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Note

Halide exchange during gas chromatography

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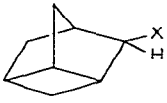
We wish to report the observation of an on-column reaction during gas chromatography (GC) which could be a source of confusion in certain analyses, and which might, in principle, have certain preparative consequences.



1a X = Br
1b X = Cl

A sample of *exo*-2-bromotricyclo[3.2.1.$0^{3,6}$]octane (1a) was chromatographed on several GC columns. Although only a single peak was observed on most of the columns tried, two components were apparent on columns with Carbowax 20 M and Ucon polar* as stationary phases. In both instances, it appeared that the composition eluted was temperature dependent, with increasing amounts of a shorter-retention-time component being observed at higher temperatures. On the Carbowax column, the shorter-retention-time component comprised only 17% of the mixture at 170°C, but up to 72% at 200°C. Both columns were ones which had seen several years of periodic usage in analysis and small-scale preparative separations of a wide variety of organic compounds.

Samples of both components were trapped and nuclear magnetic resonance (NMR) spectra were obtained. The second component had a spectrum identical with the original bromide; the first had a generally similar spectrum, and was ultimately identified as the corresponding chloride by comparison with a known sample.

It would appear that the Carbowax and Ucon polar columns, through previous interaction of the metal of the column with organic chlorides, had built up a reservoir of metal chloride which was reactive in halide exchange with the alkyl bromide. Since

* A referee has pointed out that numerous Ucon column packings are available. The one used had been purchased from Wilkens Instrument and Research, and was labelled only as "Ucon Polar". Several others (50-HB-5100 and 50-HB-2000 from Supelco and 50-HB-280X and 75H-90,000 from Anspec) were obtained and their infrared spectra (liquid smear) compared with the Wilkens "Ucon Polar" remaining from the earlier column preparation. There were various differences in intensities between the Wilkens and the other samples. Most prominently, the former had a sizable carbonyl stretch at 710 cm^{-1}, which was weak in 50-HB-2000 and absent in the others. The carbonyl and OH bands were reduced somewhat in intensity and other minor intensity changes produced by extended evacuation at 5 μ. The extent to which the spectra may reflect inherent differences in the stationary phases, volatile impurities, or changes during long storage is not clear.

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the two components gave discrete peaks, the active exchanging region of the columns must have included only their earlier portions. Formation of this active region may have resulted from pyrolysis in the injector, from greater heat leakage from the injector, or from a degradation of the column due to exposure of a hot column to the air during column interchanges over a period of years. It is likely that the polarity and perhaps hydroxylic nature of the stationary phases is significant.

In an attempt to repeat the above observations some years later, it was found that the Carbowax column failed to produce exchange. The Ucon polar column had deteriorated in quality to the extent that individual peaks were not obtained at 200°C, but the first injection of bromide produced complete conversion to the chloride. Subsequent injections led to less exchange, and finally only unchanged bromide was eluted. However, "conditioning" of the column with several injections of norbornyl chloride led to about 30% exchange of the next sample of tricylic bromide. Thus, the exchange process is reversible, and the column can be intentionally exchanged to load it with one halide.

We note that the observations reported here were puzzling to us when first seen, and so we wish to point out this possible source of confusion to others. In addition, it is possible that a halide-exchange GC column could be potentially useful on a very small preparative scale. However, bromide 1a is probably ideally suited for this type of exchange, since this system appears to undergo anchimerically assisted solvolyses, cannot eliminate hydrogen halide, and does not rearrange to a more stable carbon skeleton[1]. We did not attempt to optimize the exchange process or explore its generality, except to note that chloroform is ineffective at exchanging chloride on to the column.

EXPERIMENTAL AND RESULTS

Gas chromatograms were run on Varian-Aerograph A90P and A90-P3 instruments. Columns which led to exchange were (A) 10 ft. × 1/4 in. stainless steel, 20% Carbowax 20M on 60–80 mesh Chromosorb P; and (B) 10 ft. × 1/4in. copper, 25% Ucon polar on firebrick. NMR spectra were run on Varian T-60 and HA-100 spectrometers, and mass spectra were obtained on a Hitachi RMU-6D instrument. *exo*-2-Bromotricyclo[3.2.1.$0^{3,6}$]octane was prepared for another study as described in the literature[1]; the chloride was a gift from Professor R. R. Sauers of Rutgers University.

GC of 1a on column A at 200°C gave two peaks in relative areas of about 72.28, in order of increasing retention time. At 180 and 170°C, the ratios were 34·66 and 17:83, and at 150°C, only the longer-retention-time component was seen. The two peaks were incompletely resolved, and the earlier peak appeared to be the broader of the two. Both components were trapped from injections of *ca.* 50 μl, and their NMR spectra were found to correspond with those of 1b and 1a, in order of increasing retention time. The mass spectrum of 1b had the characteristic pair of isotopic peaks for the molecular ion at *m/e* 142 and 144. At 150°C, the two isolated components gave cleanly separated GC peaks, with no evidence of interconversion. Both halide samples were converted to Grignard reagents by reaction with magnesium in tetrahydrofuran, and then hydrolyzed. The same hydrocarbon (1, X=H) was formed from both, as determined by NMR spectra and GC retention times.

GC on column B led to similar results. At 150°C, two peaks of similar area

were present, the earlier one being broader and incompletely resolved from the later one. At 125°C, only about 10% conversion was found. In subsequent experiments several years later, the conversion to the earlier component at 200°C (as determined by NMR spectra of the material trapped from the column) was complete for the first 30 μl injection, but after eight injections of *ca.* 40 μl, only unchanged 1a was eluted. Four injections of 50 μl each of norbornyl chloride, followed by 30 μl of 1a led to a 5:3 mixture of 1a:1b. Following this, four 50 μl injections of chloroform followed by 50 μl 1a led to a 4:1 mixture of 1a:1b.

REFERENCE

1 R. R. Sauers, R. A. Parent and S B. Damle, *J. Amer Chem. Soc.*, 88 (1966) 2257.