(*6*). This is further supported by the facts that the 0.25-inch tumbler index is the only one of these measures of coke strength that is significantly correlated either with the maximum resistance developed in the Davis plastometer or with the ash content of the parent coal.

In previous work (*6*) another measure of coke strength was correlated with proximate analysis—namely, R_S, a constant measuring the uniformity of size after shatter. The range in value of R_S for the thirty-seven coals considered was too small to warrant an attempt to calculate it from the plastic indices. Since the maximum fluidity as determined in the Gieseler plastometer was not significantly correlated with the proximate analysis, it appeared possible that inclusion of another term in the regression equation might improve the correlation coefficient and reduce the probable errors of the calculated measures of coke strength. It was found, however, that there was no significant correlation between the maximum fluidity and any of the strength indices. No attempt was made to relate the other plastic indices determined by the use of the Gieseler plastometer to the several measures of coke strength since their correlation with proximate analysis was so similar to that found for the indices as determined by the use of the Davis plastometer.

FROM the preceding discussion, it does not seem unwarranted to conclude that knowledge of the various plastic indices considered, as determined by use of either the Davis or Gieseler plastometer, does not enable a closer prediction of several measures of coke quality to be made than is provided by the simpler proximate analysis.

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BICYCLO[2,2,1]HEPTANE and BICYCLO[2,2,1]-2-HEPTENE

Bicyclo[2,2,1]-2-heptene is formed by heating technical dicyclopentadiene with ethylene in a bomb at 200° C. and at pressures up to 120 atmospheres. Presumably the dicyclopentadiene depolymerizes to cyclopentadiene, and this reacts with the ethylene under the reaction conditions to give bicycloheptene. Bicyclo[2,2,1]heptane is formed by hydrogenating the bicycloheptene at 50° C. in the presence of a nickel catalyst. A small amount of methylcyclohexane is formed at the same time. Both of the bicyclo compounds are white crystalline solids. A.S.T.M. octane numbers have been determined on blends of 2,2,4-trimethylpentane, *n*-heptane, and the hydrocarbon. The bicycloheptene has a blending octane number of 95 ± 5; the bicycloheptane, a blending octane number of 56 ± 5.

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THE formation of bicyclo[2,2,1]-2-heptene by the reaction of cyclopentadiene with ethylene was recently reported (*7*). The reaction was carried out at 190–200° C. and at pressures to 395 atmospheres.

A considerable amount of the bicycloheptene was desired for study, but the rather high pressure of 395 atmospheres was a deterrent to making large preparations. The preparation and storage of large quantities of cyclopentadiene also presented difficulties. In the present work it was found that both of these difficulties could be overcome by charging technical dicyclopentadiene and ethylene to the pressure vessel. Apparently the dicyclopentadiene cracks to cyclopentadiene, which reacts with the ethylene. Under the conditions used, the maximum pressure encountered was 120 atmospheres.

The bicycloheptene was readily hydrogenated catalytically with a nickel catalyst. The expected bicyclo[2,2,1]heptane was obtained, together with a minor amount of methylcyclohexane. Both of the bicyclo compounds had been previously prepared by other methods (*8*).

The combustion characteristics of these materials in internal combustion engines is of interest, especially when compared with the combustion characteristics of hydrocarbons that might be considered related to bicycloheptane. The octane numbers of such hydrocarbons follow:

Compound	Octane No.	Compound	Octane No.
2,3-Dimethylpentane	90 (*2*), 82 (*5*)	*n*-Pentane	64 (*9*)
2,4-Dimethylpentane	90 (*2*), 80 (*5*)	Cyclopentane	85 (*2*)
n-Hexane	28 (*2*)	Bicycloheptane	56 ± 5[a]
Cyclohexane	80 (*3*)		

[a] Blending octane number.

Bicycloheptane contains two tertiary carbon atoms and might be expected to resemble 2,3- or 2,4-dimethylpentane and have an octane number in the 80–90 range. Or since it can be considered as containing two cyclopentane rings, it might be expected to resemble cyclopentane and have an octane number of about 85. Or since *n*-pentane has an octane number of 64 and this is raised, on conversion to cyclopentane, to 85, then further cyclicizing might be expected to give a still higher octane number. Bicycloheptane can also be related to cyclohexane which has an octane number of 80. It might be expected to have a somewhat higher octane number if the *n*-hexane series is valid, since *n*-hexane with 28 goes to 80 on cyclicizing to cyclohexane. A continuation of the cyclicizing process might lead to still higher octane numbers. All of these analogies lead to the prediction of an octane number of 80 or higher for the bicycloheptane. The observed blending octane number of 56 is far below the anticipated value. This seems to prove that generalizations found in the aliphatic series relating structure to combustion characteristics are not necessarily applicable to the cycloparaffins.

Ordinarily the blending octane numbers of saturated compounds in saturated compounds are very close to the unblended octane numbers. Only in rare cases is the blending octane number lower than the unblended. It is therefore felt that the above value of 56 is not far from the true value for bicycloheptane.

The blending octane number of bicyclo[2,2,1]-2-heptene was 95 ± 5. Any prediction of this octane number is difficult. The blending octane numbers of olefins in saturated compounds are higher than the unblended octane numbers. Further, the blending octane number of the olefin is a function of its concentration in the blend. For these reasons no value is easily assignable to the pure bicycloheptene for comparison with related olefins. It does seem that the octane number of the pure bicycloheptene is higher than the value for bicycloheptane, as might be expected. Also the susceptibility to tetraethyllead is higher (Table I) for the blend containing the bicycloheptane than for that containing the bicycloheptene. This is also what would be expected.

PREPARATION OF BICYCLO[2,2,1]-2-HEPTENE

In a typical experiment 800 grams of technical dicyclopentadiene (supplied through the courtesy of the Koppers Company) was charged to a 3-liter Ipatieff rotating bomb. The bomb was closed, flushed with nitrogen, and charged to 50 atmospheres at 20° C. with ethylene. The bomb was rotated and gradually warmed. Preliminary experiments indicated that the reaction is exothermic. When the bomb is heated too rapidly, the temperature is likely to rise above 200° during the exothermic reaction. A typical time-temperature-pressure relation follows:

Time, Hr.	Temp., ° C.	Pressure, Atm.	Time, Hr.	Temp., ° C.	Pressure, Atm.
0	20	50	4.5	30	50
1	85	65	5	80	50
2	198	98	6	198	78
3	200	40	7	200	80
3.5	200	40	8	23	32
4.5[a]	30	20			

[a] The bomb was cooled and repressured to 50 atmospheres with ethylene.

The bomb was cooled, the ethylene released, and 1025 cc. (960 grams) of product were recovered. In several runs a total of 3040 cc. (3000 grams) of technical dicyclopentadiene was charged, and 4050 cc. (3800 grams) of reaction product recovered. A total of 800 grams (28.6 moles) of ethylene reacted. Distillation gave:

Cut 1	50–94.7° C.	154 grams
Cut 2	94.7	1968
Cut 3	> 94.7	1598
	Loss	80 grams

Cut 1 was a liquid and contained some cyclopentadiene; it was not examined further. Cut 2 was a solid that melts at 46° C. and boils at 96.1°, corrected. These properties are consistent with those reported by Joshel and Butz (*7*). The melting point is lower than the values in the range 50–53° C. obtained by other methods of synthesis (*8*). Cut 3 was a liquid from which a small amount of unidentified crystalline material separated. A major part of the liquid was unreacted dicyclopentadiene. The yield of bicycloheptene was 46% of theory if one assumes that the dicyclopentadiene charged was pure and if no credit is taken for unconverted dicyclopentadiene.

TABLE I. PROPERTIES OF BLENDS

Property	Blend Containing Bicycloheptene	Blend Containing Bicycloheptane
d_4^{20}	0.7283	0.7253
n_D^{20}	1.4045	1.4038
$(n_F^{20} - n_C^{20}) \times 10^4$	77.5	72
Sp. dispersion × 10^4	106.5	99
Bromine number	42	1
Octane number		
Of blend	67.1	59.2
Blending No. of hydrocarbon	95 ± 5	56 ± 5
Of blend + 3 cc. tetraethyllead/gal.	79.8	79.3

PREPARATION OF BICYCLO[2,2,1]HEPTANE

Eight hundred sixteen grams of the bicycloheptene and 50 grams of Universal Oil Products nickel hydrogenation catalyst (*6*) were added to a 3-liter Ipatieff rotating bomb. The bomb was flushed with hydrogen and then pressured to 100 atmospheres with hydrogen. Upon heating to 50° C., hydrogenation was rapid. The bomb had to be repressured twice before hydrogenation was complete. The product in the cold bomb was a white volatile solid except where discolored with catalyst. The solid was recovered by dissolving in technical pentane and filtering to remove catalyst. The solvent was removed by distillation. Between 90 and 105° C., 55 grams of liquid were recovered and were shown to be mostly methylcyclohexane (d_4^{20} 0.7705, n_D^{20} 1.4237). The main product distilled at 105.3–105.5° C., corrected. The melting point of the product was 86–87° C. The yield of 747 grams (90% of theory) was low, primarily as a result of handling losses.

Both the bicycloheptene and bicycloheptane are white crystalline solids that have a high vapor pressure and sublime readily. The crystals are slightly gummy, in that they can be bent and stretched as contrasted to brittle crystals. Both compounds have odors that are strongly reminiscent of cyclopentadiene with a little camphor odor superimposed. The odors of the two compounds are not identical but the difference is not easily described. The bicycloheptene has a "warm" taste, while the bicycloheptane is tasteless but gives the sensation of a piece of paraffin wax. The bicycloheptane is stable to equal parts of concentrated nitric plus sulfuric acids and to dilute permanganate solution. The bicycloheptene reacts with both.

OCTANE NUMBERS

Octane numbers were determined according to A.S.T.M. procedure (*1*). So that liquids could be used in determining the antiknock properties, blends were made. The base for the blend was 60% 2,2,4-trimethylpentane plus 40% *n*-heptane that has an octane number of 60 by definition. The final blend of 20% bicyclo compound in the base stock was made by thermostating the base stock at 15.5° C. and adding the solid bicyclo compound until the desired volume increase was obtained at equilibrium.

The base stock had the following properties: d_4^{20}, 0.6884 [calculated to be 0.68858 from 0.69182 (*4*) for 2,2,4-trimethylpentane and 0.68372 (*4*) for *n*-heptane]; n_D^{20}, 1.3897 [calculated to be 1.39004 from 1.39157 (*4*) for 2,2,4-trimethylpentane and 1.38774 (*4*) for *n*-heptane]; $(n_F^{20} - n_C^{20})$, 68 × 10^{-4}; specific dispersion, 99 × 10^{-4}; bromine number, 0. The properties of the blends are given in Table I.

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