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Preparation of Carbonyl-Free Solvents

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► A method is described for the preparation of carbonyl-free solvents. A Celite column impregnated with 2,4-dinitrophenylhydrazine, phosphoric acid, and water is used to effect a rapid quantitative reaction with the carbonyls in the solvent. Partially deactivated alumina is employed to

isolate the monocarbonyl fraction which is subsequently estimated. The procedure is theoretically applicable to all nonoxygenated, water-immiscible solvents on a continuous basis. The aliphatic monocarbonyl content of 13 solvents is presented.

ORGANIC SOLVENTS for use in the microanalysis of carbonyls are usually purified by refluxing a derivative of hydrazine in the solvent in the presence of an acid catalyst. The most common derivative employed is 2,4-dinitrophenylhydrazine (DNPH) since it is highly nonspecific, reacts rapidly,

and yields hydrazones which are relatively acid stable. In the instance where the reagent is insoluble or only very slightly soluble in the solvent, other methods must be resorted to. These, for the most part, consist essentially of reaction with an oxidizing agent or reaction with DNPH at the interface of a two-phase system.

Begemann and DeJong (1) evaluated the more popular methods of forming 2,4-dinitrophenylhydrazones and found them unsuitable for quantitative micro-analysis. They described a two-phase quantitative method in which the aqueous phase (containing DNPH and HCl) was supported on Celite, and the nonpolar phase (petroleum ether containing the carbonyl) was permitted to flow over the support. In this manner they purified petroleum ether, but indicated that small amounts of acetone still remained unreacted. Their technique, although giving excellent yields was rather slow and ostensibly practical (as far as solvent purification is concerned) where only small volumes of solvents are employed. However, the method appeared to have excellent potentialities and considerable time was spent in this laboratory in a study of improvising modifications without impairing its sensitivity and quantitative aspect.

REAGENTS AND APPARATUS

Alumina, Grade F-20, Aluminum Co. of America. Activated by heating 24 hours at 150° C., then partially deactivated by the addition of 6% (w./w.) distilled water. The wet alumina was shaken until all lumps were broken and allowed to equilibrate overnight.

Chromatographic tubes, Type 1, approximately 2.5 cm. i.d. × 30-cm. length, with or without coarse sintered-glass disk; Type 2, approximately 12 mm. i.d. × 30-cm. length, with or without coarse sintered-glass disk.

Solvents Investigated. Table I lists the solvents which were investigated.

All solvents except chloroform were analyzed directly from the container. Chloroform was washed six times with half its volume of distilled water, then dried 24 hours over CaCl₂ before purification. Unwashed chloroform could not be purified (see discussion).

METHODS

Preparation of Reaction Column. Five tenths gram of DNPH is dissolved in 6 ml. of 85% H₃PO₄ by grinding in a 6-inch mortar. Four milliliters of distilled water is added to the clear yellow solution and the precipitated DNPH is redissolved by grinding. Ten grams of Celite (Johns-Manville, analytical grade) is then ground with the solution until a homogeneous damp preparation is obtained. This is best attained by grinding, scraping the sides with a spoon

Table I. Solvents Investigated

Solvent	Grade	Supplier	Lot
Benzene	ACS	J. T. Baker	9299
Carbon tetrachloride	ACS	Fisher	794616
Chloroform	ACS	Fisher	705603
Cyclohexane	Reagent	Fisher	700004
Ethylene chloride		Fisher	705088
<i>n</i> -Heptane	High purity	Phillips	828
<i>n</i> -Hexane		Fisher	54547
<i>n</i> -Hexane	High purity	Phillips	
Methyl cyclohexane	Yellow Label	Eastman Kodak	
Methylene chloride	Cert. reagent	Fisher	
<i>n</i> -Pentane	Blue Label	Eastman Kodak	
Petroleum ether (35.3-52.8)	ACS	Fisher	794575
Toluene	ACS	Fisher	705514

or spatula, and regrinding. The bright yellow impregnated Celite is then transferred to a Type 1 chromatographic tube which is clamped at the outlet and contains about 25 ml. of carbonyl-free hexane. The impregnated Celite is transferred in about four equal portions. Each portion is tamped tightly before addition of the next. In this laboratory an all-stainless steel tamping rod similar to that described by Corbin, Schwartz, and Keeney (3) is used, except that the disk clears the sides of the chromatographic tube by about 2 mm. The flow rate of the column can be varied by the tightness of the packing. Although this is not reproducible exactly from column to column, and, of course, varies with the physical characteristics of the solvent to be purified, the desired flow rate can be approximated by varying the head pressure or by incorporating an inert valve assembly on the outlet of the tube. With a little experience, columns can be prepared in 5 to 10 minutes with flow rates close to those desired.

Removal of Impurities from Column. The 2,4-dinitrophenylhydrazine reagent contains a small amount of colored impurities, some of which behave like aliphatic monocarbonyl dinitrophenylhydrazones on alumina (see below). These impurities are removed before addition of the solvent by flushing the column with 50 ml. of carbonyl-free benzene using air pressure.

Purification of Solvents. The solvent to be purified is stirred with excess DNPH for 15 minutes, and an aliquot is removed to serve as a blank. The solvent containing DNPH is then added to the column, and the first 50 ml. of effluent is discarded. The remainder is collected, and an aliquot taken for analysis of its aliphatic monocarbonyl content.

Isolation and Estimation of Aliphatic Monocarbonyls. To ascertain the degree of purification of the solvent, the aliphatic monocarbonyl content of the effluent is determined as follows: To about 10 ml. of hexane in a chromatographic tube (Type 2) is added 5 grams of alumina, a little at a time, with shaking and the column packed by using light air pressure, leaving about 2 cm. of hexane above the

top of the bed. An aliquot of the solvent containing the dinitrophenylhydrazones is then added. Aliquots of hexane, heptane, carbon tetrachloride, pentane, cyclohexane, and methyl cyclohexane may be added directly. However, solvents of greater polarity (e.g., benzene, toluene, chloroform, methylene and ethylene chloride) are first taken to dryness and the residue wetted with 2 ml. of benzene (per 25-ml. aliquot evaporated) and then diluted with 20 ml. of hexane and transferred to the alumina along with hexane rinsings. Following adsorption of the hydrazones, the aliphatic monocarbonyls are eluted with 50 ml. of a 1:1 benzene-hexane solution. This volume of benzene-hexane solution will elute 8 μmoles or less of aliphatic monocarbonyl hydrazones from the alumina. Studies on 40 model compounds, all of which contained no other functional group, revealed that quantitative recovery was achieved, and that no artifacts were produced.

In the analysis of the solvents in this study no band was detected which moved more than 2 cm. from the top of the column after elution of the monocarbonyl fraction. The reagent (DNPH) will not move off of the column even after 100 ml. of the benzene-hexane solution has been put through.

The absorbance of the monocarbonyl fraction was read in chloroform after removal of the eluting reagent on the steam bath. The blank (solvent saturated with DNPH) was carried through all steps except the reaction column. The purpose of the blank is to correct for any decomposition of DNPH which might occur on standing in solution or on contact with the alumina to give products which emerge with the monocarbonyl fraction. Also any optical absorption of the impurities in the residue of the solvents is accounted for when the absorbance of the monocarbonyl fraction is determined.

The remainder of the solvent was distilled at atmospheric pressure, and subjected, if necessary, to the exact same procedure again.

Table II. Aliphatic Monocarbonyl Content of Various Organic Solvents

Solvent	Flow Rate (Ml./Hr.)	Aliphatic 2,4-Dinitrophenylhydrazones Found ^a				
		1st pass (μmole/l.)	Max. ^b (mμ)	2nd pass (μmole/l.)	Max. ^b (mμ)	3rd pass (μmole/l.)
benzene	50	8	362	0
Carbon tetrachloride	58	0
Chloroform	47	7	362	0
Cyclohexane	30	12	362	0
Ethylene chloride	56	371	362	0
<i>n</i> -Heptane	47	128	362	11	362	1
<i>n</i> -Hexane (Fisher)	55	391	362	7	362	0
<i>n</i> -Hexane (Phillips)	47	11	362	1	362	...
Methyl cyclohexane	37	333	362	14	362	0
Methylene chloride	50	0
<i>n</i> -Pentane	58	130	362	0
Petroleum ether	43	129	355	3	355	...
Toluene	47	7	362	0

^a Calculations based on readings at maxima using a molar absorptivity of 22,500 for saturated aldehydes and ketones.

^b Maxima in CHCl₃ on total derivatives.

RESULTS AND DISCUSSION

Results of the study are presented in Table II.

The efficiency of the reaction column in removing carbonyl contaminants from the various solvents studied is readily evident from the data in Table II. Although it is to be expected that different lots of a given solvent will vary in their degree of contamination with carbonyls, relative contamination for the different solvents of a given grade should be fairly constant. The data in Table II could, therefore, sensibly be used as an index for selection of a solvent.

Although the work reported here was pertinent to the aliphatic monocarbonyl contaminants in the various solvents, limited experiments with aromatic carbonyls dissolved in hexane indicate that these react instantaneously on contact with the reaction column. This is manifested by the formation of a

red band at the top of the column. This phenomenon takes place only when the aromatic carbonyl is put on the column in a solvent in which the resulting hydrazone is insoluble or feebly soluble. The data of Cheronis and Levey (2) suggest that aromatic carbonyls react more rapidly than aliphatics with DNPH.

Vicinal dicarbonyls which form bis(hydrazones) also precipitate as a red zone when the parent carbonyl is put on the column in an aliphatic hydrocarbon solvent.

As mentioned earlier, unwashed chloroform could not be purified on the reaction column. This is attributed to the formation of acetaldehyde via the dehydrogenation of DNPH of the ethyl alcohol used as a preservative (4).

Theoretically, doubling the constituents making up the column while keeping the flow rate the same as reported in Table II, should be as efficient as making two passes of the

solvent over a standard column. This was not attempted, since, as the data show, one pass over a standard column will purify most solvents to a satisfactory degree.

The data in Table II were obtained on two reaction columns. In theory a reaction column can be used indefinitely, at least for the purification of some solvents, since DNPH from the DNPH-saturated solvent displaces any DNPH lost from the column through reaction. In this laboratory a single column has been used over 6 months for the purification of benzene with no loss in efficiency. However, columns used for the purification of hexane become dark with time. This is attributed to the accumulation of decomposition products of DNPH, these being virtually insoluble in hexane. As a consequence, new columns are constructed periodically for purification of this solvent.

Purification of solvents can be put on a continuous basis. At the flow rates given in Table II, approximately 1 liter per 24 hours per column can be obtained.

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