Determination of Mono- and Dialkylacetylenes

CHARLES D. WAGNER, THEODORA GOLDSTEIN, AND EDWARD D. PETERS
Shell Development Company, Emeryville, Calif.

A method is described for determining mono- and dialkylacetylenes, of four and five carbon atoms, in the presence of related paraffins, olefins, or diolefins. The method is based on the reaction of the alkynes with methanol in the presence of a catalyst mercuric oxide–boron trifluoride to produce ketals which are subsequently hydrolyzed to ketones. Allenes and high concentrations of peroxides and cyclopentadiene interfere; they are the only materials known to undergo interfering reactions. Interference by carbonyl compounds originally present is obviated by suitable blank determinations, omitting the catalyst. Although the method does not generally give stoichiometric results, recoveries of about 92% are consistently obtained, making possible use of an empirical correction factor (1.09). On samples containing as little as 0.5% acetylenes, accuracy is ±3% and on samples containing 0.1% acetylenes ±10% of true value. Elapsed time for one analysis is 2 to 3 hours; actual operator time is 40 to 60 minutes.

IN THE production of isoprene for use in the synthetic rubber program, a method was desired to determine small concentrations of 2-butyne, 1-pentyne, and 3-methyl-1-butyne in the crude isoprene product. A search of the literature revealed no physical or chemical methods for the determination of mono- plus dialkylacetylenes in the presence of olefins. (Mass spectrometry, which the authors have used to check the purity of the alkylacetylene samples, offers some promise for the determination of 2-butyne in mixtures of moderate complexity.) In many laboratories, monoalkyl acetylenes are commonly determined by a method similar to that used by Hill and Tyson (*3*) for the determination of 1-heptyne. In this latter method, which is similar to the one devised by Chavastelon (*1*) and modified by Ross and Trumbull (*7*) for the determination of acetylene, the monoalkyl acetylene is treated with silver nitrate and the resulting nitric acid is titrated. This acidimetric method cannot be used for the direct determination of alkynes containing no hydrogen atom replaceable with silver, but if such substances have a low molecular weight—e.g., 2-butyne—they can be determined in the presence of monoalkyl acetylenes by the difference between values obtained by the acidimetric silver procedure and the methanol method given in this paper.

Nieuwland and his co-workers (*4*) reported that dimethyl ketals of methyl alkyl ketones may be prepared and isolated in good yield (about 80%) by reaction of monoalkyl acetylenes with methanol in the presence of a catalyst prepared from mercuric oxide and boron trifluoride. Michael (*5*) and Mowat and Smith (*6*) succeeded in hydrating 2-hexyne and 2-pentyne, respectively, to form the ketones in good yields, using 80% sulfuric acid. These results suggested that the mercuric oxide–boron trifluoride catalyzed reaction with methanol might be quantitative for the formation of dimethyl ketals from 2-butyne, 1-pentyne, and 3-methyl-1-butyne under suitable conditions. Preliminary tests verified this possibility and a systematic investigation resulted in a quantitative procedure that was found to be applicable to acetylenes with four and five carbon atoms.

The method devised depends upon the following essentially quantitative, consecutive reactions:

$$\text{R—C}\equiv\text{C—R}' + 2\text{MeOH} \xrightarrow[\text{BF}_3]{\text{HgO}} \text{R—C(OMe)}_2\text{—CH}_2\text{—R}'$$

$$\text{R—C(OMe)}_2\text{—CH}_2\text{—R}' + \text{H}_2\text{O} \longrightarrow \text{R—CO—CH}_2\text{—R}' + 2\text{MeOH}$$

$$\text{R—CO—CH}_2\text{—R}' + \text{NH}_3\text{OH}^+ \longrightarrow \text{R—C(=NOH)—CH}_2\text{—R}' + \text{H}_3\text{O}^+$$

The alkyne sample is treated at room temperature with methanol containing the mercuric oxide–boron trifluoride catalyst. The acid reagent is neutralized and the ketal is hydrolyzed by addition of aqueous sodium bicarbonate solution. The ketone produced is steam distilled into hydroxylamine hydrochloride solution and the liberated acid is titrated, giving a measure of ketone formed and, hence, of the amount of the acetylene from which it was derived.

Olefins and diolefins (except 1,2-diolefins) do not interfere, since they do not form derivatives of ketones. Paraffins, alcohols, and most other compounds generally cause no interference. Cyclopentadiene in very large amounts interferes by precipitating the mercury catalyst. Peroxides in large concentrations may degrade during the analysis to form volatile carbonyl compounds, thus producing high results.

Under the conditions of the method, 1,2-butadiene interferes, apparently rearranging partially to form an acetylene (a sample of 1,2-butadiene, analyzing 99.9% by the mass spectrometer, gave about 50% of the amount of ketone which could theoretically be obtained by complete rearrangement). Carbonyl compounds that distill under the conditions of the test give high values, requiring the use of an appropriately determined correction.

Tests on known mixtures of each of the three acetylenes under consideration indicate a consistent recovery of approximately 92% for samples containing 0.5% or more of the alkyne; therefore, it is necessary to multiply results by a correction factor of 1.09.

APPARATUS AND REAGENTS

Boron trifluoride in methanol, 45 to 50 weight %, prepared by passing boron trifluoride into cold methanol with shaking in an ice bath. The solution remains satisfactory for use for at least one month.

Methyl orange–xylene cyanol indicator, prepared by dissolving 0.10 gram of methyl orange and 0.14 gram of xylene cyanol FF in 500 ml. of 50% ethyl alcohol.

Simple distillation apparatus, consisting of a spray trap attached to a standard-taper 24/40 inner joint and connected at the other end to an efficient vertical condenser by means of a spherical joint.

ANALYTICAL PROCEDURE

With gentle heating, dissolve 0.1 gram of red mercuric oxide in 60 ml. of methanol containing approximately 2 grams of the methanolic boron trifluoride solution (1 gram of boron trifluoride). Place this catalyst solution in a 500-ml. round-bottomed flask equipped with a 24/40 standard taper joint and immerse the flask in ice. Introduce the sample portion containing 1 to 12 millimoles of the alkyne, in one of the following manners: if the sample contains less than 5 millimoles of alkyne per ml., measure the sample in a pipet; if the sample contains more than 5 millimoles of alkyne per ml., introduce an appropriate amount of sample into a weighed thin-walled glass bulb, seal the bulb, weigh, place beneath the surface of the catalyst solution, and break the bulb with a glass rod, rinsing the rod with a few milliliters of methanol. Stopper the flask loosely, swirl it gently, and allow it to stand at room temperature (about 25° C.) for 75 to 110 minutes.

Table I. Recoveries of Methyl Ethyl Ketone from Typical Reaction Mixtures Containing Various Concentrations of Catalyst

HgO	BF_3	Diluent (20 Ml.)	Ketone Present	Ketone Found	Recoveries
Grams	*Grams*		*Millimoles*	*Millimoles*	%
0.2	2	None	5.15	4.91	95
2.0	3	None	6.76	4.81	71
2.0	3	None	13.18	10.15	77
0.2	2	Pentane	13.18	12.44	95
2.0	3	Pentane	13.18	10.12	77
0.2	2	Isopentane	5.16	4.84	94
0.2	2	Isopentane	13.18	12.28	93
2.0	3	Isopentane	5.16	3.67	71
2.0	3	Isopentane	13.18	9.86	75
0.2	2	2-Pentene	5.15	5.05	98
2.0	3	2-Pentene	5.15	5.00	97
0.2	2	Crude isoprene	5.15	4.99	97
2.0	3	Crude isoprene	5.15	5.06	98

Cool the flask in an ice bath and slowly add 200 ml. of cold saturated sodium bicarbonate solution. Add a boiling stone, connect the flask to the still, and distill until approximately 200 ml. of the distillate have been collected in 100 ml. of 2.5% hydroxylamine hydrochloride solution contained in a 500-ml. glass-stoppered Erlenmeyer flask immersed in an ice bath. Stopper the receiving flask and shake well. Remove the stopper, warm the distillate to room temperature, pass a vigorous current of air through the solution for 10 minutes, add 0.70 ml. of the indicator solution, and titrate to the color of the blank (below), using either 0.1 *N* or 0.5 *N* sodium hydroxide solution. Make an appropriate blank titration, correct the sample titration for the blank titration, and calculate the stoichiometrical alkyne concentration; multiply the result by 1.09 to obtain the true value.

If carbonyl compounds are known to be absent, make the blank determination by mixing 60 ml. of methanol, 140 ml. of water, 0.70 ml. of indicator solution, and 100 ml. of the same hydroxylamine hydrochloride solution used for the sample and titrating the mixture with standard base to the disappearance of the pink color. If the carbonyl compounds present are known to be entirely volatile in the tests, add to the mixture used for the blank titration a weighed amount of sample containing approximately the same quantity of sample used in the determination (above); shake the mixture, and titrate with the appropriate standard base to the disappearance of the pink color. If it is suspected that relatively nonvolatile carbonyl compounds are present, apply the alkyne method to an appropriate amount of sample, omitting the catalyst; use the titrated distillate as the blank.

EXPERIMENTAL AND DISCUSSION

Studies were made of effects of changing the variables in the procedure. Experiments carried out in sealed bottles at 60° C. demonstrated that no advantage in accuracy was gained by working at the higher temperature, the attendant inconvenience representing a distinct disadvantage. Varying the reaction time at 25° from 1 to 5 hours had a negligible influence on the result. The arbitrary quantitities of reagents employed—i.e., 60 ml. of methanol, 200 ml. of saturated sodium bicarbonate, 1 to 12 millimoles of alkyne, and 20 ml. of sample diluent, such as pentane and isoprene—were selected on the basis of being reasonable and convenient. The diluents were employed in the experiments to simulate actual analyses of typical materials.

Variation in the amount of catalyst employed proved to be rather critical, particularly when the method had to be adaptable for use with a variety of hydrocarbon diluents and alkynes. Some difficulty was experienced in dissolving the mercuric oxide unless the boron trifluoride was present in considerable quantity; therefore, in most cases, the ratio of boron trifluoride to mercuric oxide was 10 to 1. In order to determine whether low results with certain of the catalyst amounts were due to destruction of ketone by the catalyst, known amounts (approximately 6 to 12 millimoles) of methyl ethyl ketone in 20 ml. of methanol were added to the reaction mixture and the distillation and ketone determination were made according to the procedure. The results of these experiments (Table I) showed that recovery of the ketone was good, except that only approximately 75% recovery was found when large amounts of catalyst were used in the absence of an olefin. In the presence of 20 ml. of an olefin or diolefin recoveries of 97 to 98% were found, regardless of the amount of catalyst used.

The samples of 2-butyne, 1-pentyne, and 3-methyl-1-butyne which were to be used in preparation of known mixtures had been analyzed by the mass spectrometer and found to be 99, 99, and 90% pure, respectively. *n*-Pentane was the contaminant found in the 3-methyl-1-butyne. Samples of these alkynes were sealed in small glass bulbs which were broken under the surface of reaction mixtures containing various amounts of catalyst and various hydrocarbon diluents (the latter to simulate diluents to be encountered with alkyne samples subjected to routine analysis). Analyses were then made following the prescribed procedure except for variation in catalyst quantity. Results obtained are tabulated in Table II. The empirical factor (1.09) was not applied in calculating the alkyne found, but corrections were made for the traces of carbonyl compounds in the diluents. The olefins used as diluents were found by analysis to contain less than one milliequivalent of peroxide oxygen per liter.

The data in Table II indicate the following conclusions:

1. With 2-butyne, low results were obtained with less than the prescribed amounts of catalyst, particularly in the presence of pentene. Low values were also obtained with very large amounts of catalyst in the absence of an olefin. Results with the prescribed amount of catalyst were 90 to 93% of the theoretical.
2. With 1-pentyne, good results were obtained except with larger amounts of catalyst in the absence of an olefin. Results according to the method were 91 to 94% of the theoretical.
3. With 3-methyl-1-butyne, results 91 to 94% of theory were obtained using the prescribed amounts of catalyst. Limited results with smaller and larger amounts of catalyst were similar to those obtained on 1-pentyne.

It appears from these results and from those with methyl ethyl ketone (Table I) that the use of large amounts of catalyst gives

Table II. Determinations of Alkylacetylenes Using Varying Catalyst Concentration and Different Sample Diluents

Alkyne	Diluent (20 Ml.)[a]	HgO	BF_3	Alkyne Present[a]	Alkyne Found	Recovery
		Grams	*Grams*	*Millimoles*	*Millimoles*	%[a]
2-Butyne	None	0.01	0.5	7.64	6.52	85
		0.05	0.5	6.90	6.36	92
		0.1	1	5.44	5.04	93[b]
		0.2	2	11.05	10.28	93
		2.0	3	4.80	1.69	35
	Pentane	2.0	3	7.80	4.73	61
	Isopentane	0.1	1	4.82	4.33	90[b]
		0.2	2	2.23	2.06	92
		2.0	3	6.50	3.16	48
	Pentene	0.01	0.5	4.95	2.21	45
		0.05	0.5	5.05	3.97	79
		0.1	1	7.39	6.78	92[b]
		0.2	2	4.45	4.09	92
	Isoprene	0.1	1	5.91	5.39	91[b]
		0.2	2	6.74	6.17	92
1-Pentyne	None	0.01	0.1	3.90	3.71	95
		0.01	1.0	3.15	2.96	94
		0.05	0.5	4.69	4.42	94
		0.05	2	2.19	2.05	94
		0.1	1	6.59	6.05	92[b]
		0.2	2	3.94	3.52	89
		2.0	2	6.61	3.41	52
	Isopentane	0.1	1	3.53	3.22	91[b]
		0.2	2	2.82	2.58	92
	Pentene	0.01	0.1	5.17	4.86	94
		0.01	1	4.81	4.59	95
		0.05	0.5	3.71	3.50	94
		0.05	2	4.48	4.29	96
		0.1	1	4.81	4.53	94[b]
		0.2	2	4.26	4.04	95
	Isoprene	0.01	0.5	5.07	4.74	93
		0.1	1	7.10	6.47	91[b]
		0.2	2	3.47	3.15	91
3-Methyl-1-butyne	None	0.01	0.5	5.59	5.24	94
		0.1	1	6.11	5.71	93[b]
		0.2	2	4.27	3.72	87
	Isopentane	2.0	3	5.76	1.63	28
	Pentene	0.1	1	4.54	4.24	94[b]
		0.2	2	2.64	2.35	89
	Isoprene	0.1	1	5.57	5.07	91[b]
		0.2	2	4.37	3.78	87

[a] 5 millimoles of alkyne in 20 ml. of diluent correspond to about 2% concentration and a 50-ml. titration with 0.1 *N* base.

[b] Results obtained with prescribed amount of catalyst.

low recoveries partially because of the destruction of ketone and partially because of side reactions involving the alkyne or ketal. Results on recovery of methyl ethyl ketone using large amounts of catalyst indicate that olefins and diolefins seem to exert a protective action in preventing side reactions. The hypothesis that this is due to decrease in effective concentration of the catalyst by formation of olefin-mercury complexes is borne out by the fact that in the presence of olefins no significant precipitation of basic mercury salt occurs upon neutralization of the normal amounts of catalyst. However, results with 2-butyne show that removal of catalyst by an olefin can be undesirable if very small amounts of catalyst are used.

Nieuwland and his co-workers (*4*) generally used the boron trifluoride–ethyl ether addition compound as a source of boron trifluoride for the methanolic catalyst solution. It was considered possible that by-products formed in preparing the catalyst from methanol, mercuric oxide, and boron trifluoride were contributing to the low results, but use of the boron trifluoride–ether addition compound in place of boron trifluoride itself gave results exactly comparable to those tabulated above.

Interferences by peroxides were noted in two ways. In one experiment a portion of a mixture of isoprene and 1,3-pentadiene (containing small amounts of the above acetylenes and essentially no peroxides) was analyzed and found to contain 100 millimoles of the alkynes per liter. The remainder of the mixture was then exposed to oxygen and sunlight until it had a peroxide number of about 5 milliequivalents per liter as determined by the Yule and Wilson method (*8*). Analysis of this oxidized sample for alkynes gave a value of only 50 millimoles per liter. Although peroxide numbers obtained by the ferrous ion method may not have any absolute significance, the result from this one experiment does indicate rapid autoxidation of alkynes, even in the presence of great concentrations of dienes.

Peroxides can interfere by degradation during the course of the procedure to give volatile carbonyl compounds. This was noted when 20 ml. of a sample of pentene with a peroxide number of about 120 were added to a known amount of pure butyne-2 followed by determination of the latter according to the prescribed method. Variable results up to 119% of theory were obtained, whereas with pentene containing no peroxide, values 90 to 93% of theory were consistently obtained.

Since allenes are convertible to alkynes under certain conditions (*2*), the method was applied to a sample of 1,2-butadiene found to be 99.9% pure by the mass spectrometer. From a sample of 11.4 millimoles of allene, 6.28 millimoles of ketone were determined, representing a conversion of 55%.

One milliliter of pure cyclopentadiene was added to a mixture of 20 ml. of pentene and 2.00 millimoles of butyne-2 before determination of the alkyne. Addition of the sample to the catalyst produced a copious yellow precipitate, and results found were 87% of theoretical (no empirical factor used). This indicated that large amounts of cyclopentadiene interfere by precipitation of the mercury catalyst from the field of action.

ACKNOWLEDGMENT

The work reported was performed under sponsorship of the Rubber Reserve Corporation, United States Government. Appreciation is also expressed for advice and help rendered by Victor Zahn, Louis Lykken, and others of this laboratory.

LITERATURE CITED

(1) Chavastelon, M., *Compt. rend.*, **125**, 245 (1897).
(2) Ellis, C., "Chemistry of Petroleum Derivatives", pp. 301, 632, New York, Chemical Catalog Co., 1934.
(3) Hill, A. J., and Tyson, F., *J. Am. Chem. Soc.*, **50**, 172 (1928).
(4) Killian, D. B., Hennion, G. F., and Nieuwland, J. A., *Ibid.*, **56**, 1384 (1934).
(5) Michael, A., *Ber.*, **39**, 2143 (1906).
(6) Mowat, E. L. R., and Smith, J. C., *J. Chem. Soc.*, **1938**, 19.
(7) Ross, W. H., and Trumbull, H. L., *J. Am. Chem. Soc.*, **41**, 1180 (1919).
(8) Yule, J. A. C., and Wilson, C. P., Jr., *Ind. Eng. Chem.*, **23**, 1254 (1931).

Estimation of Aloe-Emodin and the Aloins in Curaçao Aloes

K. G. STONE[1] AND N. HOWELL FURMAN, *Frick Chemical Laboratory, Princeton University, Princeton, N. J.*

A polarographic method has been developed for estimating aloins and aloe-emodin in Curaçao aloes.

THE estimation of the aloins and aloe-emodin in aloes has long been of importance to the pharmaceutical industry. Viehoever (*5*) has summarized the methods that are available for the estimation of the aloins, but none are done directly on the aloes. A polarographic study, described below, showed that the aloins could be estimated by the polarographic method.

APPARATUS AND MATERIALS

A Leeds & Northrup electrochemograph equipped with the cell arrangement described by Furman, Bricker, and Whitesell (*2*) was used for the polarographic measurements. The work was done at room temperature (23° to 26° C.). The capillary had the following characteristics: m = 0.8173 mg. per second; t = 7.60 seconds at −1.34 volts against the saturated calomel electrode (S.C.E.) in the buffer solution; the head of mercury was 46.5 cm. Oxygen was removed by passing purified nitrogen through the solution for 15 minutes. All polarograms were taken at $^1/_{20}$ sensitivity unless otherwise indicated.

The 0.25 M acetate buffer of pH 4 was prepared by neutralizing 0.25 mole of acetic acid in 600 ml. of water with concentrated sodium hydroxide to pH 4 measured against a glass electrode and diluting to 1000 ml. A polarogram of the buffer alone showed no appreciable amount of reducible material before hydrogen evolution.

Merck U.S.P. aloin was used without further purification. A standard solution of aloin, prepared by dissolving 1.000 gram of aloin in 1000 ml. of 20 volume % ethanol, was stable for about one week when protected from light and air. Samples of Curaçao aloes were supplied by the Wallace Laboratories, Inc. Barbaloin and isobarbaloin were prepared according to the directions of Gardner and Joseph (*3*). Aloe-emodin was prepared by the ferric chloride oxidation of aloin by the procedure of Cahn and Simonsen (*1*). The standard solution of aloe-emodin for spectrophotometric studies contained 0.50 mg. per ml. in chloroform; lower concentrations were prepared by dilution. The concentrated solution was stable if the bottle was kept closed. Because there was a tendency to deposit aloe-emodin at the air-chloroform interface owing to evaporation, the standard solution was prepared fresh every day, but this is not necessary if proper protection is provided.

The chloroform for the extraction of aloe-emodin should preferably be free from alcohol, but it is not an absolute necessity. Colorimetric measurements were made with a Cenco-Sheard spectrophotelometer, using an effective slit width of 10 millimicrons and 1.0-cm. Corex cells.

PRELIMINARY EXPERIMENTS

Polarographic measurements on solutions of barbaloin and isobarbaloin showed that the same half-wave potential and current-concentration ratio were obtained for both molecules.

---

[1] Present address, Sun Chemical Corporation, New York, N. Y.