

Anal. Calcd. for $C_8H_{10}N_6$: C, 50.4; H, 5.3; N, 44.2; mol. wt., 190. Found: C, 50.2; H, 5.5; N, 44.2; mol. wt., (Rast) 185.

1,4-Bis(cyanoformimino)-2-methylpiperazine from 2-methylpiperazine. A cold solution of 10.0 g. (0.1 mole) of 2-methylpiperazine in 200 ml. of dry ether was treated with approximately 0.3 mole of cyanogen. Crystal deposition began almost immediately and continued throughout the cyanogenation. The crystals were collected, washed with ether and air-dried. The yield was 12.0 g. (58.8%).

Recrystallized from a chloroform-carbon tetrachloride solvent pair, the white solid melted at 113–113.5°. The pure product appeared to be stable.

Anal. Calcd. for $C_8H_{10}N_6$: C, 53.0; H, 5.9; N, 41.1; Found: C, 53.2; H, 5.3; N, 41.4.

Attempts to prepare the *hydrochloride* from an ether solution of the free base produced an oil which would not crystallize.

1,4-Bis(cyanoformimino)-cis-2,5-dimethylpiperazine from (cis) 2,5-dimethylpiperazine. A cold ether solution of 11.4 g. (0.1 mole) of (*cis*) 2,5-dimethylpiperazine was treated with cyanogen and worked up in the manner described above. The yield of tan crystals was 19.2 g. (88.1%). Recrystallized from a chloroform-carbon tetrachloride solvent pair, the white product melted at 124–125°. The purified material was quite stable.

Anal. Calcd. for $C_{10}H_{14}N_6$: C, 55.0; H, 6.4; N, 38.5. Found: C, 55.4; H, 6.1; N, 38.4.

The *hydrochloride* was prepared by saturating a very dilute ether solution of the free base with dry hydrogen chloride. The salt decomposed very rapidly in air and could not be analyzed.

1,4-Bis(cyanoformimino)-trans-2,5-dimethylpiperazine from (trans) 2,5-dimethylpiperazine. A cold solution of 9.0 g. (0.079 mole) of (*trans*) 2,5-dimethylpiperazine in 50 ml. of water was treated with about 0.3 mole of cyanogen. Crystallization began when about half of the cyanogen had been added. Seven g. (40.7%) of dark brown solid was recovered. Recrystallized from a chloroform-carbon tetrachloride solvent pair, the white crystals melted at 166–167°. The pure product was very stable.

Anal. Calcd. for $C_{10}H_{14}N_6$: C, 55.0; H, 6.4; N, 38.5. Found: C, 54.7; H, 6.7; N, 38.6.

The limited solubility of the free base prevented the preparation of the *hydrochloride* or other derivative.

Unsuccessful Reactions. Pyrrole. One-tenth mole (6.7 g.) of pyrrole in each of the following solvents was cyanogenated without success: water, ether, 50% ethanol, benzene, ethyl acetate. In some cases tars resulted; in others the unreacted pyrrole was recovered. A suspension of pyrrole in *N* NaOH was also unreactive, as was pure pyrrole. Δ^2 -Pyrroline. One-tenth mole (6.9 g.) of Δ^2 -pyrroline was treated with cyanogen (a) in the absence of a solvent, (b) in ether solution, (c) in ethyl acetate solution. Only paracyanogen was recovered.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE AMERICAN OIL COMPANY]

Reaction of the Saturated Dimer of α -Methylstyrene with Aluminum Chloride. The Preparation of a Substituted Tetrahydroindenoindene

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When the saturated dimer of α -methylstyrene is heated in the presence of anhydrous aluminum chloride, attack on the five-membered ring occurs followed by condensation reactions. The products of the reaction are benzene, cumene, 1,1,3-trimethylindene, 1,1,3-trimethylindan, 4b,9,9,10,10-pentamethyl-4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, and polymer.

Most of the chemical reactions of the saturated dimer of α -methylstyrene (I) have been confined to the two aromatic rings, as the five-membered ring and its methyl groups appear to be very unreactive. The aromatic rings can be nitrated, sulfonated, and chlorinated without any effect on the five-membered ring. It is noteworthy that vigorous oxidation, with chromic acid, of the related saturated dimer of *p*, α -dimethylstyrene does not result in attack on the five-membered ring or its methyl groups; only the methyl groups on the aromatic ring are oxidized.¹

No reference to the effect of anhydrous aluminum chloride on the saturated dimer of α -methylstyrene has been found. In this study, the saturated dimer was treated with aluminum chloride, and condensations involving the five-membered ring occurred. The products were benzene, cumene,

1,1,3-trimethylindene, 1,1,3-trimethylindan, indene polymers, and a compound having a melting point of 132°. The latter compound has been shown to be 4b,9,9,10,10-pentamethyl-4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene (VII). The yield of crude compound VII was 27 wt. % based on the saturated dimer charged when the reaction was carried out with 20% aluminum chloride at 80° for 24 hrs. or 100° for 6 hr. If the reaction time was increased to 72 hr. at 80°, the yield of compound VII decreased to 16 wt. %. It was demonstrated that this decrease in yield was due to further reaction of compound VII in the presence of aluminum chloride to produce lower and higher boiling compounds.

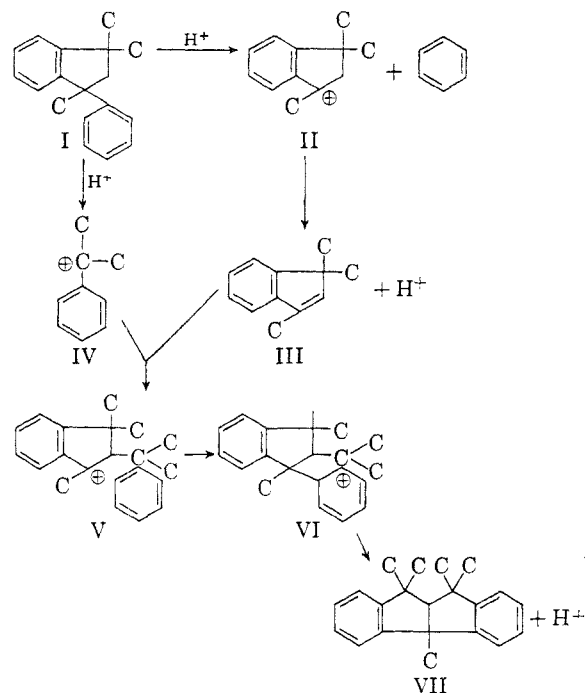
The addition of a solvent, such as benzene, to the reaction mixture had no effect on the course of the reaction. Saturation of the reaction mixture with anhydrous hydrogen chloride prevented the formation of compound VII and increased polymer yield, although it had only little effect on the amount of saturated dimer reacting. Water had a

(1) V. N. Ipatieff, H. Pines, and R. C. Olberg, *J. Am. Chem. Soc.*, **70**, 2123 (1948).

similar effect, while the addition of diethyl ether decreased both the yield of compound VII and the amount of saturated dimer reacting.

The fraction boiling below compound VII contains some unconverted saturated dimer of α -methylstyrene and would be expected to form more compound VII on treatment with aluminum chloride. The material boiling above compound VII contains polymers or a copolymer of 1,1,3-trimethylindene and α -methylstyrene. This fraction will degrade to compounds such as those described in the proposed mechanism with subsequent reaction to give more compound VII. Recycling of these fractions could therefore be used to increase the over-all yield of compound VII.

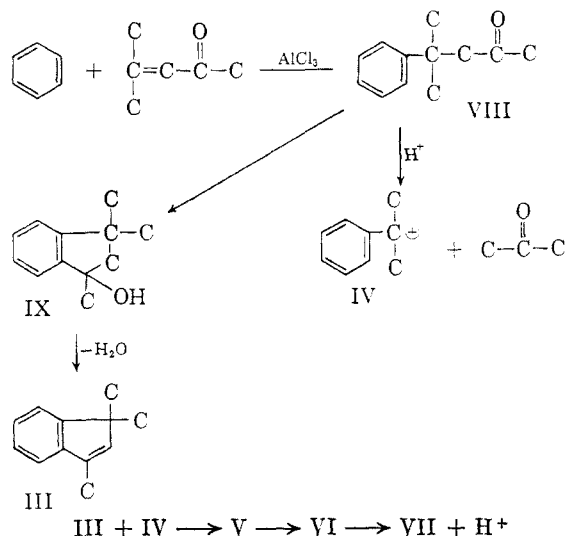
The following mechanism is proposed for the conversion of the saturated dimer to compound VII. Benzene is cleaved from part of the saturated dimer (I) to yield a carbonium ion (II), which may split off a proton to form 1,1,3-trimethylindene (III). A part of the saturated dimer reacts with a proton to form the cumyl carbonium ion (IV) which then adds to the 1,1,3-trimethylindene to yield the carbonium ion (V) with subsequent ring closure to carbonium ion (VI). This then eliminates a proton to yield compound VII.



Compound VII has also been prepared by Barnes and Beitchman² by another method. They started with a ketone (VIII) obtained by reacting mesityl oxide with benzene in the presence of anhydrous aluminum chloride. The mechanism described involves the formation of 1,1,3-trimethylindene (III) by ring closure of the ketone with subsequent elimination of water from the indanol (IX). The

(2) R. A. Barnes and B. D. Beitchman, *J. Am. Chem. Soc.*, **76**, 5430 (1954).

cumyl carbonium ion (IV) is produced by cleavage of the ketone and reacts with III to form VII.



The infrared spectrum of compound VII (Fig. 1), prepared in the present work from the saturated

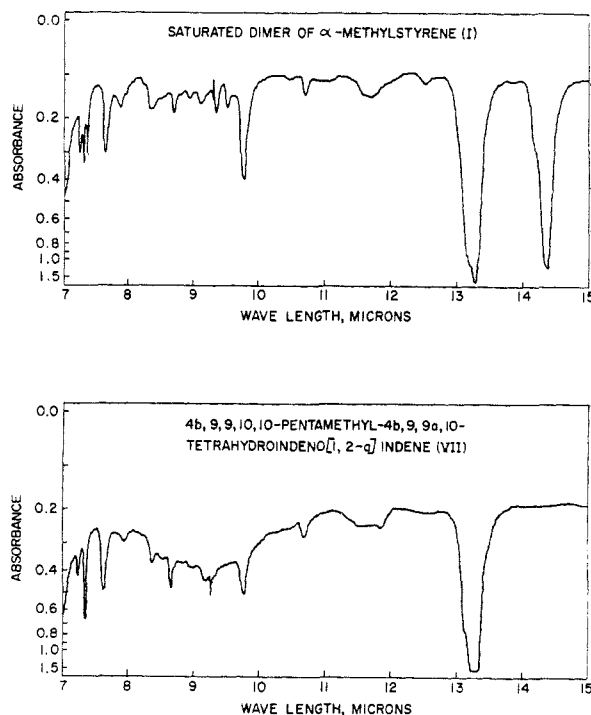


Fig. 1. Infrared spectra in CS_2

dimer of α -methylstyrene, was identical with the infrared spectrum of the compound prepared as described by Barnes and Beitchman. The strong absorption in the 13.0–13.5 μ region showed the presence of a large amount of ortho-disubstituted aromatic bonds, while the absence of absorption in the 14.0–14.5 μ range showed that monosubstituted aromatic bonds were not present in detectable amounts. Melting points, as well as a mixed melting point, of the two products indicated them to be

identical. The mass number was 276 which is consistent with the assigned structure.

Complete hydrogenation of compound VII prepared by both procedures yielded viscous liquids which had identical refractive indices and infrared spectra. The molecular weight of the hydrogenated compound was greater than the parent compound by 12 units, as determined by mass numbers from a mass spectrographic procedure. This indicated that hydrogenation had brought about saturation of two aromatic rings.

EXPERIMENTAL

Saturated dimer of α -methylstyrene. α -Methylstyrene (100 parts) and UOP phosphoric acid-on-kieselguhr catalyst (10 parts) were heated, with agitation, for 4 hr. at 200–250°. The reaction product was filtered hot and the filtrate distilled at a pressure of 10 mm of Hg. The fraction boiling from 158° to 160° was the saturated dimer which was used in the work described hereafter. The yield was 90% and the melting point 52°.

Reaction of the saturated dimer of α -methylstyrene with anhydrous aluminum chloride. The saturated dimer of α -methylstyrene (100 parts) was heated, with good agitation, at 100° for 6 hr. with anhydrous aluminum chloride (20 parts). The reaction mixture was cooled, hydrolyzed with ice, and steam-distilled. The steam distillate contained benzene, cumene, 1,1,3-trimethylindene, and 1,1,3-trimethylindan. The residue from the steam distillation was dissolved in benzene, washed, and dried. After removing the benzene at atmospheric pressure, the remainder was vacuum-distilled. The over-all product distribution is shown in Table I along with the product distribution from runs at 80° for 24 and 72 hr.

The fraction distilling at 80–83° at 10 mm. of Hg contained 60% 1,1,3-trimethylindan and 40% 1,1,3-trimethylindene. Identification was made by infrared spectrum and comparison of physical properties with those obtained by Pines.³

The material boiling from 83° to 170° at 10 mm. of Hg is mostly unreacted saturated dimer.

Compound VII was obtained from the 170–210° at 10 mm. of Hg fraction. On recrystallization from isopropyl alcohol, it had a melting point of 132°. The mixed melting point of

(3) H. Pines and J. T. Arrigo, *J. Am. Chem. Soc.*, **79**, 4958 (1957).

TABLE I
REACTION OF SATURATED DIMER OF α -METHYLSTYRENE WITH $AlCl_3$

Product Fraction	Wt % Yields on Dimer Charged			Major Component
	6 Hr. at 100°	24 Hr. at 80°	72 Hr. at 80°	
80–85° at 760 mm.	21.8	21.8	28.1	Benzene
85–160° at 760 mm.	3.4	3.4	2.9	Cumene
80–83° at 10 mm.	8.2	8.2	9.2	Trimethylindene and trimethylindan
83–170° at 10 mm.	7.1	7.1	7.2	Unreacted dimer
170–210° at 10 mm.	27.5	27.5	16.0	Compound VII
to 209° at 0.5 mm.	8.0	8.0	9.1	Polymer
Residue	24.0	24.0	27.5	Polymer

this material with the compound prepared by Barnes and Beitchman was 132°. Infrared spectrum indicated only ortho-disubstituted aromatics, and the spectra of compound VII from both procedures were identical. Other analytical data are shown as follows:

Anal. Calcd. for $C_{21}H_{24}$: C, 91.25; H, 8.75; mol. wt., 276. Found: C, 91.53; H, 8.75; mol. wt., 276 by mass spectrometer.

The fraction boiling to 209° at 0.5 mm. of Hg appears to be a mixture of polymer or a copolymer of indene and α -methylstyrene (by infrared). On treatment of this fraction with anhydrous aluminum chloride (20%) at 100° for 6 hr., 40% of compound VII along with 60% of lower and higher boiling materials was obtained.

Hydrogenation of compound VII. Compound VII was mixed with an equal weight of Harshaw Ni 0104 catalyst and hydrogenated at 200° and 2,000 lb./sq.in. of hydrogen pressure for 24 hr. The product was a liquid which had an n_D^{25} of 1.5002 and a molecular weight of 288 (mass spectrometer).

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