TABLE IV

REVERSIBLE NATURE OF CARBON MONOXIDE INHIBITION

% CO in atm.	Controls[a]	Treated[b]
0.00	32.40	
.01	17.38	22.96
.02	7.86	18.20
.05	4.51	13.68
.1	4.97	10.57
.2	4.54	11.84

[a] In CO atmospheres from 12/14/40 to 1/11/41. [b] In CO atmospheres from 12/14/40 to 12/28/40; in air from 12/28/40 to 1/11/41.

bon monoxide in the presence of ammonium nitrate—for example, by chance contaminating microörganisms—since estimation of this gas in the atmospheres during the course of the experiments showed no detectable change.

To settle these points definitely would require many carefully controlled experiments in which the external environment, including source of nitrogen, would be varied. Such investigations would be laborious, time-consuming and possibly indecisive, since accurate control of all variables is very difficult in long-time experiments. Another method, however, is available which offers less experimental limitation. Wyss and Wilson[9] have recently demonstrated that the symbiotic nitrogen fixation system in red clover is probably identical with that in *Azotobacter*. Consequently, carbon monoxide should likewise inhibit fixation by this organism. Preliminary experiments have shown this to be true and, although the actual ranges differ, the results are entirely analogous: at low concentrations of carbon monoxide, uptake of free nitrogen is inhibited—at higher levels, uptake of combined nitrogen is inhibited as well. Since *Azotobacter* can be used in short-time trials (two to five hours in the Warburg respirometer), the use of this organism affords definite advantages for more precise and detailed investigation of the mechanism of carbon monoxide inhibition. Further study of this reaction is accordingly being made with *Azotobacter*.

Summary

Evidence from experiments in which total nitrogen fixed was estimated, as well as others in which rate of fixation was measured, shows that uptake of free nitrogen by inoculated red clover plants is inhibited by as little as 0.01% carbon monoxide. The fixation process is practically stopped by 0.05% carbon monoxide. In this range of *p*CO, no effect on assimilation of ammonium nitrate by uninoculated plants is observed, but at higher concentrations definite inhibition is detectable. The inhibition of nitrogen fixation appears to be reversible and non-competitive.

MADISON, WISCONSIN RECEIVED OCTOBER 14, 1941

(9) Wyss and Wilson, *Proc. Natl. Acad. Sci. U. S.*, **27**, 162 (1941).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MISSOURI]

The Action of Aluminum Chloride on Aromatic Hydrocarbons. III. The Polyethylbenzenes and Tetramethylbenzenes

BY DOROTHY NIGHTINGALE AND FRANCIS WADSWORTH[1]

Previous work on the action of aluminum chloride on aromatic hydrocarbons in this Laboratory has been with trialkylbenzenes of the type 1,3-dimethyl-4-R-benzenes where R = C_3H_7 and C_4H_9.[2,3] We have now completed a similar study of the triethylbenzenes, the tetraethylbenzenes and the tetramethylbenzenes.

The *sym*- and *unsym*-triethylbenzenes were each converted into a mixture of these two hydrocarbons along with some diethylbenzene and tetraethylbenzene by the action of aluminum chloride at 70–75°. In the case of the 1,3,5-triethylbenzene, the ratio of the two isomers as separated from the trialkyl fraction was approximately 1 part 1,2,4-isomer to 2.5 parts 1,3,5-isomer, while from 1,2,4-triethylbenzene the ratio was 1:1.5. Losses of hydrocarbon during sulfonation and subsequent hydrolysis of the triethylbenzene sulfonic acids were about the same for each of the two hydrocarbons so these ratios should be representative of the composition of the total triethylbenzenes present in the mixture. This is the first time that it has been possible to obtain a 1,2,4-hydrocarbon from a 1,3,5-hydrocarbon.

The *sym*- and *unsym*-tetraethylbenzenes were each partially converted into the other, as were

[1] Abstract of a dissertation presented by Francis Wadsworth in partial fulfillment of the requirements for the Degree of Master of Arts at the University of Missouri.

(2) Nightingale and Carton, THIS JOURNAL, **62**, 280 (1940).

(3) Nightingale and Smith, *ibid.*, **61**, 101 (1939).

durene and isodurene, along with small amounts of trialkylbenzene, pentaalkylbenzene and a high boiling residue. The tetraethylbenzene fraction from 1,2,3,4-tetraethylbenzene was a mixture of equal amounts of 1,2,3,5-isomer and 1,2,4,5-isomer, while the tetramethylbenzene fraction from prehnitene was 83% isodurene and 17% durene. Freezing point data indicated that little if any of the original 1,2,3,4-hydrocarbon was present. These rearrangements of 1,2,3,4-tetraalkylbenzenes into mixtures of *sym*- and *unsym*-isomers are striking and may explain why none of the vicinal isomer has been found in mixtures of tetraalkylbenzenes from Friedel-Crafts alkylations.

Penta- and hexaethylbenzenes yielded lower polyethylbenzenes along with unchanged hydrocarbon. Very little hexaethylbenzene was recovered.

These data are not entirely comparable to those reported by Jacobsen[4] on the action of aluminum chloride on polymethylbenzenes other than tetramethylbenzene. He used more drastic conditions —more aluminum chloride, longer time and higher temperatures.

The two triethylbenzenes were ethylated with ethyl chloride and aluminum chloride under various experimental conditions in an effort to determine whether or not there was any relation between the structure of the triethylbenzenes and the tetraethylbenzenes formed from them. Alkylation of either 1,2,4-triethylbenzene or 1,3,5-triethylbenzene at 70–75° led to mixtures of tetraethylbenzenes of nearly the same composition with the 1,2,3,5-isomer predominant. This is in agreement with the results of Smith and Guss[5] in the preparation of polyethylbenzenes from benzene, ethyl chloride and aluminum chloride. The formation of both tetraisomers can be explained by rearrangements of the triethylbenzenes prior to alkylation, or by rearrangement of the tetraethylbenzenes after alkylation, or a combination of both. If no rearrangements took place, the 1,3,5-triethylbenzene should yield only 1,2,3,5-tetraethylbenzene, and the 1,2,4-isomer should yield largely 1,2,4,5-tetraethylbenzene by analogy with other substitution reactions of 1,2,4-trialkylbenzenes. Jacobsen[6] reported only isodurene from mesitylene, methyl chloride and aluminum chloride at 75–80°, and only durene from pseudocumene under the same conditions.

Alkylation of 1,2,4-triethylbenzene at 20–21° led to a tetraethylbenzene containing 68% of the 1,2,3,5-isomer, an increase of 10%, but it was necessary to increase the time from fifty minutes to two hours and thirty-five minutes to complete the reaction. The lower temperature may be largely responsible for the increased yield of 1,2,3,-5-hydrocarbon, for, at 70–75°, increasing the time to two hours and thirty-five minutes changed the composition of the tetra fraction only slightly.

Because of the ease with which these hydrocarbons rearrange, it is difficult to make any definite correlations between the structures of the hydrocarbons and the products formed from them by alkylation or by the action of aluminum chloride. The fact that the 1,2,3,5-tetraethylbenzene was always present in larger amounts than the 1,2,4,5-isomer when either of the triethylbenzenes was ethylated may be interpreted as indicating that the formation of the unsymmetrical hydrocarbon is favored. Once they are formed, the two tetraethylbenzenes appear to be equally stable toward aluminum chloride, for the tetraethylbenzene fraction from both of them contained 58–59% of the original hydrocarbon. The data from this investigation and Jacobsen's[4] data indicate that the polymethylbenzenes are more stable toward aluminum chloride than are the polyethylbenzenes.

Acknowledgments.—The authors wish to thank the Dow Chemical Company for the commercial triethylbenzene which they have so generously furnished for this investigation, and which made it possible to carry out the reactions with much larger quantities of hydrocarbons than had been practical in previous work. The other special chemicals were purchased through a grant from the University Research Council, University of Missouri.

Experimental

Commercial triethylbenzene was separated into the 1,2,4- and 1,3,5-isomers by the method of Dillingham and Reid.[7] The procedures of Smith and Guss[5] were used for the separation and identification of the other polyethylbenzenes. The two triethylbenzenes were each sulfonated twice, and the sulfonic acids steam distilled after the initial separation to be sure that the two hydrocarbons were as pure as possible. It was more convenient to alkylate commercial triethylbenzene for the preparation of the higher polyethylbenzenes than to start with benzene.

The sodium salt of 1,2,4,5-tetraethylbenzene sulfonic acid was recrystallized twice prior to hydrolysis to obtain pure 1,2,4,5-tetraethylbenzene.

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(4) Jacobsen, *Ber.*, **18**, 338 (1885).

(5) Smith and Guss, THIS JOURNAL, **62**, 2625 (1940).

(6) Jacobsen, *Ber.*, **14**, 2624 (1881).

(7) Dillingham and Reid, THIS JOURNAL, **60**, 2606 (1938).

Isodurene was made from bromomesitylene by the method of Smith and MacDougall.[8] Durene was purchased from Eastman Kodak Company. Prehnitene was made by the Jacobsen rearrangement of mixtures of durene and isodurene by the method of Smith and Cass.[9]

The composition of the mixtures of the tetraethylbenzenes and of the tetramethylbenzenes was determined by their freezing points. In a few cases the isomers were also separated to verify the accuracy of the freezing point determinations. The slight variation was due to mechanical losses during separation.

To be certain that little or no unchanged hydrocarbon was present in the tetraethylbenzene mixture from 1,2,3,4-tetraethylbenzene after treatment with aluminum chloride, a sample of the mixture was made up to 69.4% of *sym*-isomer by the addition of 1,2,4,5-hydrocarbon. The freezing point of −0.5° corresponded to 69% *sym*-isomer on the freezing point curve of Smith and Guss.[10] To another sample, enough of the *unsym*-isomer was added to make it 43.9% of *sym*-isomer. The freezing point of −13° corresponds to 43% on the curve.

To the mixture of tetraethylbenzenes from prehnitene after treatment with aluminum chloride enough durene was added to make 76% isodurene. The freezing point of 18° corresponded to 75% isodurene on the freezing point diagram of Smith and MacDougall[8] for mixtures of durene and isodurene.

Alkylation of the Pure Trimethylbenzenes and Commercial Triethylbenzene.—The alkylations were carried out in a three-necked flask equipped with a motor stirrer, an inlet tube for ethyl chloride reaching to the bottom of the flask, and an exit tube for hydrogen chloride. The triethylbenzene and aluminum chloride were placed in the flask which was warmed in a water-bath. Ethyl chloride distilled into the reaction mixture from a graduated cylinder. At the end of the reaction the complex was decomposed with ice, the hydrocarbon washed, dried and vacuum distilled through a column packed with single turn glass helices.

The data for the tetraethylbenzene fractions (IV) from typical experiments are summarized in Table I. The ratio of moles of aluminum chloride to moles of hydrocarbon was constant except where noted. Some triethylbenzene was recovered, along with varying amounts of penta- and hexaethylbenzenes. All of the tetraethylbenzene could not be separated from the reaction products due to the formation of mixtures with triethylbenzene and pentaethylbenzene which could not be separated conveniently by distillation.

Action of Aluminum Chloride on Polyethylbenzenes and Tetramethylbenzenes.—The hydrocarbon and aluminum chloride were placed in a three-necked flask fitted with a reflux condenser and motor stirrer. The ratio of aluminum chloride to hydrocarbon was the same as in the alkylations. In most cases the mixtures were stirred fifty minutes at 70–75°. The complex was decomposed with ice, the hydrocarbon washed, dried and vacuum distilled. The data for the tetraalkylbenzene fractions (IV) from typical experiments are summarized in Table II. Various amounts of lower and higher alkylated benzenes were formed in most cases. The data from the two triethylbenzenes are typical.

The following fractions were obtained from 248 g. of *1,2,4-triethylbenzene* and 27 g. of aluminum chloride: (II-III) 20.7 g.; (III) 132.8 g.; (III-IV) 58.9 g. The triethylbenzene (III) is 76.5% 1,3,5-triethylbenzene and 23.5% 1,2,4-isomer.

From 230 g. of *1,3,5-triethylbenzene* and 25.2 g. of aluminum chloride the products were (II-III) 18.4 g.; (III) 121 g.; (III-IV) 35 g.; (IV) 11.4 g.; residue, 7 g. The triethylbenzene (III) is 16.5% 1,2,4-triethylbenzene and 83.5% 1,3,5-isomer. The tribromo derivative of the 1,2,4-triethylbenzene melted at 86°, the recorded value.

Pentaethylbenzene.—The hydrocarbon (183 g.) and aluminum chloride (14 g.) reacted at 70–75° for fifty minutes. The product was a mixture of tetra-, penta- and hexaethylbenzene which could not be separated completely.

Hexaethylbenzene.—The hydrocarbon (181 g.) and aluminum chloride (13 g.) were heated at 145–150° for fifty minutes. The product (127 g.) yielded 69 g. of pentaethylbenzene, 12 g. of hexaethylbenzene and 45 g. of a mixture of tetra- and pentaethylbenzenes.

TABLE I

COMPOSITION OF TETRAETHYLBENZENES FROM ALKYLATION OF TRIETHYLBENZENES AT 70–75° FOR FIFTY MINUTES

Hydrocarbon	g.	$AlCl_3$, g.	IV, g.	1, 2, 4, 5, %	1, 2, 3, 5, %
1,3,5-	205	22.4	61.2	48.3	51.7[c]
1,2,4-	205	22.4	83.4	46.6	53.4[c]
Com. tri-	200	21	46.7	40	60
1,2,4-[a] (20–21°)	130	14.2	18.8	32	68
1,2,4-[a]	130	14.2	22.7	42	58
Com. tri-	100	48.2	26.9	33	67
Com. tri-[b]	100	11	22.5	33	67

[a] Time 155 minutes. [b] 33.4 g. of tetrachloroethane [c] Isomers separated.

TABLE II

ACTION OF ALUMINUM CHLORIDE ON POLYALKYLBENZENES AT 70–75° FOR FIFTY MINUTES

Hydrocarbon	g.	$AlCl_3$, g.	IV, g.	1,2,4,5- %	1,2,3,5- %
1,2,3,5-Ethyl-	154	14	69	41	59
1,2,4,5-Ethyl-	165	15	117	58	42
1,2,4,5-Methyl-	100	13.2	57.9	70	30
1,2,3,5-Methyl-	78	16.3	53.9	5	95
1,2,3,4-Methyl-	10	1.3	2.7	17	83
1,2,3,4-Ethyl-	81.2	13	39	50	50

Summary

The significant changes which take place when the polyalkylbenzenes are warmed with aluminum chloride at 70–75° are as follows:

The 1,3,5-triethylbenzene yields appreciable quantities of 1,2,4-triethylbenzene.

The 1,2,3,5- and 1,2,4,5-tetraethylbenzenes are each partially converted into the other. Durene and isodurene react similarly.

The 1,2,3,4-tetraethylbenzene is converted into

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(8) Smith and MacDougall, THIS JOURNAL, **51**, 3001 (1929).

(9) Smith and Cass, *ibid.*, **54**, 1614 (1932).

(10) Smith and Guss, *ibid.*, **62**, 2630 (1940).

a mixture of equal amounts of the 1,2,3,5- and 1,2,4,5-isomers.

Prehnitene is converted into a mixture of 83% isodurene and 17% durene.

All of the hydrocarbons yield varying amounts of lower and higher alkylbenzenes in addition to the principal product.

COLUMBIA, MISSOURI RECEIVED AUGUST 8, 1941

[CONTRIBUTION FROM NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING]

Vapor Phase Thermal Isomerization of α- and β-Pinene*

BY L. A. GOLDBLATT AND S. PALKIN

Thermal isomerization studies of α- and β-pinene in the past have been confined largely to the liquid state (below 160°) or to the vapor phase at relatively high temperatures (above 450°).[1] Interest in the intermediate range was stimulated by Arbuzov's discovery[2] that pyrolysis of α-pinene yielded, in addition to dipentene, the chain triolefin *allo*-ocimene (2,6-dimethyl-2,4,6-octatriene), the best yield of about 26% being obtained at 340–350°. Later, similar results were reported[3] with respect to β-pinene (20% yield of *allo*-ocimene). This finding, as will be shown presently, is erroneous.

Dupont and Dulou,[4] repeating the work of Arbuzov on α-pinene but using a copper tube filled with copper gauze, obtained in addition to *allo*-ocimene and dipentene two new monocyclic conjugated diolefinic terpenes (up to 50%) which they designated as α-pyronene (1,1,2,3-tetramethyl-3,5-cyclohexadiene) and β-pyronene (1,1,-2,3-tetramethyl-2,4-cyclohexadiene). However, Charlton and Day[5] operating chiefly in the range 380–425°, both with and without a thorium catalyst, did not find *allo*-ocimene or any of its derivatives in the pyrolysate of α-pinene.[6]

Experimental

Special precautionary measures were taken to purify the pinenes used, in view of the apparently contradictory findings of Charlton and Day, the erroneous character of the conclusions of Arbuzov with respect to the products of thermal isomerization of β-pinene,[7] the known difficulties frequently encountered in obtaining the initial terpenes in a pure state, and the consequently confusing conclusions, This included repeated fractionation *in vacuo* in efficient columns. The purified pinenes for this investigation (except for preliminary trials in which the pinenes were of somewhat lower purity) had the following characteristics

α-pinene $[\alpha]_D$ $+32.06°$; n^{20}_D 1.4645; d^{20}_4 0.8600
β-pinene $[\alpha]_D$ $-21.81°$; n^{20}_D 1.4782; d^{20}_4 0.8712

Apparatus.—The reaction apparatus was an all-glass (Pyrex) assembly (Fig. 1), consisting essentially of a charging flask (C), preheater (F), jacketed reaction tube (I) and water condenser (N_1), backed up by a packed condenser (N_2), dry-ice trap (P) and receivers (O). Hot pinene was vaporized with the aid of nitrogen gas as a carrier which was admitted through a fritted glass distributor (D), and the rate of vaporization was varied by changing the rate of flow of nitrogen or the temperature of the liquid pinene or both.

Procedure.—The pinene vapors were passed through the preheater where the temperature of the vapor (measured at Q_1) was raised to 250–300° and were then passed through the reaction tube. For the range 338–375° the temperature in each case was maintained relatively uniform along the entire length of the tube by a jacket of mercury vapor (J) from the mercury boiler (K). With the mercury vapor jacket in operation, the temperature along the entire length of the reaction tube was found to vary less than 5° and usually less than 2°, despite the fact that the reaction is strongly endothermal. The boiling point of the mercury was varied by varying the pressure [gaged by the manometer (L)] from 0.5 to 1.5 atmospheres. Temperature was measured at four points Q_1 to Q_4, by thermocouples leading to a potentiometer through ice junctions. For temperatures above 375° the outer jacket was heated electrically. In such cases, however, the temperature could not be kept uniform along the entire length of the tube, extreme variations sometimes reaching 30° or more. The maximum temperature indicated by any thermocouple was in each case recorded as the temperature of the reaction.

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(1) More than 50 literature citations on thermal reactions of the pinenes and turpentine (β-pinene constitutes about a third of American gum turpentine) are given in *Chem. Rev.*, **14**, 349–352 (1934).

(2) Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

(3) Arbuzov, *ibid.* (U. S. S. R.), **6**, 297 (1936).

(4) Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935).

(5) Charlton and Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

(6) *Ibid.*, p. 95. They state: "It was not possible to isolate such a hydrocarbon [*allo*-ocimene], and it was extremely doubtful that the physical constants for the various fractions gave much indication of its presence. When the pinene was passed through the Pyrex tube without the catalyst, other conditions being the same, there was no indication of the presence of an unsaturated open chain compound."

(7) Arbuzov's findings were probably due to working with impure β-pinene, the *allo*-ocimene resulting from α-pinene present as an impurity. This is indicated by the physical constants reported: "b. p. (10.5 mm.) 44.5°; d^{14} 0.8670; n^{14}_D 1.4740; α_D -13.50; α_V/α_j 1.09." The low rotation and high dispersion indicate the presence of a considerable proportion of an impurity which, from the characteristics cited, may well be suspected of being α-pinene.