

# ADAMANTANE AND ITS HOMOLOGUES

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It is indeed a very difficult task to ascertain the individual hydrocarbons which are present in crude oils, and whose boiling points are above 200° C. It may be pointed out that even attaining the 200° C. boiling range and ascertaining the individual composition of petrol has needed about forty years of research by highly qualified workers in this field of study. With the rising boiling points of crude oil fractions there occurs the possibility of not only an increase in the number of isomers present but also, simultaneously, a decrease in the differences in the physical properties of the isomers or their homologues. Thus the difficulties of their separation as well as their identification substantially increase. Moreover, it is possible that there may be present new groups of hydrocarbons which have not been found in the lower boiling fractions, or even hydrocarbons with hitherto completely unknown structures and properties. As an example I would like to quote the crude oil of Hodonin the composition of which I began to study thirty years ago. The crude oil of Hodonin is a very heavy crude oil which does not contain petrol at all and is very viscous (119 cSt/20° and 25 cSt/50°).

Crude oils of similar character occur frequently, as can be seen from technical data quoted in literature. It may be presumed that some of the crude oils of Louisiana described by Coates, Best and Mabery may belong also to the same group of crude oils.

In the crude oil of Hodonin I, together with V. Machacek, found a quite new hydrocarbon, *adamantane*, the fundamental member of a new series of hydrocarbons. The isolation of adamantane consisted in thoroughly rectifying the fraction of crude oil

which is obtained by steam distillation, and freezing out. Adamantane separates out in beautiful octahedral crystals.

Adamantane is a hydrocarbon of formula  $C_{10}H_{16}$ . The carbon atoms are arranged in the same way as the carbon atoms in a diamond molecule. We could imagine that adamantane could be formed by the hydrogenation of the diamond or that the diamond could be formed by the dehydrogenation of the adamantane. It is of interest that the American scientist Bridgewater tried to obtain diamond by dehydrogenation of adamantane under high pressure. Adamantane is a compound interesting not only as regards its structure but also its properties. From the molecule of adamantane shown by means of a Stuart model it can be seen that four cyclohexane rings in saddle forms are bound together in such a manner that they form a very rigid spherical system. This symmetry becomes evident from the fact that among the 200 compounds of the formula  $C_{10}H_{16}$  only camphen, tricyclane and bornylane are solids melting at 53°, 68° and 98°, respectively, while the octahedrals of adamantane melt at 271° C. This high melting point is caused by the very rigid system of four cyclohexane rings which needs for melting a considerable quantity of heat energy for the transformation of the crystals to liquid. The spherical form of the molecule is characterized by a very small surface of the molecule. The forces binding the lattices together in the crystal are so feeble that the molecules can easily pass from the solid to the vapor state. Therefore, adamantane sublimates easily and the melting point can be determined in a sealed tube only.

If only adamantane were present in crude oil, its presence would be of significance only

as a curiosity. The relatively small quantity of adamantane in crude oil could hardly explain the special properties of some crude oils, especially of the crude oil of Hodonia: boiling point  $239^\circ$ , only 4% up to  $250^\circ$  and unusually low flash points of the heaviest oil fractions. It is worthy to mention that by means of water vapor at  $100^\circ$  it is possible to distil 30% of distillate from this crude oil. Therefore, as early as 1932, I presumed the presence of the homologues of adamantane in this crude oil.

The fact that, e.g., in Oklahoma crude oil only 0.05% of cyclopentane together with 22% of homologues of cyclopentane were found supports the presumption of the presence of homologues of adamantane to a higher extent.

In order to prove the presence of the homologues of adamantane, it was necessary to synthesize them and to determine their properties, because the known methods of isolation gave no hope in the successful isolation of the individual homologues of adamantane, the more so because the properties of the homologues of adamantane could not even be guessed at. The stated syntheses could have been accomplished after the Second World War only. In the meantime V. Prelog and Seivert succeeded in preparing adamantane from the malonic methylester in a yield sufficient to compare the melting point with the values found by us in the year 1932.

We began to prepare the homologues of adamantane by two methods:

Monotopic homologues were prepared from adamantane isolated from crude oil, whereas the di- and tetratopic homologues were synthesized from the methylester of malonic acid by a tedious method applied by Böttger for the adamantane derivatives, and also by Prelog for adamantane itself. We have improved this method in such a manner that the quantities obtained have been sufficient

for the determination of the essential (fundamental) data of the homologues.

Adamantane can be easily converted with yields up to 90% to bromoadamantane (by heating with bromine in  $\text{CCl}_4$  solution under reflux) which serves as raw material for the preparation of the monotopic homologues of adamantane (Fig. 1). Using mostly the

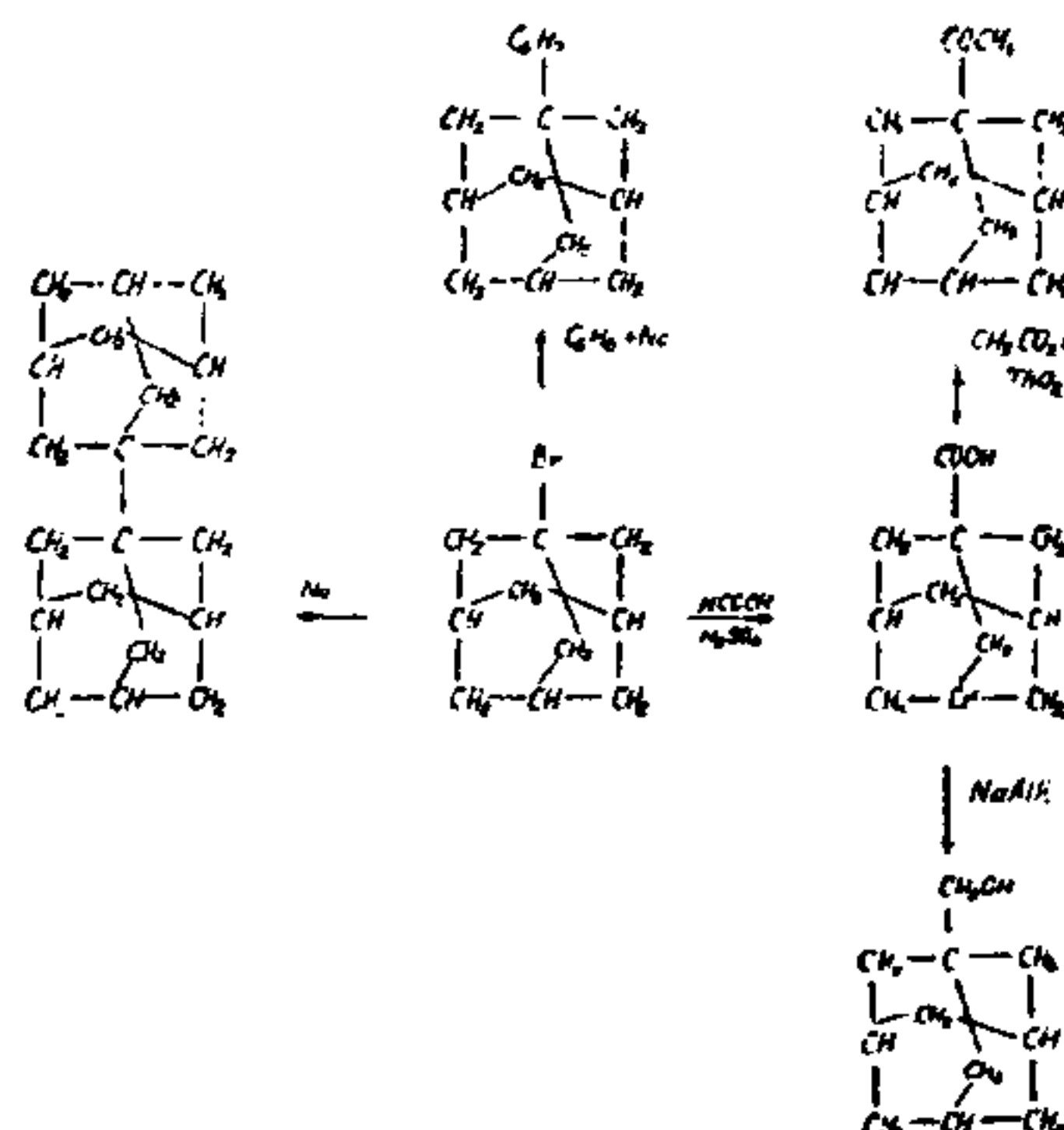


FIG. 1. Synthesis of Monotopic homologues of Adamantane.

Wurtz-Fittig procedure we prepared 5 monotopic homologues of adamantane and further 4 homologues by Grignard synthesis from adamantane carbon acid. 1-Ethyladamantane was prepared also by the reduction of methyladamantylketone. The monotopic homologues of adamantane are summarized in Table I. Preparation of the di- and tetratopic derivatives and homologues of adamantane is shown in Fig. 2.

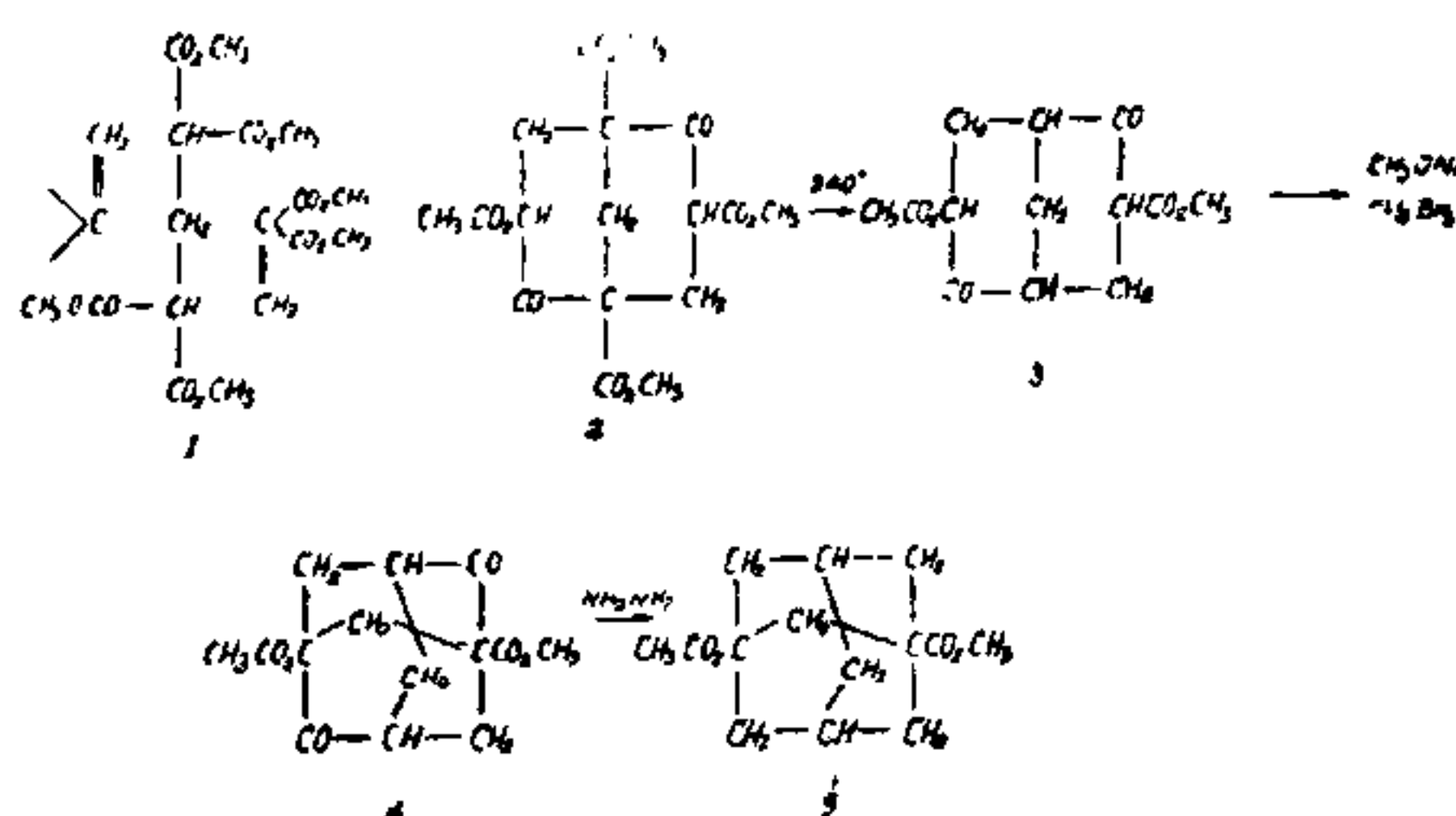


FIG. 2. Synthesis of ditopic homologues of Adamantane.



TABLE I  
Properties of homologues of adamantane

Hydrocarbon	Melting point	Boiling point	$n_D^{20}$
1-Methyladamantane .. ..	103	..	..
2-Methyladamantane .. ..	143.8-146	..	..
1-Ethyladamantane .. ..	-58	240	1.4955
1- <i>n</i> -Propyladamantane .. ..	-1	251	1.4962
1-Phenyladamantane .. ..	82	..	..
1-Cyclohexyladamantane .. ..	105	..	..
1, 1'-Diadamantyl .. ..	296	..	..
2-Adamantyl-1-propane .. ..	-20	105-107.8 mm.	1.4969
2-Adamantyl-1-butane .. ..	-44	119-121.8 mm.	1.5010
2-Adamantyl-1-pentane .. ..	under -50	235-240.8 mm.	1.4978
3-Adamantyl-1-pentane .. ..	-23	133-134	1.5000
1, 3-Dimethyladamantane .. ..	..	100-110/15 mm.	..
1, 3-Diisopropenyladamantane .. ..	..	155-158/15 mm.	1.5190*
1, 3-Diisopropyladamantane .. ..	under -70	294-296	..
1, 3, 5, 7-Tetramethyladamantane .. ..	66-67	159/15 mm.	..
$n_D^{17}$			

We have replaced the original way of isolation of adamantane which consisted in thoroughly rectifying and freezing out the fractions containing adamantane by another, more effective method. Schiessler and Flitter found that hydrocarbons with a cross-section of  $5.8 \times 6.8 \text{ \AA}$ , which value represents the size of the channel in the thiocarbamide clathrate lattice, give crystalline clathrates with thiourea. On the model of adamantane we can see that according to its dimensions adamantane could give a clathrate with thiourea. This fact has been fully confirmed. A benzenic solution of adamantane mixed with a methanolic solution of thiourea immediately gave needle-like crystals of the clathrate. The clathrate is relatively stable, which is caused by the fact that the absolutely symmetric molecule of adamantane fits closely to the spaces of the lattice of the clathrate; this enables a mutual binding of covalent forces. Adamantane can be isolated even from those fractions of crude oil from which it does not separate any more when cooling to  $-70^\circ \text{C}$ . This means that formation of a clathrate with thiourea is a more effective way for the separation of adamantane from crude oil than the freezing out of a sharp fraction.

Not only adamantane, but also all its homologues prepared by us, e.g., diadamantyl, phenyladamantane, cyclohexyladamantane, ethyladamantane, propyladamantane and even dimethyladamantane form a clathrate with thiourea, which is caused by the fact that the substituents increase the dimension of the molecule in one direction only.

The clathrates were prepared by heating an 8% methanolic solution of thiourea with adamantane or with a mixture of its homologues in a sealed tube up to  $100^\circ \text{C}$ . On cooling, needle-like crystals of clathrate appeared, which—when cooled slowly—attained a length of several centimetres. 1, 1'-diadamantyladamantane and 1-cyclohexyladamantane yielded crystals of clathrate even from a warm solution, while the clathrate of phenyladamantane, ethyladamantane and propyladamantane needed some hours of standing at room temperature. This is caused by the fact that the substituents of 1-cyclohexyladamantane and diadamantyl contribute to form the clathrate. Phenyl-, ethyl- and propyl-groups are not clathrate-forming and if bound to a clathrate-forming molecule, they do not hinder the forming of the clathrate, but reduce its stability. This fact facilitates considerably the isolation of

adamantane and its homologues from crude oil. Thus it is possible to obtain a concentrate of hydrocarbons forming clathrates with thiourea which includes all monotopic homologues of adamantane and even some ditopic ones, as it results from preliminary experiments.

The great stability of the adamantane clathrate is the reason why from the mixture of hydrocarbons forming a clathrate with thiourea the adamantane passes with preference into this crystalline clathrate.

On this fact we based the method of the quantitative determination of adamantane in crude oils, which enables the determination of adamantane during 6 or 8 hours with a precision of 0.001%. In this way we have ascertained the presence of adamantane in further kinds of the Czechoslovakian crude oils.

It is worthy to mention that the clathrates of adamantane and its homologues represent the lowest ratio of weight of thiourea to hydrocarbons.

According to a paper by Rossini, in which he generalizes the results of the analysis of petrol from seven different crude oils, all crude oils contain substantially the same hydrocarbons and the main compounds in the petrol fraction of each crude oil can be divided into five groups, i.e., *n*-paraffins, *i*-paraffins, alkylcyclopentanes, alkylcyclohexane and alkylbenzenes. In each of these five groups of hydrocarbons, individual compounds occur in ratios of equal rank for different crude oils. The different crude oils differ only by the different ratios of the groups of hydrocarbons, but in all crude oils each group contains the same hydrocarbons; also the mutual proportion of the different homologues remains the same.

The presence of adamantane was proved also in French crude oil of Le Lacque by Croxier, in U.S.A. crude oils by Mair and Rossini, and recently in U.S.S.R. crude oils. In Iraq crude oil thioadamantane was dis-

covered by Birch. It seems that the presence of adamantane and adamantane derivatives will not be limited only to some of these crude oils, but will occur in all naphthenic crude oils.

Although the formation of clathrates is a very effective method for the separation of adamantane and its homologues, many hydrocarbons forming clathrate with thiourea pass also into the precipitate so that the isolation is unsatisfactory. Therefore we have tried to separate the homologues of adamantane from other hydrocarbons forming clathrates with thiourea by means of chromatography. For this study 1-ethyladamantane has been chosen as a characteristic representative of this series. It had been prepared in a larger quantity by reduction of methyladamantylketone.

The chromatographic separation has been studied by S. Hala on binary mixtures with *n*-dodecane, decaline, dicyclohexylmethane and 1,2,4,5-tetramethylcyclohexane. On percolation we ascertained that some separation of ethyladamantane from the cyclic naphthenes occurred, but the separation was not sufficiently sharp. From this it can be deduced that crude oil fractions containing the lower homologues of adamantane could be enriched in this way by chromatography and at the same time the homologues of adamantane would follow behind the simple cycloparaffins and would accumulate among the dicycloparaffins and polyalkylcycloparaffins.

Thermodiffusion was found to be a much more effective method than chromatography for the separation of the homologues of adamantane from other naphthenes, eventually from *i*-paraffins.

From the crude oil of Hodonin about 10% were vaporized by means of steam. From this fraction we separated hydrocarbons forming clathrates with thiourea and consisting mostly of naphthenes, 74-88% of carbon atoms of the total number of carbon atoms



are present in naphthenic structures. The decomposed clathrates were freeze-dried, adamantane filtered off and the filtrate rectified. Six fractions boiling from 100°/15 mm. Hg up to 150°/15 mm. Hg were submitted to a repeated thermodiffusion in a batch equipment of current construction, consisting of two vertical concentric tubes 50 cm. high with a slit width of 0.4 mm. At the thermal gradient of 50° the equilibrium was reached in six hours. Five thermodiffusion fractions were collected and submitted to gas chromatographic analysis.

Until now only two of the five fractions, i.e., No. 1 and No. 3, have been analyzed by infra-red spectroscopy and both show seven distinct peaks. Peak No. 1 belongs to adamantane, peak No. 2 to 2-methyladamantane, peak No. 3 probably to 1-methyladamantane, No. 4 to 1-ethyladamantane, as could be proved by the injection of standards. Fraction No. 1 contains mostly adamantane and 2-methyladamantane, whilst fraction 3 mostly 1-ethyladamantane.

Mass spectra of these two fractions which were carried out by Messrs. Hanus and Dolejšek confirm the presence of the above-mentioned homologues of adamantane.

The mass spectra show that not only homologues of adamantane with 1 and 2 carbon atoms in side chains are present, but

also higher homologues with 3 and 4-carbon atoms are present. The investigated thermodiffusion fractions contain 20 to 80% of the homologue of adamantane.

Finally, a word may be said about the possible practical use of adamantane and its homologues. As it is known, the range of flight calculated according to Breguete formula

$$R = k.f. Q. \log \left( 1 - \frac{V}{P_0} \right)$$

depends first of all on the heating value and density of fuel, considering the fuel only. The heating value of a fuel is given by the hydrogen content according to the relation  $Q = 8650 + 122.2 H$ , where  $H$  is the percentage hydrogen. But the higher the hydrogen content the lower is the density.

This requirement which seems to be contradictory is fulfilled by naphthenes with several rings because they are fully saturated and the greater is the number of rings the higher is their density.

Adamantane and its homologues have nearly a heat calorific value of 10,000, and their density is approximately 1.00.

Supersonic fuels should be very heat stable, and the heat stability of some homologues of adamantane is extraordinary compared with other hydrocarbons.

## SEARCH FOR SUBMUONS

**T**HE field of high-energy physics has seen the discovery of a large number of new particles and resonances, all with mass larger than the mass of the  $\pi$  meson. However, the mass region between the muon and the electron has not been extensively studied. In a paper communicated to the *Physical Review*, 15 August 1963, D. H. Coward and coworkers report the results of an experiment designed to search systematically for singly charged particles (submuons) with rest masses between that of the electron and muon, produced by electromagnetic pair production.

The incident photon beam was obtained by bombarding a one-inch thick block of carbon

with an 80 MeV electron beam from the Stanford Linear Electron Accelerator. The momentum of the secondary particles was determined by using a double-focusing, zero-dispersion magnetic spectrometer.

The results of this experiment which had high sensitivity rule out any but very short-lived singly charged particles in the mass range 5–175  $m_e$ . This result when combined with theoretical electrodynamics results on the vacuum polarisation leads to the conclusion that it is very unlikely that charged particles with rest mass' between that of the electron and muon exist.—(*Phys. Rev.*, 1963, 131, 1782.)