

THE ACTION OF LIGHT ON TRUE NITROSO COMPOUNDS

by

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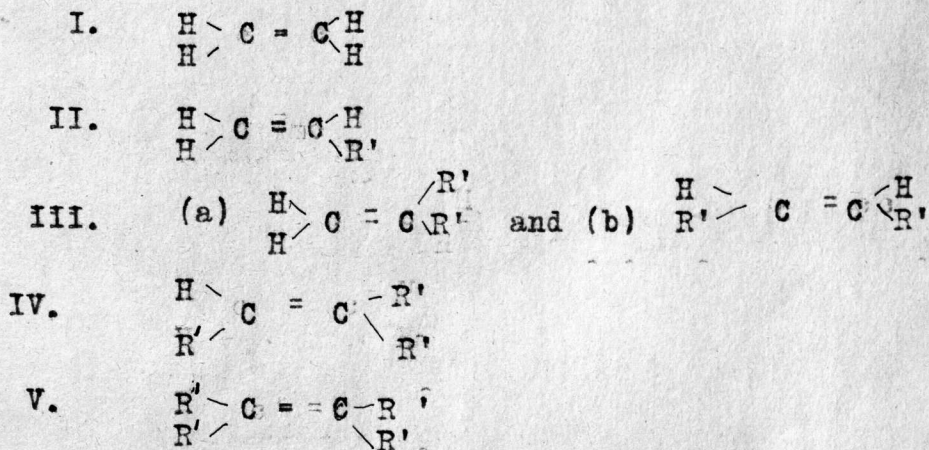
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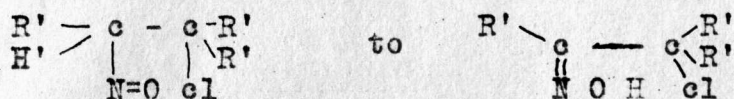
The addition of elements or groups of elements to unsaturated carbon compounds has always afforded valuable material for study in organic chemistry. The addition of nitrosyl chloride, nitrosyl nitrite and nitrosyl nitrate constitutes one of the most interesting chapters in the study of addition products at large, for reasons that will become apparent from the statements of problems to be made later.

The attribute unsaturated is used here in its strictest sense as applying to lack of saturation between carbon and carbon. Restricting it still more to so-called double linkage between carbon and carbon, it will become apparent that the following possibilities exist in so far as the carbon atoms, between which the lack of saturation occurs, and their immediate surroundings are concerned.



In these configurations more remote influences are left out of consideration, likewise the influence of substituted groups other than alkyl radicals.

If, as has been observed the more negative radical goes to the more differentiated carbon atom, the nitroso group will in each instance but case V to go a carbon atom with which at least one hydrogen atom is connected. The possibility is therefore given of a comparatively easy rearrangement of the nitroso group to an isonitroso or oxime group, e.g. thus (case IV).



As a matter of fact, in the formation of most of the nitroso chloride, nitroso-nitrite and nitroso nitrate addition products the first step of the reaction is indicated by a blue color of the solution in which the reaction takes place. The compound which crystallizes out, however, is white. While in the beginning these white compounds were regarded as nitroso compounds, as is indicated by the misnomers still in use, it was soon ascertained that at least some of them were isonitroso compounds, e.g. limonene nitroso chloride, and nitroso limonene, which latter is identical with carvoxime. \*(1) Moreover, even such compounds like pinene, nitroso chloride and nitroso pinene which

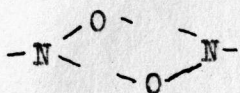
time were regarded as true nitroso compounds, were later shown to be isonitroso compounds. \*(2) Indeed, the changed character of so-called pinene nitroso chloride can readily be demonstrated by gently heating a chloroform solution of a carefully purified compound. Gentle heat not only brings the compound into solution but also colors it blue. Upon reformation of the white crystals, the blue color of the solution disappears.

As a further step in this line of argument, the formation of a blue nitrosochloride from a hydrocarbon of type V by Thiele <sup>\*(3)</sup> should be mentioned. In this instance there is no hydrogen atom with which the nitroso group can itself to an isonitroso group, hence the formation of blue crystals of methyl-ethylene.

From these observations the conclusion has been drawn that the formation of a blue compound is in itself evidence of the configuration represented in formula V. While such generalizations are very suggestive and even useful when taken with a grain of allowance, several other factors must be born in mind.

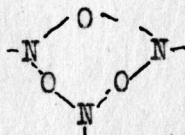
In addition to the possible change of a nitroso group to an isonitroso group it must be remembered that the  $-N=O$  group indicates a lack of saturation like that expressed by the  $R'_2 = C = C = R'_2$  and similar groupings in which this

lack of saturation is indicated graphically by a double bond between carbon and carbon. The double between nitrogen and oxygen is indicative of a like absence of saturation although this want of saturation may find expression in a different manner, at least in part. As is the case with the carbonyl(= C - O ) it may primarily find expression in the additive capacity for like molecules, namely in polymerization, forming heterocyclic compounds. Such polymerization may involve two, three, or possibly more molecules, though it is not likely that more than three are involved.



Bis nitroso

and

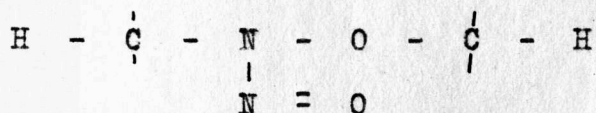


Tris (?) nitroso.

As a matter of fact, these names, the bis nitroso having been suggested first by v. Baeyer<sup>(4)</sup>, are misnomers quite as much as the designation nitroso for compounds possessing the characteristic of an oxime.

An explanation of the rearrangement for which no analogue can be found and which, therefore, seems far fetched because not supported by experimental data, is the one suggested by Lewinsohn,<sup>(5)</sup> viz., for isonitroso compounds  $\text{>C} = \text{N} \text{O} \text{H} + \text{H} \text{O} \text{N} = \text{C}$  the hydrogen goes to the carbon atom  $\text{H} - \overset{|}{\underset{|}{\text{C}}} - \text{N} = \text{O} + \text{O} = \text{N} - \overset{|}{\underset{|}{\text{C}}} - \text{H}$  and

the N = O group of the second molecule fastens to the N atom of the first molecule while the free bond of the C atom of the second molecule unites with the O atom of the first molecule giving the arrangement



If the double bond lies between two tertiary carbon atoms, a blue monomolecular compound is obtained, since the complex  $\text{:C} = \text{N O H}$ , which could bring about the formation of a bis - molecule in the above sense, does not develop.

The blue nitroso compounds, however are of interest not only because of their blue color and because this enables to draw conclusions (with due allowance) regarding the configuration of atoms to which the nitroso group has been added; but primarily because of the change which these compounds undergo when subjected to the influence of light under the proper conditions. It is because of the latter peculiarity that the study of these compounds especially that of the caryophyllene nitrosite were resumed after a lapse of more than ten years.

A perusal of the literature of nitroso and so-called nitroso compounds has revealed the isolation of ten blue compounds. They are herewith catalogued in the order of discovery.

- 1887, Monobromamylene nitrosate, <sup>(6)</sup> Wallach.
- 1894, Tetramethylethylene nitrosite, <sup>(7)</sup> J. Thiele.
- 1894,  $\Delta^4$ <sup>(8)</sup> - Terpen - 1-ol acetate nitrosochloride, <sup>(8)</sup>  
A Baeyer.
- 1895, Humulene nitrosite, A Chapman.
- 1899, Caryophyllene nitrosite, <sup>(10)</sup> Schreiner and Kremers.
- 1902, Trimethylethylene nitrosite, <sup>(11)</sup> J. Schmidt.
- 1902, Trimethylethylene nitrosate, <sup>(12)</sup> J. Schmidt.
- 1908, Caryophyllene nitrosochloride, <sup>(13)</sup> A. Lewinsohn.
- 1908, Caryophyllene nitrosobromide, <sup>(14)</sup> A. Lewinsohn.
- 1908, Caryophyllene nitrosochloride, (amorphous) <sup>(15)</sup>  
A. Lewinsohn.

### The Action of Light on Blue Nitroso Compounds.

The effect of light on caryophyllene nitrosite was first studied in a preliminary way by Schreiner,<sup>(16)</sup> He identified the gas given off, when sun light was allowed to act on the nitrosite suspended in benzene, to be nitrogen monoxide. He also ascertained the effect of different colored lights. This qualitative work was supplemented by Brandel whose results demonstrate quite conclusively that the action of light gives rise to a distinctly quantitative reaction.<sup>(17)</sup> Indeed, the results are so striking that it seemed well worth while to repeat them with other batches of nitrosite, especially since such material had been prepared by L. Dustin.<sup>(18)</sup>

An attempt was made to determine the reaction of light on the nitrosite when exposed suspended in hexane. About .6 gm of nitrosite was put into a small pycnometer of about 3 cm diameter which was then completely filled with hexane. The neck of the flask was attached to a Lunge nitrometer, also filled with hexane, by means of a rubber tube. It was then exposed to the sun light. After about a minute a slight cloudiness appeared and soon bubbles of gas were given off. Since the nitrosite was not very soluble in hexane the bubbles adhered about the crystalline masses causing them to float. In this way

much of the decomposition material was carried over mechanically into the nitrometer. The reaction was complete after about fifty minutes exposure to strong sun light. Since the hexane seemed to contain a considerable amount of gaseous hydrocarbons the volume of gas was somewhat large, to partially overcome this trouble the nitrometer was set in a cool place for a time to allow the gases to become condensed. The reading was then taken and the weight of the gas calculated as  $N_2O$  taking the vapor density of hexane into consideration. In spite of this it can be seen from the results that the lower temperature at which the reading was taken the lower would be the yield of gas. Compared with the results of Brandel the per cent of gas obtained was almost twice as great. According to Schreiner and Kremers 28.94% of the total amount of nitrogen present is liberated when the benzol solution of the nitrosite is exposed to sunlight, of which the total per cent of nitrogen is 10.2%.

(For results, see following page.)



A small quantity of the compound which had been prepared by I. Dustin was recrystallized from hexane. Several different forms of crystals were obtained which had different melting points thus indicating a mixture. The melting point before recrystallization was  $87 - 89^{\circ}$ .

After recrystallization crystals with the following melting points were obtained:  $92^{\circ}$ ,  $107^{\circ} - 109^{\circ}$ ,  $111^{\circ}$ ,  $92.5^{\circ} - 95^{\circ}$

Since the quantity of material was not sufficient for fractional crystallization to give enough for an analysis, no further work was done.

## APPENDIX.

1. Goldschmidt, Berichte, 18 p 2220.
2. Urban, A. C. J., 16, p. 404.
3. Thiele, B., 27, p. 454.
4. v Baeyer, B., 28, p. 648.
5. Lewinsohn, Inaugural Dissertation, p. 20.

6. Wallach, C., 241, p. 312. Nitrosite of Monobromamylene.

Dibromamylene was prepared and decomposed with alcoholic potash. The product was an oily mixture, insoluble and heavier than water. According to bromine estimations the fraction boiling at 115 to 125 degrees was richest in monobromamylene. This product was mixed with two volumes of glacial acetic acid and the solution saturated with nitrous oxide ( $N_2O$ ) which then turns blue. After complete saturation the liquid is poured into water when an ultramarineblue crystalline mass slightly contaminated by oily products separates out. The crystals dried on porcelain plates are very soluble in ether and benzol, insoluble and in petroleum ether. The product was purified by precipitating it from a concentrated solution of benzol with petroleum ether. In this way feathery crystals were obtained colored like copper sulphate. When heated decomposition sets in between 130 and 140 degrees, with the elimination of red brown vapors leaving a colorless solid with a high melting point.

The analysis obtained was unsatisfactory.

When mixed with piperidine in the cold reaction begins to take place which is readily completed by warming. The addition of water to this almost colorless liquid precipitates an oil which after being washed with water and

hydrochloric acid becomes crystalline. The recrystallized substance from alcohol is colorless, contains much bromide, can be sublimed, when heated alone with water has a camphor-like odor and has neither basic nor acid properties. In the aqueous mother liquids there remained considerable nitrous acid.

7. J. Thiele, B, 27, p. 455. Tetramethylethylene-nitrosochloride.

The hydrocarbon is dissolved in an excess of strong alcoholic hydrochloric acid and concentrated sodium nitrite is slowly added in slight excess under constant cooling in a freezing mixture. The liquid is colored blue and with an excess of nitrite green. An excess of water is added and the nitrosochloride precipitated as a light blue powder.

For analysis the compound was redissolved in alcohol and precipitated with water.

Analysis	Theoret. per cent	Cl.	23.41	N	9.36
	Found	"	23.55	N	9.61

Molecular weight determination in glacial acetic acid.

Analysis	Theoret. $C_6-H_{12}$	N	O	Cl	149.5
	Found	"			150; 153.

Tetramethylethylene nitrosochloride is a powder having the color of blue vitriol and a camphoraceous pungent odor. It melts at 121 degrees with slight evolution of gas. It is quite volatile and can be sub



9. A. Chapman, J.C.S., 67, p. 782. Nitrosite of Humulene.

To a mixture of equal volumes of humulene and light petroleum a concentrated aqueous solution of sodium nitrite was added and the mixture thoroughly cooled; a volume of glacial acetic acid equal to that of humulene was then added little by little with frequent shakings. The upper hydrocarbon layer rapidly acquired a deep blue color which, on standing for some time became somewhat green. From this green layer deep blue needles soon separated, which after some hours, were collected and purified by one recrystallization from boiling alcohol, from which solvent it separated in the form of magnificent blue needles.

Two separate preparations gave the following results on analysis;

0.2085 gave 18.5 cc moist N at 18° and 762 mm N = 10.24  
 0.207 gave 17.8 cc moist N at 15° and 756 mm N = 10.24

$C_{15}H_{24}N_2O_3$  requires N = 10.00 per cent.

The oily mother liquors yielded a second crop of crystals, which, when recrystallized from alcohol were colorless. This compound gave the following numbers on analysis:

0.203 gave 17.5 cc moist N at 18° and 758 mm N = 9.93

$C_{15}H_{24}N_2O_3$  requires N = 10.00 per cent.

From this it appears that the white compound is isomeric with the blue, the latter former the isonitroso derivative of humulene.

The blue compound recrystallized from alcohol melted at 120 degrees, the effect of each subsequent crystallization being to increase the melting substance paler in color. The melting point of the colorless compound was 166 to 168 degrees with decomposition.

10; Scheiner & Kremers, Pharm. Archives, 2, p. 282.  
Caryophyllene Nitrosite.

Equal parts of caryophyllene, low boiling petroleum ether, a saturated solution of sodium nitrite and lastly, glacial acetic acid are mixed, continually agitating the solution. This solution is allowed to stand for a few minutes and then strongly cooled in a freezing mixture. Upon agitation the upper blue layers solidify to a mass of deep blue crystals. Crystallization usually took place when so treated, but <sup>should</sup> it fail the merest trace of solid nitrosite brought in contact with the cold solution will cause it to solidify immediately to a mass of crystals. The magma is transferred to a force filter, first washed with cold alcohol, then with water, and lastly with a little more cold alcohol, in which the nitrosite is but sparingly soluble. The yield obtained is from 12 to 14 per cent. The solutions must not be exposed to white light as the blue compound is thereby decomposed.

The nitrosite can be recrystallized from hot alcohol in the dark, in which it is very soluble and deposits the nitrosite in beautiful deep blue needles on cooling, which melt at 113 degrees.

11: J. Schmidt, B. 35, p. 2327. Trimethylethylene Nitrosite.

A solution of 20 gm of trimethylethylene in 60 cc of ether are cooled to 0° and a slow stream of the moist gases formed from 80 cc of concentrated nitric acid and about 120 gm arsenic trioxide is passed into the solution. The liquid becomes warm but should be kept below a temperature of 10 degrees. When the liquid has a blue green color the reaction is complete. It is washed 10 - 12 times with cold water to remove the excess of nitrous acid. If the reaction has taken place properly the liquid should have a blue, not blue green. color. After drying with fresh anhydrous sodium sulphate the liquid is evaporated at a moderate heat in a water bath while stirring continually. A very mobile blue liquid remains which may be concentrated still more in a vacuum dessicator. The yield is about 35. g (41.5 g theoretical.)

Trimethylethylene nitrosite when freshly prepared is a deep blue oil with a pungent odor, volatilizes and decomposes readily. It can be kept for a length of time only in a dark cool place. It decomposes in diffused daylight and very rapidly in direct sunlight. After a time it is completely converted to an almost colorless liquid.

12. J. Schmidt. B., 35, p. 23. Trimethylethylene Nitrosate.

A solution of 20 gm of trimethylethylene in 66 cc of ether is cooled in a freezing mixture and nitric oxide, formed from heating lead nitrate, is gradually passed in until the solution is saturated. The solution becomes green and after <sup>a time</sup> white crystals begin to separate. (Bis - Trimethylethylene nitrosate ).

The filtered mother liquor is washed ten to twelve times with water, dried with anhydrous sulphate and concentrated on a water bath at moderate heat. The remaining blue green trimethylethylene nitrosate is freed from ether in a vacuum dessicator.

The yield is 30 to 35 gm of liquid nitrosate and 2 to 6 gm of crystalline bis - nitrosate.

13. Lewinsohn, Inaugural Dissertation, p. 43. Caryophyllene Nitrosochloride.

Prepared according to Kremers and Schreiner's method it was observed that a considerable part of the nitrosochloride separated when standing in the cold. The nitrosochloride had a very light blue color which did not disappear even after washing with ice cold ether or alcohol. Preparations did not bleach until after several months, after being kept in light or darkness without changing the melting point. He found the melting points of several trials to be  $160^{\circ}$ ,  $162^{\circ}$ ,  $163^{\circ}$ ,  $158^{\circ}$ .

14. Lewinsohn, Inaugural Dissertation, p. 59.  
Caryophyllene Nitrosobromide.

A mixture of equal volumes (5 cc) of caryophyllene acetic ether, alcohol and ethylnitrite was cooled to  $-20^{\circ}$  and 5 cc of a saturated ethereal solution of hydrobromic acid was added very slowly while stirring continually. During the reaction the nitrosobromide separated out. The product when washed with cold alcohol was a coarse crystalline powder with a light blue color.

It melted at  $140^{\circ}$ , undergoing decomposition.

15. Lewinsohn, Inaugural Dissertation, p. 93.  
A Green Amorphous Nitrosochloride of Caryophyllene.

A mixture of 5 cc caryophyllene and a like amount of ethylnitrite were cooled to  $-20^{\circ}$  to which 5 cc of alcoholic hydrochloric acid was very gradually added, keeping the mixture below  $-10^{\circ}$ . The product is a tough green blue mass which was triturated with alcohol a few times and then pressed on porcelain plates. After a few days the mass becomes solid so that it may be powdered. The bright green product is treated with twice its weight of low boiling petroleum ether. A pale yellow constituent remains undissolved which when purified and recrystallized from chloroform was identified as inactive nitrosochloride.

The green petroleum ether mother liquor was diluted with ether, shaken out ten times with a 1% solution of sodium bicarbonate and then ten times with water; the ether was evaporated and again treated with petroleum ether to separate brown resinous substances. The addition of petroleum ether is continued so long until a filtered portion remains clear on the addition of a large excess of petroleum ether. About twenty-five times as much petroleum ether was used as the original crude product. The petro-

leum ether is distilled off at a very gentle heat almost completely and the last traces are removed in a vacuum desiccator. A light green fragile substance remains which is readily soluble in most solvents. All attempts at obtaining a crystalline compound were of no avail.

100 gm of crude caryophyllene yielded amorphous substance which was analysed.

Theoret. Found.

$C_{15}H_{24}N O Cl$						
C	66.75	65.97;	65.85			
H	8.97	9.17;	9.13			
N	5.21			5.97	5.05	5.65
Cl	13.145					13.48; 13.23; 13.07

This compound melts at 67 to 69 degrees and decomposes at 95 degrees with the evolution of gas.

16. The Action of Light on Caryophyllene Nitrosite.  
Phar. Arch. 2, p 286.

By boiling humulene nitrosite with alcohol until the blue color was gone Chapman prepared the white nitrosite of humulene. This same method was tried for caryophyllene nitrosite but did not give good results. The quantity of white compound which separated was exceedingly small and accompanied by a large amount of oil. It was thought that long boiling was detrimental so the blue nitrosite was allowed to stand in contact with alcohol for a time. The same was done with benzol in which the nitrosite is very soluble. After standing several weeks, no change was noticed.

It had been observed that the reaction with the boiling alcohol took place much more readily on bright days than on cloudy. Therefore it was thought that light played some part in this reaction and the above benzol solution and magma in alcohol were exposed to the sun light. Almost immediately the bright blue benzol solution began to give off a gas and to become paler in color, while small felt like white crystals began to separate. In less than an hour the reaction was complete, the color had disappeared and white crystals had separated. The nitrosite in the alcohol did not begin to change as readily, after a short

time bubbles arose and the blue crystals began to disappear. Before an hour the color had completely disappeared and a layer of oil had formed in the bottom. This oily product was called the  $\alpha$  compound and the above white crystals the  $\beta$  compound.

An investigation of the colorless gas liberated from a benzol solution showed it to be nitrogen since it is non-combustible nor capable of supporting combustion, neither was it absorbed by potassium hydrate solution.

A quantitative estimation of the gas liberated was made by placing 0.5gm of nitrosite into the funnel of a nitrometer which was completely filled with mercury. A few cubic centimeters of Benzol were added and the solution allowed to flow into the nitrometer. The completely filled nitrometer was exposed to sunlight. The amount of nitrogen liberated was found to be 28.9% of the total nitrogen present.

The average yield of  $\alpha$  compound obtained by exposing the blue nitrosite to light in benzol solution was about 12%. The melting point was 146 - 148 at which temperature it decomposed. It is sparingly soluble in the different solvents.

To determine the action of colored light on the blue nitrosite in benzol solution, narrow test tubes were passed through the corks of wide mouthed bottles which con-

tained the colored solutions. A few cubic centimeters of a solution of the blue nitrosite in benzol were placed in each test tube and stoppered with a notched cork. The colored solutions were all of about the same intensity. The bottles were then set in the sunlight and results were recorded in the following table:

Colored Solution	Evolution of Gas.	Separation of Crystals	Color of Sol. 30 m.
Aniline Violet		19 minutes.	Very Blue.
Amm. Copper Sulph.	No change after several days.		
Copper Sulphate.	Crystals separated after five hrs		
Chromium Sulph.		13 Minutes.	Quite blue
Nickel Nitrate,	5 min.	29 min.	Very blue
Potass. Chrom.	1 Min.	8 Min.	Almost colorless. 40 min. complete.
Potass. Dichrom.		9 min.	" "
Cobalt Nitrate.	10 min.	12 min.	Quite blue.
Eosin		13 min.	Light blue
Water.	6 min.	9 min.	Almost colorless. 40 min. complete.

The results show that the yellow and orange rays of the spectrum are the most active while the blue rays of the copper solutions had practically no effect.

5 g of the blue nitrosite were mixed with 20 cc of absolute alcohol and exposed to the sunlight until colorless. The solution was then allowed to evaporate continuously and the white crystals separated from an oily residue which were collected and dried on a porous plate. The yield of this substance was 5%. The melting point of this  $\alpha$  compound was 113 to 114 degrees. A nitrogen determination gave the following: 0.1151

0.1151 gr substance gave 10.8 cc moist N at 25°

Theoret for C H N O . N = 10.03% found 10.19%

A molecular weight determination indicated a monomolecular compound.

The blue mother liquor from the nitrosite was washed with the water and placed in a flask with a rubber stopper connected by bent glass tube to a gasometer so as to collect the gas over water. It was then exposed to sunlight. The liquid changed to a yellow color from which a solid crystalline substance separated which, when collected, washed with petroleum ether and alcohol had a melting point of 144, almost the same as the  $\beta$  compound to which it is very similar.

To determine roughly how much nitrosite might still be contained in the mother liquor, from another portion 65 cc of caryophyllene which had yielded 6.1 g of nitrosite,

was treated as above. 850 cc of gas were obtained corresponding to about 36.6 g of nitrosite which still remained in the mother liquor

17) Unpub. Results. by I.W.Brandel.

Wt of Nitrite	Vol of Gas.	Temp.	Pres- sure.	Vol. of Gas at 0 & 760 mm	Wt. of Gas as N O	Wt. Residue Filtered off	Wt. Res. from Vap-	P C. of Gas.	P C. Res. of	P.C. of 2nd.res.	Total per cent
0.8900	37.4	24.0	738	33.37	0.06557	--	--	7.36	--	--	--
0.6135	26.0	24.5	738	23.16	0.04450	--	--	7.25	--	--	--
0.9570	42.0	25.0	740	37.46	0.07360	0.2465	0.5990	7.69	25.75	62.59	96.03
0.9148	37.8	25.0	740	33.70	0.06622	0.2231	0.6185	7.23	24.38	67.61	99.22
1.4045	58.6	24	741	52.50	0.10316	0.4485	0.8490	7.34	31.93	60.44	99.71
1.2775	52.8	23.5	740	47.33	0.09300	0.3120	0.8530	7.28	24.42	66.77	98.47
0.8000	32.8	22.5	740	29.50	0.05726	0.2505	--	7.24	--	--	--

## 18) PREPARATION OF CARYOPHYLLENE NITROSITE, By L. Dustán.

The nitrosite was prepared according to the directions of Schreiner and Kremers, with this exception, that the low temperature of the freezing mixture was used from the very beginning. The theoretical yield of nitrosite from 10 cc of caryophyllene (weighing 9.033 grams) is 12.39 grams. Inasmuch as the yield of nitrosite is an important factor in the interpretation of results obtained in certain experiments conducted with the mother liquids the amounts are herewith tabulated. Schreiner and Kremers had obtained a yield of 12 to 14 per cent.

Expt.	Amt. of Nitrite	% of Theoretical Yield.
1	1.125 g.	9.1
2	1.195	9.6
3	1.289	10.4
4	1.306	10.5

Approved

Edward Keener

Prof. of Pharm. Chemistry