleus; the increase is larger when the substituent is in a position ortho to the free hydroxy.

Gleim and Chenicek (6) showed that butylation of 5-hydroxycoumaran, *i.e.*, introducing a butyl group in the position ortho to the hydroxy, markedly increases inhibiting potency. Since 5-hydroxycoumaran, an analog of 3,4-methylene dioxyphenol (sesamol) was found to be an effective inhibitor (4), it was worthwhile to investigate the effect of introducing a tert-butyl group into 3,4-methylenedioxyphenol and related compounds of this type. If the increase in potency is comparable to that for 4-methoxyphenol, it should be possible to produce very effective antioxidants since the 3,4-methylenedioxyphenol is initially more potent than 4-methoxyphenol.

The investigation of compounds related to methylenedioxyphenol wherein a polymethylene chain or two alkyl groups were substituted for methylene should also be of interest.

Although methylene dioxyphenol and similarly constituted compounds may be regarded as derivatives of hydroxyhydroquinone, this trihydric phenol is an unsatisfactory starting material for synthesis. The following equations show the method used in the synthesis of all the compounds of this type.



None of these reactions is difficult to carry out although the introduction of the methylene group and hydrolysis of the diazonium chloride give yields in the order of 40–60%. Butylation, unlike the butylation of p-methoxyphenol wherein a mixture of isomers is produced (14), gives only one product. No proof of structure of the butylated compounds was made, but their low solubilities in aqueous caustic and the presence of a hindered hydroxy group as shown by the infrared spectrum leave little doubt but that the tert-butyl group is ortho to the hydroxy. Formation of diethers, in which, instead of methylene, dimethyl, diethyl, dimethylene, or trimethylene is used, gave materials that underwent the same series of reactions without difficulties.

The compounds of this series were tested as antioxidants in gasoline and lard. The results in gasoline shown in Table I can be examined most easily by consideration of the last column wherein the potency of the materials is compared on an equimolar basis. The standard is taken as 2-tert-butyl-4-methoxyphenol to which a ratio of 1.00 is assigned.

On the basis of molar ratio, introduction of the tert-butyl group into 4-methoxyphenol increases the