obtained the compounds $C_{11}H_{20}$, $C_{10}H_{18}$ and C_8H_{14}, all showing the same properties as the series C_nH_{n-2} referred to above. The results of this work will be published shortly.

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A FULLER STUDY OF THE NEUTRAL SULPHITE METHOD FOR DETERMINING SOME ALDEHYDES AND KETONES IN ESSENTIAL OILS.

BY S. S. SADTLER.

Received August 14, 1905.

PAPERS on this subject have been read at two different times by the author, as follows: October 15, 1903, published in the *Journal of the Franklin Institute*, December 1903, and February 19, 1904.[1] The work was based upon work of Tiemann,[2] Dodge[3] and Heusler,[4] in which neutral sulphites were used to react with the aldehydic constituents of certain essential oils, and the amount of aldehyde present was determined by differences of volume as measured in cassia flasks, etc. Alkali was formed by the reaction, and was indicated by phenolphthalein and, by neutralizing the alkali as formed, the end of the reaction could be ascertained.

The author measured the amount of standard acid required to neutralize the alkali and by calculating the amount, was able to determine the percentage with a fair degree of accuracy. He was in error, however, in judging the extent of the application of the reaction, as in his earlier experiments only citral, cinnamic aldehyde, benzaldehyde, vanillin and formaldehyde were tried, all of which react, although they, as now shown, react differently. These successes were a little misleading.

Burgess,[5] in a paper read December 28, 1903, several months after the reading of the earliest one by the author, but almost coincident with its publication, points out the reactions with citral, cinnamic aldehyde, carvone and pulegone, and states that the same would probably be true of citronellal and olefinic aldehyde.

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[1] *J. Soc. Chem. Ind.*, March 31, 1904.

[2] *Ber.*, **31**, 3334.

[3] *Am. Chem. J.*, **12**, 55 (1890).

[4] *Ber.*, **24**, 1805.

[5] *Analyst*, p. 78, 1904.

He does not describe any titration method, however, and refers to measuring in a cassia flask.

His conclusions with regard to the substances that will react are most of them confirmed by the author's coincident or more recent work. He states, however, that carvone reacts with one molecule of sulphite, while the author has abundant experimental evidence to show that it reacts with two molecules and he states that citronellal reacts. The author obtained such feeble results with oil of citronella, that he believes the reaction observed was caused by the small amount of citral contained in this oil, and, furthermore, doubts its activity because of theoretical consideration which will be advanced in this paper. Tiemann[1] only claims that citronella reacts in the presence of sodium bicarbonate.

The substances tried by the author were:

Name.	No. of double bonds.	Class.	No. mols. sulphite.	Remarks.
Citral	2	fatty	2	Reaction slow.
Cinnamic aldehyde	2	aromatic	2	Reaction most energetic.
Benzaldehyde	..	"	1	Reaction moderate.
Vanillin	..	"	1	....
Carvone	1	ketone	2	Reaction moderate.
Pulegone	1	"	2	"
Formaldehyde	..	fatty	2	Reaction instantaneous.
Citronellal	1 (remote from CHO group)	"	..	No reaction.
Camphor	none	......	..	"
Menthone	"	......	..	"
Fenchone	"	......	..	"

The method given by the author[2] has been used for subsequent work. Precautions and observations will be given herewith for the substances studied.

In nearly all cases the flask containing the oil and neutral sulphite was allowed to stand over night to be sure that no more alkali formed. Rosolic acid was used as indicator, and the oils were carefully neutralized with tenth-normal potassium hydroxide before adding the sulphite solution. An important indication of the end of the reaction in most cases is the disappearance of the characteristic odor, noticeable in the cases of cinnamic aldehyde, citral, carvone, pulegone and benzaldehyde. Kerosene was used as a diluent for aldehydes and ketones used by themselves and for oils with high percentages of the same.

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[1] *Ber.*, **31**, 3336.

[2] *J. Soc. Chem. Ind.*, March 31, 1904.

CITRAL.

On going over the results with oils containing citral, no additional points of particular interest were found. With lemon oil it was found well to take 15 grams when half-normal hydrochloric acid was used, and heating (immersed in boiling water) was resorted to as soon as the first color that formed with shaking was discharged by the half-normal hydrochloric acid.

The sample of lemon oil was an old one which had previously been found to contain considerably more aldehyde.

Percentage of citral	3.69	3.80	3.75

Lemon-grass oil almost 1.5 grams used in 10 cc. of kerosene.

Percentage of citral	72.8	72.2	71.7

CINNAMIC ALDEHYDE.

With oils of cassia and cinnamon the reaction was very much quicker than with citral, especially in the case of the cassia, and in fact some way of rendering it less rapid should be found. The author considered, after getting the material together for this paper, adding the sulphite, to be used, slowly as the sodium hydroxide formed was neutralized so that the alkali could not polymerize or otherwise act upon the aldehyde or its addition product. Heating is only necessary to complete the reaction.

Percentages of cinnamic aldehyde in a sample of nearly pure cinnamic aldehyde.

Cinnamic aldehyde (1.5 grams)	95.5	94.6	94.6	94.0
Oil of cinnamon (2 grams)	72.8	72.5	73.8	......
Oil of cassia (2 grams)	77.6	78.3	81.5	......

CARVONE AND PULEGONE.

With compounds containing carvone, such as caraway and dill oils, the reaction is about midway in rapidity between the oils containing cinnamic aldehyde and those containing citral. Heating completes the reaction, after neutralizing several times in the cold.

Carvone (97 per cent.)	96.4	97.5
Carvone, another sample	87.7	89.0
Oil of caraway	52.6	53.6

With pulegone the action is very slow and the reaction is probably 2:1, but this point has not yet been verified by the author. It smelled very strongly of menthol, after the pulegone had been removed by the reaction.

BENZALDEHYDE.

In the case of benzaldehyde it is absolutely necessary to carry out the operation entirely in the cold by violent shaking, and in this case the analyses were carried out by adding the sulphite in small amounts at first. A relatively large amount of rosolic acid or phenolphthalein (as it can be used equally well in the cold) must be used and even then the pink color is very faint, but additions of acid must be kept up until it is completely dissipated. It is especially important to allow the flask to stand over night to see if any additional amount forms.

To further standardize the reaction with benzaldehyde, the clear filtrate was in several cases distilled with steam, and 98 per cent. of the amount taken was recovered. Carbon dioxide was passed through the warm solution to evaporate off the ether.

Steam distillation of the aqueous layers was tried with other substances, but benzaldehyde was the only case where more than a small amount could be recovered. This difference in action may be partly due to the form of combination, but is probably largely due to the different action of steam on the particular aldehydes and ketones themselves.

To standardize the reaction for benzaldehyde, it was thought best to measure the amount of standard alkali (half-normal) used to neutralize the sample and to calculate this to benzaldehyde as the oxidation to acid is so extensive.

Results: 93.5 (not completely decolorized), 96.8, 98.0, 99.0 (fully decolorized).

VANILLIN.

In the case of vanillin there seemed to be a reaction, but the author found difficulty in indicating it. With rosolic acid and phenolphthalein it did not show any formation of alkali, but as pure vanillin dissolved readily in neutral sulphite, it was believed that reaction took place with one molecule of sulphite, as was the case with the benzaldehyde, and the alkali was at once taken up by the vanillin. Previous neutralization of vanillin with alkali, darkened up the solution so that the results were uncertain.

It was found that by taking different amounts of neutral sulphite and vanillin, with more than about one molecule of sulphite to one of vanillin a formation of red color could be observed with a little carefully neutralized cinnamic aldehyde, and with appreciably less that the color did not undergo much change.

A microscopical examination of the residues showed the presence of needle-like crystals of vanillin when in excess at one stage, apparently hygroscopic bunches of very fine crystals of the addition product, with no vanillin at another stage, and then the showing of long effloresced crystals of neutral sulphite itself when more sulphite than the 1 : 1 portion was present.

It is therefore believed by the author that vanillin reacts with one molecule of neutral sulphite.

REAGENTS AND BLANKS.

If the titration is performed hot, it is very hard to decide about the correction to be made for the blank, as the amount of acid necessary to completely discharge the color in the sulphite solution when hot is considerable, but when largely used up in the reaction, would undoubtedly not be so much. The amount of free alkaline reaction in the cold is small and probably even less should be deducted. In this paper, the deductions were about 0.24 cc. of half-normal acid and when 40 cc. were used for titrations; this would not give a large error, if a smaller figure were correct.

The samples of sulphite used by the writer did not vary much, and it is an unexplained fact that the most carefully purified samples showed the stronger alkaline reactions.

NEUTRALIZATION OF SULPHITE SAMPLES.

	Cold. cc.	Hot. cc.
Mallinckrodt sample (anhydrous)	0.24	2.32
General Chemical Co (pure cryst.)	0.22	2.37
General Chemical Co (commercial cryst.)	0.14	1.86
Powers-Weightman-Rosengarten Co. (large, clear crystals)	0.78	2.92

A point to be observed is that correspondingly more of the crystallized salts should be taken as compared with the anhydrous.

THEORETICAL CONSIDERATIONS.

Probably enough substances have now been studied to begin to formulate an opinion as to what influences tend toward combinations of aldehydes and ketones with neutral sulphites.

It may be noticed that double bonds seem to aid in bringing about a reaction when close to the CHO group, as is the case with citral and cinnamic aldehyde.

Proximity of the benzene nucleus to the CHO group as in the case of benzaldehyde and vanillin is probably a factor. It may be noticed that in the case of the most active aldehyde of high molecular weight, cinnamic aldehyde, both the benzene ring and the double bond are near the CHO group.

Citronellal, $C_{10}H_{18}O$, is like citral, $C_{10}H_{18}O$, except that it lacks two double bonds and the one it has is furthest removed from the CHO group, so if it does not react, as seems to be the case, it would not be anomalous.

With ketones, the only ones the author has found active probably contain double bonds and as near as possible to the CO group. Ketones which probably do not contain any double bonds, such as Japan camphor, menthone and fenchone, do not seem to react.

It might be inferred from the fact that formaldehyde reacts so readily, that the smaller the molecular weight, the more readily the reaction takes place.

The author means to look into the reaction with formaldehyde as the analyses he has made point to two molecules of sulphite reacting, which would mean a rearrangement of the CHO group and not merely saturating double bonds in accordance with Tiemann's reaction. The reactions of benzaldehyde and vanillin, however, seem to indicate that the saturation takes place in the CHO group, as it is unlikely that any of the double bonds of the benzene ring would be saturated, and furthermore there is only one molecule of sulphite entering into the reaction.

Similar to benzaldehyde are salicylic, anisic, cuminic aldehydes and heliotropin which promise well for reacting with one molecule of neutral sulphite.

As Tiemann claimed that citronellal reacted with neutral sulphites in the presence of bicarbonate of soda, a line of investigation with its use should be tried with aldehydes and ketones not reacting with neutral sulphite alone. The author, however, does not see his way clear to do this in the near future.

As heat brought about reaction more rapidly than in the cold, slight pressures were tried with several oils, but it was not found to be useful.

In this paper the author has endeavored to make a few additional analyses of compounds containing citral and cinnamic aldehyde so as to corroborate his previous claim as to the proportions of the reacting substances, to investigate the reaction with benzaldehyde and vanillin, to obtain a satisfactory assay method for benzaldehyde, and to get further light on the extent of the reactions.

The author regrets that with a very limited amount of time available for this work he has not been able to analyze more samples and obtain more analytical results on those examined, and that, not being directly connected with essential oil interests, he has not had available the fresh samples he would have preferred, and all the varieties he would have liked to examine.

The author wishes, however, to express his thanks to Dr. F. D. Dodge for additional samples, besides those that had been kindly furnished previously.

LABORATORY OF SAMUEL P. SADTLER & SON.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 113.]

THE SYNTHESIS OF 7-NITRO-2-ALKYL-4-KETODIHYDROQUINAZOLINES FROM 4-NITROACETANTHRANILIC ACID, AND FROM 4-NITROACETANTHRANIL.

BY MARSTON TAYLOR BOGERT AND S. H. STEINER.

Received September 14, 1905.

OF THE four possible Bz-nitro-2-methyl-4-ketodihydroquinazolines, three have been described already: the 5-nitro compound by Bogert and Chambers,[1] the 6-nitro by Dehoff[2] and Thieme,[3] and the 8-nitro by Zacharias.[4] In the present paper, the 7-nitro compound is described, thus completing the series.

We have also prepared the 4-nitroacetanthranil, and find that it resembles the 6-nitro isomer[5] in general properties.

The starting-point for these syntheses was *o*-toluidine. This was converted into 4-nitro-2-acetaminobenzoic acid by two slightly different methods.

I. *o*-Toluidine was nitrated in presence of excess of concentrated sulphuric acid, the 4-nitro-2-toluidine thus produced acetylated, and the acetyl derivative oxidized to the nitroacetaminobenzoic acid.

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[1] This Journal, **27**, 655 (1905).

[2] *J. prakt. Chem.* [2], **42**, 347 (1890).

[3] *Ibid.*, **43**, 473 (1891).

[4] *Ibid.*, **43**, 441 (1891).

[5] See Bogert and Chambers: this Journal, **27**, 649; Bogert and Seil: *Ibid.*, **27**, 1305.