0.3743 g. requires 16.67 cc. of $N/5$ KOH. Found: 16.67 cc. Calcd.: 0.2106 g. requires 18.79 cc. of $N/10$ KOH. Found: 18.78.

Piperonylphenylsuccinic acid was obtained in poor yield by the alkaline hydrolysis and decarboxylation of $3,4\text{-}CH_2O_2C_6H_3CH(CN)CH(CN)_2$ (XXV). The product was very pale yellow and melted at 210–212°, which agrees with the melting point of 211° observed by Lapworth and McRae.[16]

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Summary

1. Several new condensation products of malononitrile with aromatic aldehydes are reported.

2. These α,β-unsaturated dinitriles closely resemble α,β-unsaturated aldehydes and ketones in that they (a) dissolve in sodium bisulfite solution, (b) are oxidized by potassium permanganate, (c) are reversed into the original components by sodium hydroxide and (d) add the elements of hydrocyanic acid.

3. The trinitriles, resulting from the addition of hydrocyanic acid to the dinitriles, function as weak acids, dissolving in bases to form salts. Acidification of the potassium, ammonium and silver salts results in regeneration of trinitrile. The potassium salt alkylates with methyl iodide to give carbon–carbon alkylation.

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[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM MONOCHLORIDE UPON FATTY OILS

BY ELLERY H. HARVEY AND H. A. SCHUETTE

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The discovery by Parkes[1] that rubber could be vulcanized by immersing it in sulfur monochloride, followed by his observation[1] that "articles having properties analagous to those from india-rubber or gutta percha" could be made from fatty oils by the action of this substance, eventually gave rise to its introduction into the field of analytical chemistry by Warren[2] and then by Fawsitt.[3] Warren's conclusions, which were based upon the nature of the reaction product, were subsequently questioned.[4] Fawsitt's

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[16] Lapworth and McRae, *J. Chem. Soc.*, **121**, 1708 (1922).

[1] Parkes, British Patents 11,147, Sept. 25, 1846, and 2359, Oct. 22, 1855.

[2] Warren, *Chem. News*, **55**, 134 (1887); **56**, 222, 231, 243, 262 (1887); **57**, 26, 43, 113 (1888); **58**, 4, 15 (1888).

[3] Fawsitt, *J. Soc. Chem. Ind.*, **7**, 552 (1888).

[4] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan Co., London, **1921**, 6th ed., Vol. I, p. 474.

suggestion that the accompanying thermal effect might be utilized after the manner of Maumené's sulfuric acid number of fatty oils[5] received but scant attention and attempts to revive the former proposal by improving the technique of the method and following closely guarded experimental conditions, which measurements of this type require, have served to indicate that this feature of the reaction is impractical in so far as it might be used as a diagnostic "number" of fatty oils.[6]

The relationships which obtain in the oxygen family of the chemical elements and the renewed interest which has centered within recent years around selenium and its compounds suggested to the authors the desirability of observing the action of its monochloride upon the fatty oils under conditions[7] which simulate those once proposed by Fawsitt,[3] except that a diluent was to be used to facilitate the formation of a homogeneous reaction mixture.

Apparatus, Materials and Procedure.—The nested beakers of Fawsitt with cotton-filled intervening space were replaced by a silvered 300-cc. Dewar flask 55 mm. in diameter and 160 mm. in height. The latter was packed in kieselguhr and covered with a flanged Bakelite cap drilled to accommodate a stirrer, thermometer and pipet, respectively.

For experimental material there were selected twenty-two fatty oils representative of nine groups in the classification of Mitchell.[8] Their purity, in the sense that they conformed in name to that for which they were sold, was experimentally verified. Selenium monochloride, b. p. 130°, was prepared from elementary selenium by the method of Divers and Shimos[9] and the sulfur monochloride was purified from a commercial preparation by that of Pope.[10]

For the purpose of measuring the thermal effect in the contemplated reaction, 25 g. of the fatty oil in question and a like amount of pure, dry xylene were weighed into the calorimeter. There was then quickly introduced (15 sec.) 1 cc. of the reagent at the same temperature as the fatty oil solution, the stirrer was started and the maximum temperature rise and the time of reaching this point were noted. Since the loss of heat through the glass is negligible from the standpoint of the purposes for which this reaction serves, and since the only escape of heat is from the surface exposed to the outer air, radiation losses were corrected for by the formula $C = 0.5t(R_1 \pm R_2)$, in which R_1 and R_2 represent the initial and maximum temperatures, respectively, and t is the number of minutes which elapsed from the moment that the reagent was added to the time at which the maximum temperature was reached.[11]

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[5] Maumené, *Compt. rend.*, **35**, 572 (1852).

[6] Harvey and Schuette, unpublished data.

[7] By making allowance for the heat capacity of the apparatus and the specific heats of the solvent, oil, sulfur monochloride and reaction product it should be possible to calculate the exact amount of heat evolved, but since this reaction was studied from the standpoint of its probable suitability for analytical purposes, the observed rise of temperature is fully efficient.

[8] Allen, "Commercial Organic Analysis," Blakiston, Philadelphia, **1924**, 5th ed., Vol. II, pp. 109–113.

[9] Divers and Shimos, *Chem. News*, **49**, 212 (1884).

[10] Pope, *J. Chem. Soc.*, **37**, 356 (1880); Harvey and Schuette, THIS JOURNAL, **48**, 2065 (1926).

[11] Stillman, "Engineering Chemistry," Chemical Publishing Co., Easton, Pennsylvania, **1910**, 4th ed., p. 137.

The experiments were repeated in that the corresponding sulfur compound was substituted for the selenium monochloride so that comparative data might be obtained in the action of these substances under similar conditions. Data pertinent to these observations are recorded in the accompanying table.

Table I

Thermal Reactions of Sulfur and Selenium Monochlorides and Fatty Oils

		Sulfur monochloride			Selenium monochloride		
Group	Fatty oil	Max. rise, °C.	Time, min.	Rise per min., °C.	Max. rise, °C.	Time, min.	Rise per min., °C.
Olive oil	Almond	13.0	65	0.20	12.95	5	2.60
	Olive	10.0	165	.06	13.10	6	2.20
	Peanut	12.6	73	.16	16.90	2	8.40
Rape oil	Rapeseed	14.3	75	.19	12.80	6	2.10
Cotton seed oil	Soy bean	12.5	100	.12	14.85	3	4.95
	Sesame	11.7	75	.15	13.75	3	4.58
	Corn	11.9	100	.11	18.80	1	18.80
	Cottonseed	11.0	160	.06	14.90	4	3.70
Linseed oil	Tung	13.5	50	.27	8.55	4	2.14
	Linseed	17.3	65	.26	15.70	3	5.20
Castor oil	Castor	17.5	8	2.10	10.50	4	2.60
Cacao butter	Palm	12.9	20	0.64	11.40	13	0.87
Lard oil	Neatsfoot	16.1	50	.32	12.75	8	1.60
	Lard (oil)	16.0	55	.29	15.10	1	15.10
Tallow and butter	Tallow (beef)	..	..	...	12.85	5	2.57
	Butterfat	5.1	80	.06	11.85	10	1.18
	Lard	8.5	95	.08	13.10	4	3.30
Whale oil	Whale	15.4	50	.30	15.80	1	15.80
	Menhaden	18.3	25	.73	13.40	2	6.70
	Codliver	13.4	45	.30	14.00	4	3.50
Fatty acid	Oleic acid	15.0	50	.30	14.80	0.5	29.60

Discussion

Selenium monochloride is, in the light of thermometric measurements, more energetic in its action upon the fatty oils than is the corresponding sulfur compound. Although on the one hand the action of the latter appears to be, under the conditions set forth in this communication, of a rather complicated nature—an action which is characteristic not of groups whose members bear some resemblance to each other in their physical properties or chemical natures, but rather of individuals and one which cannot be ascribed alone to the nature of the fatty acid radicals present—on the other hand the action of selenium monochloride is more far reaching. In addition to substitution and addition, which results wholly if not in part with the sulfur compound, here there must also be taken into consideration the effect of the decomposition of the selenium compound itself. The deposition of elementary selenium in many case points to this conclusion. Ditmar[12] advances the opinion that at low temperatures

[12] Ditmar, *Kunststoffe*, **4**, 292 (1914).

the reaction with sulfur monochloride is one of addition and that at normal temperatures substitution accompanies this phenomenon. Lack of specificity is even more pronounced in this case. The thermal rise which was observed with approximately one-half of the oils whose behavior was studied is about the same as with the sulfur monochloride, but of greater significance is the fact that the rise per minute is appreciably greater. Palm oil is the only one which showed any suggestion of a similar behavior.

Conclusions

The thermal effect which is observed when selenium monochloride acts upon fatty oils is an additive one produced not only by substitution and addition but by the decomposition of the reagent itself. In view of this situation, the use of selenium monochloride under conditions which simulate in a measure those of sulfuric acid[5] is impractical as a test which has any diagnostic value for the fatty oils.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE ACTION OF SILVER ON DIPHENYL-TERTIARY-BUTYLETHYNYLBROMOMETHANE

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It was recently[1] shown that hexa-*tert.*-butylethynylethane reacted with liquid sodium-potassium alloy and with liquid sodium amalgams to give the corresponding alkali metal derivative of tri-*tert.*-butylethynylmethyl, thus indicating that aliphatic acetylenic groups possess the properties necessary to cause weakening of the central bond in a substituted ethane. These results would lead to the prediction that the replacement of two phenyls in hexaphenylethane by acetylenic radicals would not greatly decrease the dissociation. However, Moureu, Dufraisse and Houghton[2] have shown that the action of metals on diphenylphenylethynylchloromethane gives rise to a hydrocarbon which is much more stable than would be expected of *sym.*-tetraphenyldiphenylethynylethane. To gain further knowledge of the effect of acetylenic groups on the stability of hexa-substituted ethanes, a study of the closely related tetraphenyldi-*tert.*-butylethynylethane has been undertaken.

Diphenyl-*tert.*-butylethynylcarbinol was easily prepared from *tert.*-butylethynylmagnesium bromide and benzophenone. The bromide was prepared by the action of phosphorus tribromide on the carbinol. When an ether solution of this bromide was shaken with molecular silver in an

[1] Salzberg with Marvel, THIS JOURNAL, **50**, 1737 (1928).

[2] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).