Bromination in chloroform converted the ethane to a dibromide—presumably 1,2-di-(2,4,6-triisopropyl-3-bromophenyl)-ethane. It was purified by recrystallization.

2,4,6-Triisopropylbenzyl Chloride.[17]—This compound was prepared in 85% yields by the general method of Sommelet.[18] A mixture of 300 g. of triisopropylbenzene, 200 g. of chloromethyl ether and 600 cc. of carbon disulfide was cooled to 0°, and 120 g. of stannic chloride was added gradually, with stirring, over a period of one hour. The mixture was stirred for an additional hour and poured on ice. The chloromethyl compound was purified by distillation.

(17) This compound was prepared by Mr. Norman Rabjohn.
(18) Sommelet, *Compt. rend.*, **157**, 1443 (1913).

Summary

An improved method has been developed for the synthesis of mesitaldehyde. The procedure has been used successfully to prepare 1,3,5-triethylbenzaldehyde, 1,3,5-triisopropylbenzaldehyde and guaialdehyde.

Mesitaldehyde, 2,4,6-triisopropylbenzaldehyde and guaialdehyde have been reduced bimolecularly to yield the corresponding hydrobenzoins.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Alkylation of Paraffins at Low Temperatures in the Presence of Aluminum Chloride

BY HERMAN PINES, ARISTID V. GROSSE AND V. N. IPATIEFF

The alkylation[1,2,3] of isobutane with propene and butene in the presence of aluminum chloride was studied at temperatures ranging from −40° to +150°. At the lower temperatures it was possible to carry out this reaction at atmospheric pressure, while at 0° or higher the experiments were made under increased pressure. This paper will deal only with the low temperature alkylation.

For the low temperature alkylation, a continuous-operation glass apparatus was designed with which it was possible to regulate the temperature, contact time or feed rate.

Discussion of Results

The properties of the products obtained from the reaction of olefins with paraffins in the presence of aluminum chloride–hydrogen chloride depend on several factors: concentration of olefins, temperature, time of contact, and quantities of hydrogen chloride used. When the charging stock contains a large proportion of olefins, the resulting product is of a high molecular weight; it was found that when a ratio of 4 parts of paraffins to 1 part of olefins is used, the resultant product is of the desired properties. The temperature and experimental conditions depend upon the pair of hydrocarbons used. Ethene reacts with paraffins at 0° or higher and, therefore, the experiments are preferably made under super-atmospheric pressure. For other olefins, temperatures ranging from −45° to room temperature produce satisfactory results. Very low temperatures (−100°) are not desired, since at these temperatures the paraffinic hydrocarbons are not very reactive, and the resulting product consists of high-boiling hydrocarbons due to the polymerization of olefins.

The aluminum chloride was always observed to undergo a series of changes. The fine suspended aluminum chloride first formed flocculent curds that later formed hard pieces; after a period of time these pieces softened into a heavy sticky gum which slowly became a yellow-brown viscous liquid. When the catalyst reached this stage, great difficulty was encountered in keeping the discharge tube open. In some cases plugging of the discharge tube occurred, and the experiment had to be discontinued, although the aluminum chloride showed no diminution in activity.

Isobutane–*n*-Butenes.—As an example of a continuous alkylation of isobutane with *n*-butene, a typical experiment is described in detail in Table I in the experimental part. This reaction was made at −35° in an atmospheric-pressure, continuous-alkylation apparatus (Figs. 1 and 2). The liquid product resulting from this reaction contained over 60% of octanes and 12% dodecanes. About 90% of the total product distilled below 225° and consisted of paraffinic hydrocarbons only. The exit gases did not contain any olefinic hydrocarbons; they consisted only of un-

(1) V. N. Ipatieff and H. Pines, U. S. Patents 2,112,846 and 2,112,-847, April 5, 1938.
(2) (a) V. N. Ipatieff "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, N. Y., 1937, p. 673; (b) V. N. Ipatieff, A. V. Grosse, H. Pines and V. I. Komarewsky, *ibid.*, **58**, 913 (1936); (c) H. Pines, paper presented before the Division of Organic Chemistry at the American Chemical Society Meeting, Dallas, Texas, April, 1938.
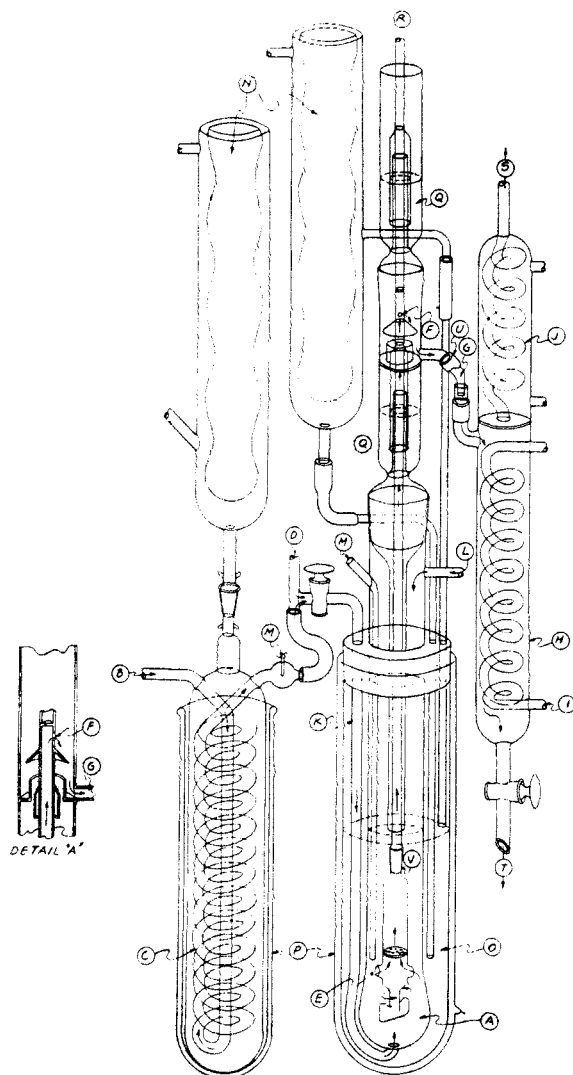(3) V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

Fig. 1.—Low temperature alkylation apparatus.

reacted isobutane which could be mixed with fresh butene and contacted again with the catalyst.

The octane fraction was distilled on a 20 theoretical plate distilling column with a reflux ratio of 10:1. The following compounds were identified by means of Raman spectra: 2,2,4-trimethylpentane, 2,2,3-trimethylpentane, 2,5-dimethylhexane and 2,3,4-trimethylpentane.

One of the primary products of the reaction of isobutane with n-butene is 2,2,3-trimethylpentane
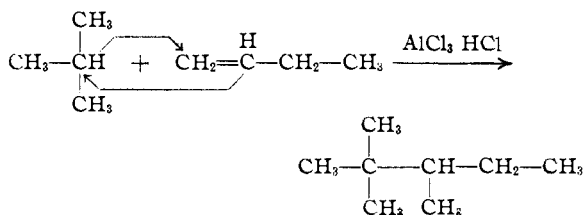
The formation of 2,2,4-trimethylpentane and 2,5-dimethylhexane is probably due to the isomerization of n-butene to isobutene and subsequent reaction of the isobutene with isobutane.
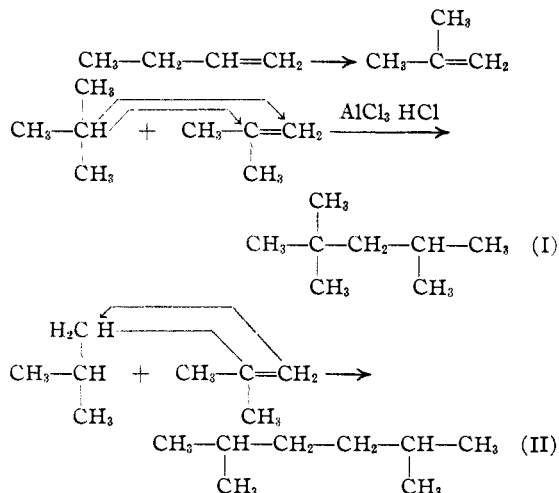
TABLE I

Hour ending	Feed rate liq. cc./hr.	Liquid product cc./hr.[a]	HCl added g./hr.	Cut	Vol. % C_8H_{18}	Vol. % boiling to 225°
1	315	93	3.6	1	52.3	75.2
2	300	99	4.2	2	62.9	94.4
3	300	108	2.0	3	65.5	91.0
4	300	118	2.5	4	65.8	88.4
5	325	110	1.7	5	65.5	89.3
6	300	105	1.0	6	63.1	89.4

[a] Unstabilized, contains about 20% dissolved isobutane.

SUMMARY OF DISTILLATION DATA

B. p., °C.	Cut 1	2	3	4	5	6
–96	7.4	12.7	5.7	2.6	2.8	3.8
96–125	52.3	62.9	65.5	65.8	65.5	63.1
125–150	3.8	2.9	3.0	2.6	3.0	3.1
150–175	0.0	0.0	0.0	0.2	0.0	0.0
175–200	5.5	10.9	12.0	12.0	13.8	12.4
200–225	6.2	5.0	4.8	5.2	4.2	7.0
Total boiling to 225°	75.2	94.4	91.0	88.4	89.3	89.4

The presence of 2,3,4-trimethylpentane could be explained only on the basis of isomerization of the octanes formed.

The structure of the dodecanes was not investigated.

Isobutane–Propene.—The reaction of isobutane with propene was carried out under conditions similar to those described for isobutane–n-butene alkylation. The hydrocarbons produced contained 42% of heptanes and 20% of decanes.
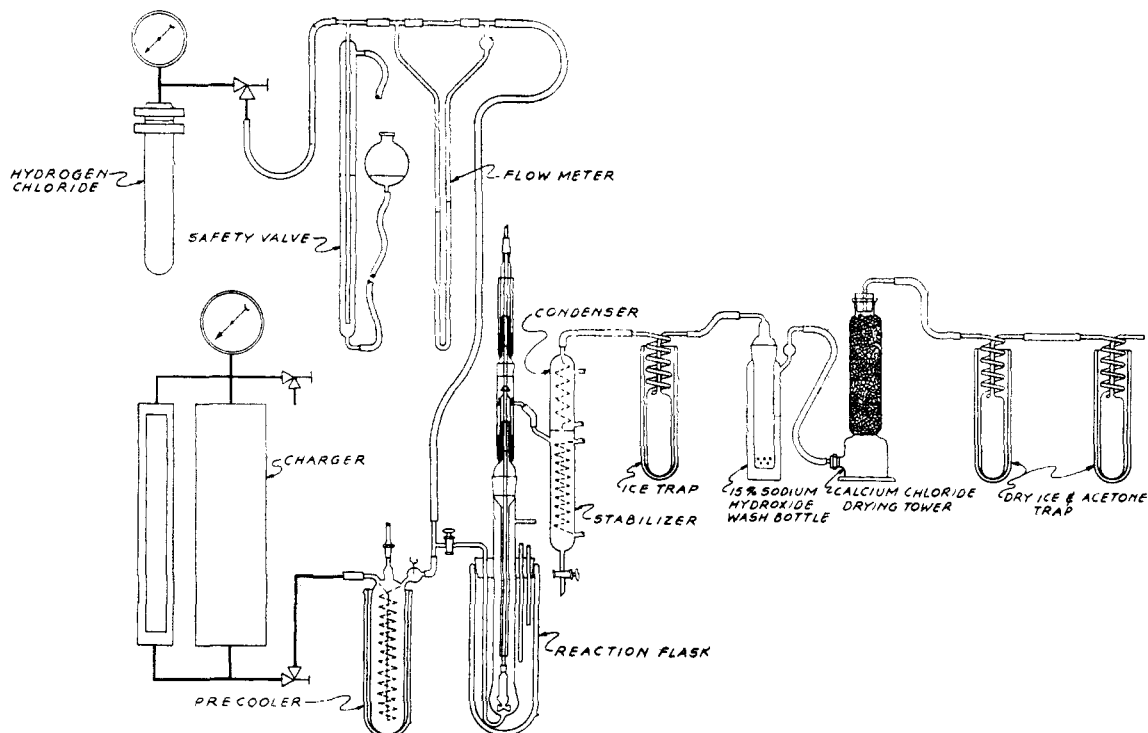
Fig. 2.—Flow diagram of low temperature alkylation.

Ninety per cent. of the catalyzate distilled below 220°. The heptane fraction consisted of 2,4- and 2,3-dimethylpentane, the latter in preponderant amounts. These were identified by the Raman spectroscopic method.[4] The identification is in full agreement with the physical constants of the cuts obtained.

The structure of the decanes was not investigated.

Experimental

Apparatus and Procedure.—The flow sheet of the low-temperature alkylation apparatus is given in Fig. 1. The main body of the apparatus is the reaction flask which is designed for a continuous withdrawal of *catalyst-free* liquid product. The separation of the liquid product from the catalyst is accomplished by centrifuging the liquid product in the stirring device itself. The catalyst is forced toward the wall of the vessel, while the relatively clear liquid is lifted by nitrogen pressure through the opening "E" of the hollow stirring shaft, through a part of the mercury seal, and through a perforation "F" in the tube where an apron spins it into a trough which drains through tube "G" into a stabilizer "H" (see detail "A").

The reaction vessel and the precooler are maintained at the desired temperature by refluxing a suitable cooling liquid such as propane, dimethyl ether, isobutane or n-butane.

The gaseous hydrocarbons are mixed in the desired proportions in a calibrated pressure charger equipped with a

(4) E. J. Rosenbaum, A. V. Grosse and H. F. Jacobson, THIS JOURNAL, **61**, 689 (1939).

Jerguson gage and pressure needle valves. The hydrocarbons from the charger pass through a precooler "C"; immediately before entering the reaction chamber the hydrocarbons are mixed with anhydrous hydrogen chloride. The latter, kept in a steel bomb, passes through a manometer and flowmeter into inlet "D." The mixture of hydrocarbons and hydrogen chloride is passed through tube "K" into the reaction flask. Before introduction of the gases, a weighed amount of anhydrous aluminum chloride is put into the reaction vessel "A," and covered with the paraffinic hydrocarbons used in the reaction. An electric motor-driven propeller stirs the reagents constantly throughout the run. As soon as the liquid reaches the level "E," the nitrogen stream lifts the hydrocarbons through the system described above into the stabilizer kept at 30° by blowing air through the coil (I) sealed into the receiver "H." The stabilized gas and the nitrogen pass through the water cooled condenser "I," and then pass through a train composed of an ice-cooled trap, a 15% sodium hydroxide wash bottle, a calcium chloride drying tower, gas traps cooled to −78° by means of solid carbon dioxide and acetone, and then put into the air.

Isobutane and n-Butene.—The experimental conditions are given in Table I. The octane fraction was distilled on a 20 theoretical plate column. The combined octane fraction was analyzed. Found: C, 83.89; H, 15.98. Calcd. for C_8H_{18}: C, 84.11; H, 15.89.

The following fractions were analyzed: *Fraction 6*, b. p. 98–99° (742 mm.), $n^{20}D$ 1.3914, d^{20}_4 0.6911. According to Raman spectroscopic analysis this fraction consists of: 80% 2,2,4-trimethylpentane, 20% 2,2,3-trimethylpentane. *Fraction 17*, b. p. 108–109° (742 mm.), $n^{20}D$ 1.3959, d^{20}_4 0.6943. According to Raman spectro-

scopic analysis the fraction consists of: 65% 2,5-dimethyl-hexane, 15% 2,2,4-trimethylpentane, 5% 2,2,3-trimethyl-pentane, 15% unknown octanes. *Fraction 23*, b. p. 114–115° (742 mm.), n^{20}D 1.4021, d^{20}_4 0.7124. The Raman spectroscopic analysis shows that it consists chiefly of 2,3,4-trimethylpentane.

Isobutane–Propene.—The reaction was made at −30° and under conditions similar to those described in detail for the isobutane–*n*-butene alkylation. The amount of aluminum chloride used and the feed rate of the hydrocarbons and the hydrogen chloride were the same. The concentration of propene in isobutane was 23% on molar basis. The contact time of the hydrocarbons with aluminum chloride was of the order of four minutes. In total 3230 cc. of liquefied gaseous hydrocarbons was contacted with the 15 g. of aluminum chloride; even at the end of that period the catalyst was still active. Six hundred and fifty cc. of liquid product was obtained which contained 42% of heptanes and 20% decanes. Ninety per cent. of the total product distilled below 220°. The liquid product was stable toward a nitrating mixture, indicating the absence of olefinic hydrocarbons. The exit gases did not contain any unreacted propene.

The heptanes were redistilled on a 20 theoretical plate column; 89% of product distilled from 84 to 89°. The following fractions were analyzed. *Fraction 4*, b. p. 86°; n^{20}D 1.3883, d^{20}_4 0.6865. Raman spectroscopic analysis: 50% 2,4-dimethylpentane; 50% 2,3-dimethylpentane.

Fraction 11, b. p. 88–89°, n^{20}D 1.3908, d^{20}_4 0.6921. *Analysis.* Found: C, 83.60; H, 16.20. Calcd. for C_7H_{16}: C, 83.90; H, 16.10. Raman spectroscopic analysis: 10% 2,4-dimethylpentane, 90% 2,3-dimethylpentane.

The decanes were redistilled; 92% of the product distilled at 150 to 154°: *Fraction 2*, b. p. 150–151°, n^{20}D 1.4099, d^{20}_4 0.7302. *Fraction 6*, b. p. 153°, n^{20}D 1.4112, d^{20}_4 0.7322. *Analysis.* Found: C, 84.25; H, 15.71. Calcd. for $C_{10}H_{22}$: C, 84.40; H, 15.60.

Summary

The reaction between isobutane and olefins at low temperature was studied. Isobutane reacts with propene in the presence of aluminum chloride–hydrogen chloride catalyst at −30°, yielding 42% of heptanes composed of 2,3- and 2,4-dimethylpentane.

Isobutane and *n*-butene under similar conditions yield 60% of octanes of which the following were identified by Raman spectroscopic analyses: 2,2,4-, 2,2,3-, 2,3,4-trimethylpentane and 2,5-dimethylhexane.

The Vapor Phase Esterification Equilibrium*

BY J. O. HALFORD AND DONALD BRUNDAGE

Studies[1] of the equilibrium in the reaction

$$CH_3COOH(g) + C_2H_5OH(g) = CH_3COOC_2H_5(g) + H_2O(g) \quad (1)$$

conducted with the aid of catalysts at 150 to 300° have yielded widely divergent results which could not be extrapolated to give reasonable values of the equilibrium constant at room temperature. The data of Jatkar and Gajendragad appear to be the most reliable. At lower temperatures, the distillation method of Edgar and Schuyler[2] has been improved by Swietoslawski and Poznanski[3] and further refined by Salcewicz,[4] who obtained uncorrected constants of 41 at 75.9° and 39 at 73.7°, using vapor samples containing acetic acid in apparent mole fractions of 0.0213 and 0.0033,

respectively. When these results are corrected for association, as described below, they yield 68 and 45 for the vapor phase constant, showing that the experimental method is still subject to large errors.

The present work was undertaken to provide further data by a new experimental method at a temperature as near to 25° as might prove feasible. The acid and ester were treated as solutes in a large excess of a solvent containing alcohol and water in a fixed ratio. The liquid phase equilibrium constant at 40° has been obtained from measurements at 40, 60, 79 and 99°, and has been transferred to the vapor phase with the aid of vapor compositions measured separately for the solvent and for dilute solutions of the acid and ester. The result is $K_{313} = 122 \pm 3$.

Table I and Fig. 1 show the logarithm of the equilibrium constant as a function of the reciprocal of the absolute temperature. No relation of the expected linear or slightly curved form is

(1) Frolich, Carpenter and Knox, THIS JOURNAL, **52**, 1565 (1930); Tidwell and Reid, *ibid.*, **53**, 4353 (1931); Essex and Clark, *ibid.*, **54**, 1290 (1932); Jatkar and Gajendragad, *ibid.*, **59**, 798 (1937).

(2) Edgar and Schuyler, *ibid.*, **46**, 64 (1924).

(3) Swietoslawski and Poznanski, *Roczniki Chem.*, **8**, 527 (1928).

(4) Salcewicz, *ibid.*, **14**, 702 (1934).