A Simple Fraction Collector for Gas Chromatography. Compatibility with Infrared, Ultraviolet, Nuclear Magnetic Resonance, and Mass Spectral Identification Techniques

JOANNE L. WITIAK, GREGOR A. JUNK, G. V. CALDER, J. S. FRITZ,* AND H. J. SVEC

Ames Laboratory—USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010

Received March 1, 1973

Isolation of the individual components of a reaction mixture in pure form by gas chromatography prior to examination by ir, uv, nmr, and mass spectroscopy is an important and recurring problem for organic chemists. The fraction collection techniques presently available are not so convenient as might be desired. The most popular devices are cold traps.[1-4] These, however, require coolants and some means of preventing aerosol formation, which lowers the collection efficiency. Other fraction collectors have been proposed in which a sample is sorbed on an inert support[5-8] or is partitioned on a chromatographic liquid phase.[9-11]

Some of these devices require relatively complicated equipment, which makes the technique inconvenient. Many require heat and/or vacuum equipment to transfer a sample from the collection device, and some cause chemical transformation of the collected components. This report will describe a simple procedure which circumvents these difficulties and is easily adaptable for use in uv, ir, nmr, and mass spectral analyses of the separated components.

A supply of collection tubes is made by loosely packing 4–12 mg of 80–100 mesh Rohm and Haas XAD-4 resin into 1.6–1.8 × 70 mm borosilicate glass capillary tubes. The resin is held in the tubes with small plugs of clean glass wool on either side. The ends of the tubes are lightly fire polished and the tubes are stored in a sealed container until ready for use.

The method of attaching the tubes to the exhaust port of the gas chromatograph will depend on the instrument used. When a Varian Autoprep A700 chromatograph is used, this is accomplished by drilling a $^1/_{16}$-in. hole, tapered on one side, into a 9 mm diameter × 3 mm thick Teflon disk. The disk is placed, taper out, inside the nut on the exhaust port of the chromatograph. The nut is tightened so that the Teflon disk holds the capillary collection tube snugly in place but loose enough that the tube can be easily inserted or removed. With other chromatographs, similar designs can be easily adapted.

For fraction collection, a packed tube is inserted into the modified exhaust port at the beginning of the gas chromatographic run and the instrument recorder zeroed. At the onset of the desired fraction, as indicated by the recording of a peak, this tube is removed and a new collection tube inserted. When the gc peak has returned to base line, the collection tube is removed and another tube is inserted to collect the next fraction. There is generally only a slight deflection of the recorder pen as one tube is removed and another tube is inserted. The time required to change tubes is less than 1 sec, so that multiple collections across a single gc peak are possible.

The efficiency of sample collection for several model compounds was tested. Typical recoveries, based on repeating the chromatography of the collected material, were between 60 and 95% for α-methylstyrene, *n*-hexyl alcohol, *n*-pentyl alcohol, benzyl chloride, benzaldehyde, toluene, anisole, and acetophenone. In view of the simplicity of the device and the ease of fraction collection and transfer, these recoveries are considered satisfactory for auxilary instrumental qualitative analysis, such as ir, uv nmr, and mass spectroscopy.

Infrared Spectra.—For infrared analyses, the sample component is eluted directly from the collection tube into the ir cell using a suitable solvent such as carbon tetrachloride. The plunger and needle are removed from a 1-ml disposable syringe which is fitted into the opening on one end of the ir cell. With the other opening of the ir cell plugged, the collection tube is eluted into the syringe until the syringe barrel contains ~0.1 ml of a carbon tetrachloride solution. The plug is then removed from the ir cell allowing the solution to fill the cell. Using this technique, well-resolved and easily interpretable ir spectra were obtained using a Beckman IR-33 for ~1.0 mg of each of the following compounds: α-methylstyrene, acetophenone, aniline, *n*-hexyl alcohol, toluene, and hexyl acetate.

Nmr Spectra.—For nmr analyses, the sample component is transferred from the collection tube directly into an nmr tube by elution with ~1.0 ml of carbon tetrachloride. Good quality nmr spectra were obtained using a Hitachi R20-B, 60-MHz instrument for ~4 mg of each of the following compounds: *n*-hexyl acetate, 2-methylcyclohexanol, α-methylstyrene, and toluene.

Uv Spectra.—For uv analyses, the sample component is eluted from the resin with ~0.2 ml of an appropriate solvent such as hexane or 95% ethanol. The eluate is then diluted to 25 ml and an aliquot of this solution is transferred to the uv cell. With this technique, quality uv spectra were obtained using a Cary Model 14 spectrophotometer for 0.5-mg fraction-collected samples of α-methylstyrene, toluene, acetophenone, benzaldehyde, and anisole.

Mass Spectra.—It is unnecessary to transfer the sample by elution from the collection tube to obtain a mass spectrum. The resin containing the sorbed sample is simply transferred to the direct insertion probe of the mass spectrometer for mass spectral analysis. This technique is particularly convenient for a Du Pont 21-490 series mass spectrometer, since the

(1) H. T. Badings and J. G. Wassink, *J. Chromatogr.*, **18**, 159 (1965).
(2) J. T. Ballinger, T. T. Bartels, and J. H. Taylor, *J. Chromatogr. Sci.*, **6**, 295 (1968).
(3) K. R. Burson and C. T. Kenner, *J. Chromatogr. Sci.*, **7**, 63 (1969).
(4) R. K. Odland, E. Glock, and N. L. Bodenhamer, *J. Chromatogr. Sci.*, **7**, 187 (1969).
(5) M. Cartwright and A. Heywood, *Analyst*, **91**, 337 (1965).
(6) J. N. Damico, N. P. Wong, and J. A. Sphon, *Anal. Chem.*, **39**, 1045 (1967).
(7) F. W. Karasek and R. J. Smythe, *Anal. Chem.*, **43**, 2008 (1971).
(8) D. M. Kane and F. W. Karasek, *J. Chromatogr. Sci.*, **10**, 501 (1972).
(9) J. W. Amy, E. M. Chait, W. E. Baitinger, and F. W. McLafferty, *Anal. Chem.*, **37**, 1265 (1965).
(10) M. D. D. Howlett and D. Welti, *Analyst*, **91**, 291 (1966).
(11) B. A. Bierl, M. Beroza, and R. M. Ruth, *J. Chromatogr. Sci.*, **6**, 286 (1968).

borosilicate 1.6 × 1.8 mm collection tubes are easily converted into direct insertion sample containers. After fraction collection, one end of the collection tube is sealed and the resin containing the sorbed sample is pushed to the sealed end. The unsealed end is then cut off, leaving an 18–20 mm long sample container which is identical with those supplied by Du Pont. Using this technique high-quality mass spectra were obtained for samples as volatile as toluene as well as for benzaldehyde, *o*-xylene, benzyl chloride, 1-methylnaphthalene, acenaphthylene, α-methylstyrene, 2-ethyl-1-hexanol, acetophenone, and methyl octanoate, with quantities as low as 10^{-8} g. The background spectra caused by the XAD-4 resin as it is received is significantly reduced by vacuum degassing the resin used in preparing the collection tubes at 10^{-6} Torr and ~200° for 1 hr.

Acknowledgment.—This work was supported by a grant from the National Science Foundation under Contract No. GP-33526X.

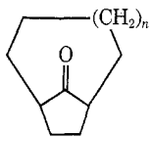
Bisdiazo Insertion in Cycloheptanone

J. D. HENION AND DAVID G. I. KINGSTON*[1]

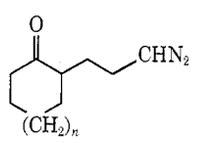
Department of Chemistry,
State University of New York at Albany,
Albany, New York 12222,
and Department of Chemistry,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061

Received February 21, 1973

In connection with an investigation into steric effects on the McLafferty rearrangement,[2] we were interested in obtaining a sample of bicyclo[6.2.1]undecan-11-one (**1**). This compound has not previously been prepared, but both bicyclo[5.2.1]decan-10-one (**2**) and bicyclo[4.2.1]nonan-9-one (**3**) have been obtained by reaction of 1,4-bisdiazobutane (**4**) with cyclopentanone and cyclohexanone respectively,[3] and also by intramolecular diazoinsertion of the side chain diazoalkyl ketones **6** and **7**, respectively.[4] In the original report describing the reactions of **4**, it was stated that reaction with cycloheptanone (**8**), which would have been expected to yield the desired ketone **1**, yielded complex mixtures, and it was inferred from a study of the vapor phase chromatographic behavior of these mixtures that the bridged ring ketones could be no more than minor constituents.[3] No information was available on the alternate route to **1** *via* the side chain diazoalkyl ketone



1, $n = 3$
2, $n = 2$
3, $n = 1$



5, $n = 3$
6, $n = 2$
7, $n = 1$

5, but a recent paper by Wiseman and Chan showed that the structures of the two major product ketones produced by reaction of 1,3-bisdiazopropane with cyclohexanone differed from those previously assigned on the assumption of double expansion of the six-membered ring.[5] It thus seemed likely that the reaction of **4** with cycloheptanone would not prove to be a good synthetic route to the ketone **1**.

In spite of this discouraging situation, we decided to investigate the reaction of **4** with **8** in order to determine whether any of the desired product at all was produced. Since our need was for only a small quantity of **1**, it was believed that sufficient material could be obtained even from a low-yield reaction. Reaction of bis-*N*,*N*′-dinitroso-1,4-butanediamine with cycloheptanone by the method of Gutsche and Smith yielded a mixture of six major products, as detected by vapor phase chromatography (vpc). In contradistinction to the findings of Gutsche and Smith, however, one of these products (and only one), representing about 20% of the total product mixture, had a vpc retention time in the region expected for the desired ketone **1**. Examination of this product by high-resolution mass spectrometry showed that it had the composition $C_{11}H_{18}O$. The presence of a cyclopentanone ring was confirmed by its infrared absorption maximum of 1731 cm^{-1}, and the bicyclic nature of the material was shown by the absence of low-field resonances in the nmr spectrum due to vinyl protons.

In spite of the similarity of the isolated product to the ketone **1**, there were some features in its mass spectrum which were not consistent with its formulation as **1**; in particular, the compound showed a moderately intense ion at *m/e* 148 $[M - H_2O]\cdot^+$ which was absent in the spectra of compounds **2** and **3**. The location of the carbonyl group in the compound was deduced by deuteration followed by mass spectral analysis of deuterium incorporation. This showed clearly that it possessed three exchangeable hydrogens, and it must, therefore, have the bicyclic structure of bicyclo[6.3.0]undecan-2-one (**13**). Other structures are incompatible with the requirement of a cyclopentanone ring in the product, the nature of the starting materials, and the absence of olefinic protons in the nmr spectrum.

A plausible rationalization for the formation of **13** from the reagents used is given in Scheme I.

Monodiazo insertion into cycloheptanone would yield the intermediate **9**, which could react to form the intermediate **10**. Rearrangement of **10** by the pinacol route (pathway A) would yield the cyclononanone **11**, while rearrangement *via* the epoxide **12** (pathway B) would yield the observed product **13**. The structure **11** is, of course, excluded for the product by the observed infrared adsorption of the latter; presumably, the angular strain in the transition state leading to a cyclobutane is sufficient to make pathway A energetically unfavorable as compared with pathway B. The latter pathway must also be favored over the bis insertion to give **1**, presumably also because of conformational restrictions when forming a medium-ring ketone by ring expansion.[6] It is well known that the formation of medium-ring alicyclic ketones by ring expansion of the lower homologs with diazomethane is

(1) Author to whom inquiries should be directed: Virginia Polytechnic Institute and State University.
(2) J. D. Henion and D. G. I. Kingston, unpublished work.
(3) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).
(4) C. D. Gutsche and D. M. Bailey, *J. Org. Chem.*, **28**, 607 (1963).
(5) J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).
(6) C. D. Gutsche, *Org. React.*, **8**, 364 (1954).