Possible Significance of the Absence of Azaadamantane and Pyridine in California Crude Oil

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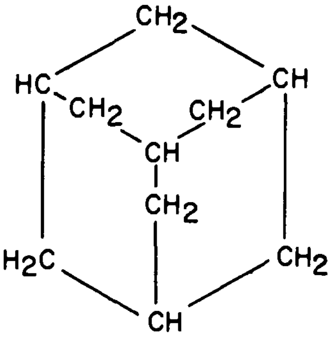
A CAREFUL SEARCH for azaadamantane and pyridine failed to indicate the presence of these bases in a California crude oil. If the oil was transported from source-bed to reservoir by water, this was to be expected as was the presence of only a trace of phenol.

Adamantane subliming at about 80° C., melting (closed tube) at 268°, steam distillable, and obtained from hydrocarbons boiling at 190-5° C. was first isolated from Moravian petroleum (*5, 6*).



Adamantane

Recently thiaadamantane, subliming at 78° C. at 3 mm., melting (closed tube) at 320° C., and distilling from Iranian kerosine at 227-8° C. has been reported (*2*).

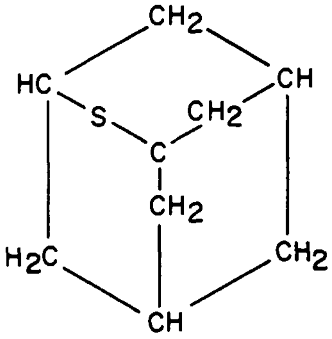
Birch and coworkers suggested at that time that azaadamantane with similar physical properties might be found in California oil. Large supplies of bases were available here from earlier work but were not used. Because the new base should be fairly strong and have properties similar to quinuclidine it would probably be fairly soluble in water and so would have been lost during isolation at the refinery or during separation processes during which solubility in water was not suspected in bases boiling well over 200° C. Furthermore, while it was predicted that azaadamantane would be isolated from oil boiling at 210° to 220° C., there appears to be no method of predicting the temperature at which it would distill from a mixture of bases. If azaadamantane were present in petroleum, it should be fairly easily isolated because it would surely be one of the strongest bases present. A moderately strong base such as *cis-trans*-perhydropyrindine when added to a natural mixture of petroleum bases can be recovered readily by counter-current fractional extraction with acid.

EXPERIMENTAL

Preliminary Experiments. Available petroleum bases boiling from 208° to 220° C. were carefully refractionated. From each 2° cut, 3% fractions representing the strongest bases in each cut were obtained by countercurrent extraction with acid. Neither the index of refraction nor the melting point of picrates indicated the presence of azaadamantane.

Meanwhile, Fusco and Bianchetti (*3*) reported the synthesis of azaadamantane. It sublimes readily and melts (closed tube) at 258° C., its picrate melts at 300° C., and its hydrochloride sublimes at 250° C. but does not melt below 360° C. The report indicates that the base has, in general, the properties predicted for it.

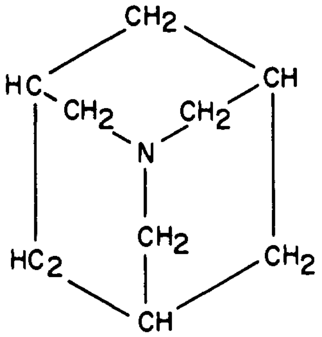
Preparation and Study of Oil Sample. A 10-gallon sample of fresh California crude oil that had not been in contact with water above ground was roughly fractionated to 240° C. The material boiling between 80° and 240° C. was carefully extracted with dilute hydrochloric acid and then with dilute sodium hydroxide. Basic compounds were recovered from the acid extracts and acidic from the basic extracts—being careful at each stage to avoid losses due to solubility in water. To recover pyridine, if present, the basic material was dissolved in 100 ml. of acid-washed refractionated hydrocarbon boiling over the same range and fractionated on a 50-plate column to 170° C. None of the fractions yielded a crystalline picrate. The bases obtained



Thiaadamantane

from the recombined fractions failed to show a peak for pyridine in gas-liquid chromatography. The authors know of no previous attempt to find it through chromatography.

Baker recently (*1*) postulated that petroleum migrated from source-bed to reservoir in solution in water from which it is then released under a change of conditions. If this theory is correct, the large volumes of water that may have been involved should have held partially soluble compounds like pyridine, phenol, the lower ketones, and presumably azaadamantane in solution so that these data as well as those of previous workers might be expected. Azaadamantane might not be in this California petroleum, or it may have been removed below ground by water with which the oil had been in contact. As adamantane and thiaadamantane are not soluble in water, they would not have been removed by water and are found in petroleum.



Azaadamantane

The sample of crude oil showed a total nitrogen content of 0.577% (*4*). A preliminary distillation to 240° C. from Claisen flasks yielded a total of 2.25 gallons of distillate which was extracted in well-stirred batches with 2*N* hydrochloric acid. The hydrocarbon layer remaining was next extracted similarly with a total of 5 liters of 10% sodium hydroxide, and basic solution was set aside for the future search for phenol while the final hydrocarbon layer was reserved.

Search for Pyridine and Azaadamantane. The solution of hydrochlorides was concentrated under water pump vacuum, made strongly basic with sodium hydroxide, and the mixture distilled to near dryness. By repeated ether extraction of the residual salt cake and the distillate, 8 ml. of basic material was obtained after evaporation of the ether.

One liter of the hydrocarbon layer, left after extraction with acid and base, was washed with several portions of concentrated sulfuric acid, with sodium hydroxide, and finally with water and was redistilled. Forty milliliters of this special hydrocarbon mixture was added to the 8 ml. residue of basic material, and the resulting mixture fractionated through a 50-plate Todd column to 170° C. The residue was saved for the search for azaadamantane.

PYRIDINE. This fractionation yielded 42 cuts of 0.3 to 1.3 ml. in volume. None formed picrate derivatives, so they were recombined. The basic material was recovered by treating with hydrochloric acid, concentrating, treating with sodium hydroxide, and removing the basic material by ether extraction. After being dried, the ether solution was chromatographed on a Perkin-Elmer fractometer at 100° C. Comparison of the graph with that obtained with ether to which minute drops of pyridine and α-picoline had been added showed that these were absent in the crude oil sample.

AZAADAMANTANE. The residual bases remaining in the Todd column after the distillation to 170° C. were fractionally neutralized in an efficient spinning rod extraction column—similar to ones described previously (*7*)—with a concentration of hydrochloric acid sufficient to remove 32 mg. of azaadamantane. The aqueous phase was concentrated under water-pump vacuum without heating, and basic material was recovered in the usual manner with sodium hydroxide and ether extraction. Because azaadamantane should sublime readily, a sublimation of the basic material was attempted. No solid sublimate could be observed even on prolonged heating. The basic material would not yield a solid picrate.

To determine whether the extraction column would have extracted azaadamantane, which should be very similar both in water solubility and in base strength to quinculidine, from the alkyl pyridines present in much larger amounts, a mixture of 42 mg. of *cis-trans*-perhydropyrindine and 6.32 grams of California bases boiling between 200° and 220° C. was dissolved in 500 ml. of carbon tetrachloride and extracted with 500 ml. of water containing 0.34 ml. of 1*N* hydrochloric acid. The synthetic perhydropyrindine gave a single peak in gas-liquid chromatography and should have a K_b of 5 to 6 while that of azaadamantane should be as low as 3 to 4. Gas-liquid chromatography of the bases, recovered from the aqueous phase in the usual manner, showed that 14% of the extracted material was *cis-trans*-perhydropyrindine. The stronger and more water-soluble azaadamantane would have been found in the aqueous layer if it had been present.

Search for Phenol. The sodium hydroxide extract mentioned earlier was acidified with concentrated hydrochloric acid solution and the acidic material was recovered by extraction with carbon tetrachloride in the spinning-rod column. After concentration and recovery of the acidic material from the carbon tetrachloride, it was distilled through a semimicro spinning-band column. Various cuts in the boiling range of 160° to 200° C. were chromatographed on the gas-liquid apparatus. A strong peak corresponding to *o*-cresol was found but no definite peak for phenol was found; if present, it was in trace amounts.

ACKNOWLEDGMENT

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