

dimer II (as judged by infrared comparison), m.p. 17–19°. Further elution with petroleum ether–benzene (1:1) yielded 4.66 g. (19%) of the tetramer IV, m.p. 82–86°.

Crystallization of the 7.95 g. of semi-solid mixture of II and VI from petroleum ether produced 1.65 g. (6.7%) of cyclohexadeca-1,3,9,11-tetrayne (VI) as hexagonal plates, m.p. 160–162° dec.;  $\lambda_{\text{max}}$  227, 239 and 254  $\mu$  ( $\epsilon$  580, 600 and 360, respectively);  $\nu_{\text{max}}$  2240 and 2154  $\text{cm}^{-1}$  (disubstituted  $\alpha$ -diacetylene); no band at ca. 3300  $\text{cm}^{-1}$  (absence of acetylenic hydrogen). The substance gave no precipitate with silver nitrate in 95% ethanol solution.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{18}$ : C, 92.26; H, 7.74. Found: C, 92.48; H, 7.62.

The residue (6.3 g.) after removal of the crystalline VI completely solidified at 0° and showed m.p. 15–18°. Infrared analysis indicated the presence of over 90% of the linear dimer II. It was dissolved in 60 cc. of ethanol and was added to a solution of 12.5 g. of silver nitrate in 240 cc. of ethanol and 12.5 cc. of water. The immediate white precipitate was collected and washed well with ethanol. The filtrate was concentrated to small volume, diluted with water and well extracted with ether. The residue obtained by evaporation of the ether extract was crystallized from petroleum ether and yielded 0.32 g. of VI, m.p. 156–158°; the total yield was 1.97 g. or 8%. The pure linear dimer II could be regenerated from the silver salt by boiling with aqueous sodium cyanide solution.

The linear tetramer, dotriaconta-1,7,9,15,17,23,25,31-octayne (IV), eluted last from the column, was best purified by slow crystallization from a dilute methanol or ethanol solution. This method produced small plates, m.p. 93–94°;  $\lambda_{\text{max}}$  226, 240 and 254  $\mu$  ( $\epsilon$  1190, 1140 and 720, respectively);  $\nu_{\text{max}}$  3305 and 2100  $\text{cm}^{-1}$  (terminal acetylene) and 2235 and 2140  $\text{cm}^{-1}$  (disubstituted  $\alpha$ -diacetylene). The substance gave a white precipitate with silver nitrate in 95% ethanol solution.

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{34}$ : C, 91.81; H, 8.19. Found: C, 92.01; H, 7.98.

**Oxidation of Hexadeca-1,7,9,15-tetrayne (II).**—The oxidation of 1.7 g. of II together with 1.6 g. of cuprous chloride, 2.6 g. of ammonium chloride in 5 cc. of ethanol and 7 cc. of water at pH 3 was carried out at 55° by bubbling through

oxygen with stirring for 6 hr. Nearly all the starting material was recovered and only 0.017 g. (1%) of the linear tetramer IV, m.p. 90–92°, was obtained.

In another experiment the oxidation was performed by bubbling oxygen for 6 hr. through a stirred mixture of 5 g. of II, 5 g. of cuprous chloride and 8 g. of ammonium chloride in 180 cc. of ethanol, 20 cc. of water, 30 cc. of benzene and 0.05 cc. of concd. hydrochloric acid, at 55°. Isolation with benzene and chromatography on alumina gave 2.57 g. (51%) of recovered II and 1.56 g. (31%) of the linear tetramer IV, m.p. 91–93°.

***n*-Hexadecane (Cetane) (III).**—The linear dimer II (233 mg.) dissolved in 10 cc. of acetic acid was shaken in hydrogen over 40 mg. of platinum oxide at atmospheric pressure and room temperature until the uptake of gas ceased. The catalyst was removed, the solvent and then the product were distilled. The resulting *n*-hexadecane showed m.p. 17–18°, b.p. 276–278° (762 mm.),  $n_{\text{D}}^{20}$  1.4355 (reported<sup>20</sup> m.p. 18°, b.p. 280° (760 mm.),  $n_{\text{D}}^{20}$  1.4352).

***n*-Dotriacontane (Dicetyl) (V).**—The linear tetramer IV (100 mg.) was hydrogenated in a mixture of 5 cc. of dioxane and 20 cc. of acetic acid (due to its insolubility in the acid alone) over platinum oxide. The resulting *n*-dotriacontane after crystallization from ether showed m.p. 70°, undepressed on admixture with an authentic specimen (m.p. 70°).

**Cyclohexadecane (VII).**—The cyclic dimer VI (150 mg.) was hydrogenated in a mixture of 20 cc. of acetic acid and 5 cc. of hexane over 40 mg. of platinum oxide, as usual. The resulting cyclohexadecane after crystallization from methanol showed m.p. 60–61°, undepressed on admixture with an authentic specimen (m.p. 60–61°); reported<sup>21</sup> m.p. 61°. Further proof of identity was provided by the fact that the infrared spectrum, measured in potassium bromide at liquid air temperature (when much fine structure appears), was completely identical with that of an authentic sample.

(20) P. J. Garner and J. H. Beynon in "Chemistry of Carbon Compounds," Vol. 1A, edited by E. H. Rodd, Elsevier Publishing Co., Houston, Texas, 1951, p. 228.

(21) L. Ruzicka, W. Brugger, C. F. Seidel and H. Schinz, *Helv. Chim. Acta*, **11**, 496 (1928).

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## Reaction of $\alpha$ -Methylstyrene Catalyzed by Sodium<sup>1</sup>

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The reaction of  $\alpha$ -methylstyrene at its reflux temperature in the presence of sodium and sodium-benzylsodium catalyst was investigated. The products of the reaction were composed of cumene (V) 18% by wt., *p*-terphenyl (VI) 2.4%, 1-methyl-1,3-diphenylcyclopentane (VII) 32% and a trimer 19%. The structure of the dimer was established by means of synthesis and degradation. Compounds V and VI were products of a hydrogen transfer reaction. The effect of temperature upon the product distribution was investigated. The mechanism of the reaction was discussed and tested. The synthesis of VII was accomplished by the reaction of 1-methyl-3-phenylcyclopentene with benzene in the presence of hydrogen fluoride. The cycloalkylation reaction was accompanied by a hydrogen transfer reaction resulting in the formation of 1-methyl-3-phenylcyclopentane and 1-methyl-3-phenylcyclopentadiene.

The dimerization of  $\alpha$ -methylstyrene in the presence of acid catalysts was reported to form compounds I, II and III, depending on the experimental condition and the nature of the catalyst used.<sup>4–6</sup>

(1) Paper XI of the series Base Catalyzed Reactions of Hydrocarbons. For paper X, L. Schaap and H. Pines, *THIS JOURNAL*, **79**, 4967 (1957).

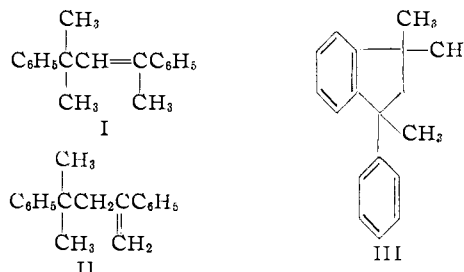
(2) Vladimir N. Ipatieff Postdoctoral Fellow 1955–1956.

(3) To whom requests for reprints should be addressed.

(4) For complete literature references see J. Hukki, *Acta Chem. Scand.*, **3**, 279 (1949).

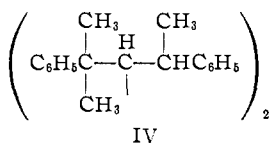
(5) F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).

(6) J. C. Petropoulos and J. J. Fisher, Division of Organic Chemistry American Chemical Society Meeting, Miami, Florida, April 12, 1957.

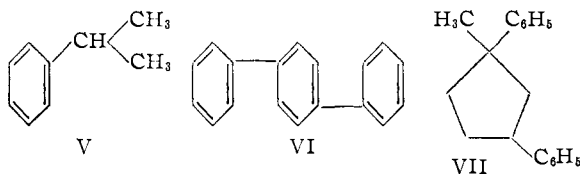


Bergmann and co-workers<sup>7</sup> reported that  $\alpha$ -  
(7) E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, **64**, 1493 (1931).

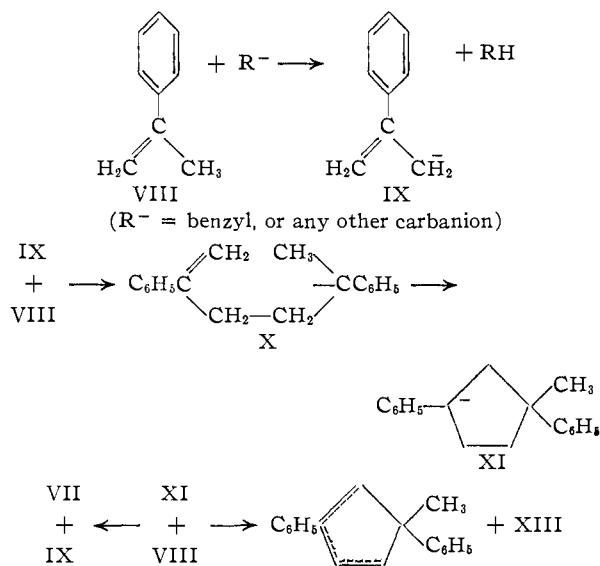
methylstyrene or its dimer I or II forms a tetramer IV on shaking with dispersed sodium for six days at room temperature.



The present study embodies the reaction of  $\alpha$ -methylstyrene at its reflux temperature in the presence of sodium or sodium-benzylsodium catalyst. The product from the reaction was composed of 18% by weight of cumene (V), 2.4% *p*-terphenyl (VI), 32% 1-methyl-1,3-diphenylcyclopentane (VII) and 19% of a trimer. About 13% of the products formed corresponded to dimers of  $\alpha$ -methylstyrene but boiling lower than VII. The remainder of the reaction product consisted of higher boiling material which could not be separated into pure compounds.

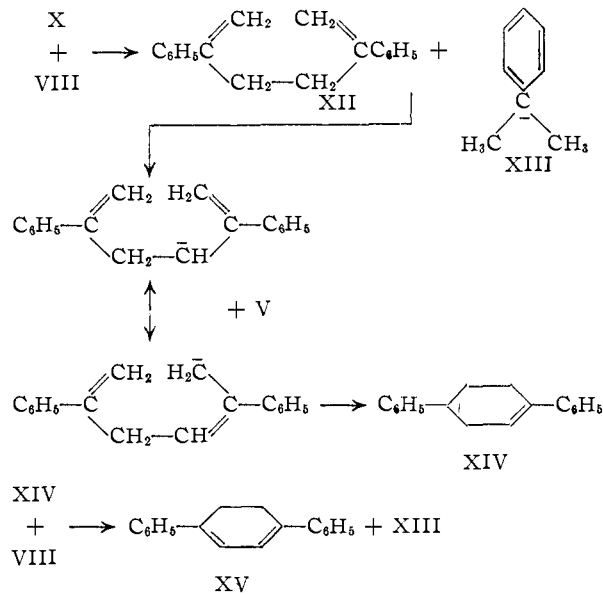


The formation of compounds V–VII can be explained by a carbanion chain mechanism which involves as the first step the removal of a proton from an allylic carbon atom of  $\alpha$ -methylstyrene (VIII) with the formation of carbanion IX. The latter adds to another molecule of  $\alpha$ -methylstyrene to form X which on cyclization forms a cyclopentylcarbanion XI. The latter can remove a proton from another  $\alpha$ -methylstyrene to produce 1-methyl-1,3-diphenylcyclopentane (VII) and generate another chain (IX).



The formation of *p*-terphenyl (VI) and of cumene (V) can be explained by assuming the intermediate formation of 2,5-diphenyl-1,5-hexadiene (XII) and of cumylcarbanion (XIII) followed by a

proton transfer reaction, cyclization and hydride elimination



Compound XV was not isolated because it is converted readily to *p*-terphenyl (VI); this can occur by means of a hydrogen transfer reaction in which  $\alpha$ -methylstyrene can act as a hydrogen acceptor. This type of reaction has been shown to occur previously.<sup>8</sup>

In order to demonstrate that compound XII can undergo cyclization and dehydrogenation reaction, the diene XII was synthesized and allowed to react at 180° in the presence of sodium-benzylsodium catalyst; about 40% of the diene was converted to *p*-terphenyl. In the absence of the catalyst the diene was recovered unchanged.

Part of the cumene must have been produced also by a hydride transfer reaction involving carbanion XI and  $\alpha$ -methylstyrene with consequent formation of the corresponding unsaturated hydrocarbons. A transfer of a hydride from a carbanion to an olefin was reported previously<sup>8-10</sup> and was presently confirmed by the results obtained from a reaction between  $\alpha$ -methylstyrene and *d*-limonene. In the latter case 50% of  $\alpha$ -methylstyrene underwent a hydrogen transfer reaction and both cumene and *p*-cymene were formed. *p*-Cymene as such does not have an effect upon this reaction since  $\alpha$ -methylstyrene under similar experimental conditions yielded only 16% of cumene, the same as in the absence of *p*-cymene. In the absence of a catalyst  $\alpha$ -methylstyrene does not form cumene or any of the hydrocarbons described above.

Unlike the reactions studied previously<sup>8-11</sup> the addition of either an organosodium compound or an additive which can form an organosodium compound *in situ* is not required in the case of  $\alpha$ -methylstyrene inasmuch as the latter *per se* can react with the sodium to form a disodium compound which can act as a chain initiator for the dimerization reaction.

- (8) H. Pines and M. Kolobielski, *THIS JOURNAL*, **79**, 1698 (1957).  
 (9) H. Pines, J. A. Vesely and V. N. Ipatieff, *ibid.*, **77**, 554 (1955).  
 (10) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956).  
 (11) H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

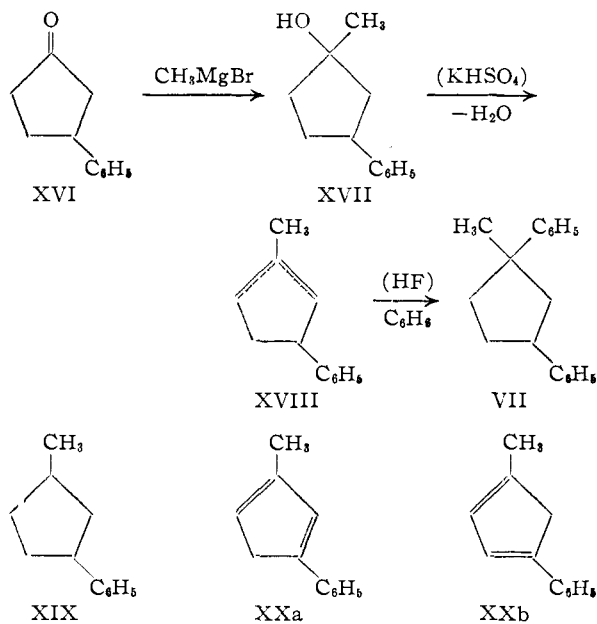
The effect of temperature between the ranges of 125 to 230° was studied upon the reaction of  $\alpha$ -methylstyrene in the presence of sodium alone. At lower temperatures the yield of compounds V, VI and VII is decreased while the yield of trimers produced is increased (Table I).

TABLE I  
EFFECT OF TEMPERATURE UPON THE REACTION OF  $\alpha$ -METHYLSTYRENE IN THE PRESENCE OF SODIUM

Temp., °C.	Composition of product, weight %				
	Recovered $\alpha$ -methylstyrene	V	VI	VII	Trimer
125	6	3	0.2	22	42
160	2	4	.2	34	39
230 <sup>a</sup>	6	5	.1	38	31

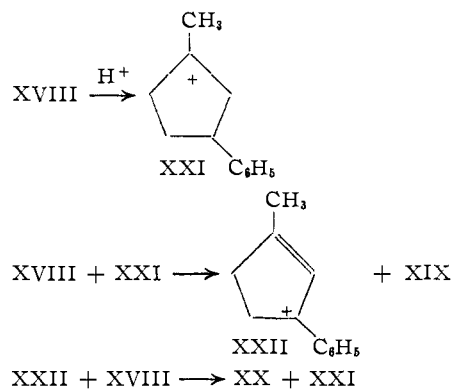
<sup>a</sup> This experiment was made in a Magne-Dasher autoclave manufactured by Autoclave Engineers, Inc., Erie, Pa.

**Proof of Structure of Compound VII.**—The structure of 1-methyl-1,3-diphenylcyclopentane was determined by means of synthesis. Compound VII was prepared by treating 1-methyl-3-phenylcyclopentene (XVIII) with benzene in the presence of hydrogen fluoride. Compound XVIII was synthesized from 3-phenylcyclopentanone (XVI) by the usual procedure. The cycloalkylation reaction forms in addition to the expected compound VII (yield 17 mole %) also 36% of 1-methyl-3-phenylcyclopentane (XIX) and 23% of 1-methyl-3-phenylcyclopentadienes (XXa and XXb).



Compounds XVIII and XX yielded on hydrogenation a hydrocarbon which was identical with XIX, which shows that skeletal isomerization did not accompany the hydrogen fluoride catalyzed reaction. The ultraviolet spectrum of XX showed  $\lambda_{\text{max}}$  256  $\text{m}\mu$ ,  $\epsilon$  6300 and  $\lambda_{\text{max}}$  307  $\text{m}\mu$ ,  $\epsilon$  3700. The low extinction coefficient probably is due to the rapid polymerization of the dienes on standing.

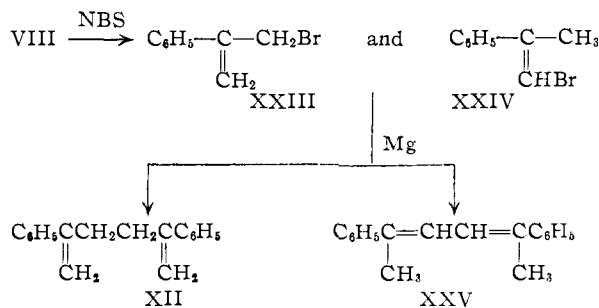
Compounds XIX and XX were formed by a hydrogen transfer reaction which can be explained as



The physical constants, ultraviolet and infrared spectra of the synthetic hydrocarbon VII were identical with those of the hydrocarbon obtained from the dimerization reaction of  $\alpha$ -methylstyrene. Compounds VII, XIX and XVII can exist in two forms, *cis* and *trans*; no attempts, however, were made to isolate the pure isomers.

The alkylation and cycloalkylation reactions in the presence of alkylating catalysts are in certain cases accompanied by a skeletal isomerization.<sup>12</sup> For that reason compound VII was partially degraded by means of a selective hydrogenolysis using a modified nickel catalyst.<sup>13</sup> This hydrogenolysis reaction reductively cleaves the phenyl group from the quaternary carbon atom, while the phenyl group attached to the tertiary carbon atom remains untouched. The hydrogenolyzed product yielded compound XIX which was identical with compound XIX obtained from the hydrogenation of XVIII. The formation of XIX by hydrogenolysis is a further proof that the synthetic compound VII has the structure indicated above.

**Synthesis of 2,5-Diphenyl-1,5-hexadiene (XII).**—This hydrocarbon was prepared from  $\alpha$ -methylstyrene (VIII) by a two-step reaction, which consisted of: (a) bromination of VIII with N-bromosuccinimide<sup>14</sup> to form mixtures of XXIII and XXIV and (b) treating an ethereal solution of the mixture with magnesium.



(12) (a) M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, *THIS JOURNAL*, **74**, 292 (1952); (b) L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954); (c) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **77**, 1774 (1955); (d) B. S. Friedman and F. L. Morrirtz, *ibid.*, **78**, 2000 (1956); (e) B. S. Friedman, F. L. Morrirtz and C. J. Morrissey, *ibid.*, **79**, 1465 (1957).

(13) H. Pines and W. S. Postl, *ibid.*, **79**, 1769 (1957).

(14) H. Pines, H. Alul and M. Kolobielski, *J. Org. Chem.*, **22**, 1113 (1957).

Most of the bromide XXIII reacted to form the desired compound XII and only a small amount of the vinylic bromide XXIV reacted to form as a main product a conjugated diene XXV. Small amounts of hydrotropic aldehyde were produced probably by the hydrolysis of the bromide XXIII either during the alkali or the acid wash.<sup>15</sup>

The structure of XII was determined by ozonolysis which gave formaldehyde and 1,4-diphenyl-1,4-butanedione.

Hydrocarbon XXV melted at 138° and its ultraviolet spectrum was in agreement with the proposed structure.

### Experimental Part

**Experiment.  $\alpha$ -Methylstyrene VIII-Sodium Benzylo-sodium.**—Freshly distilled VIII (53 g., 0.45 mole) was refluxed in the presence of a catalyst prepared from 2 g. of sodium and 1.5 ml. of *o*-chlorotoluene in 13 ml. of toluene, according to the procedure described previously.<sup>11</sup> The liquid temperature rose during the 24 hr. of refluxing from 160 to 194°. Only about 240 cc. of gas was liberated during the action.

The lower boiling hydrocarbons were separated from the catalyst and from the rest of the material by means of flash distillation under reduced pressure. The distillate, 9.5 g., consisted of isopropylbenzene.

The residue of the flask was extracted with benzene, filtered and the solvent removed by distillation. The extract was composed of a brown oil and a solid. After the addition of *n*-pentane it was possible to separate the solid by filtration. The solid, 0.9 g., melted at 211–212° and corresponded to *p*-terphenyl (VI). It did not depress the melting point of an authentic sample of VI, and its ultraviolet spectrum,  $\lambda_{\max}$  275  $\mu$ ,  $\epsilon$  31,800 (in iso-octane), was the same as reported previously.<sup>18</sup>

The filtrate was separated by means of distillation into fractions: (1) b.p. 100–130° at 2 mm., 0.5 g.; (2) 130–145°, 1.5 g.,  $n_D^{20}$  1.5570; (3–5) 145–162°, 22.5 g., 1.5632–1.5758; (6) 162–175°, 2.0 g. (oil and solid which melted at 205–207° and which corresponded to *p*-terphenyl); (7) residue, 14 g.

Fractions 3–5, which contained, according to the bromine number determination,<sup>17</sup> 13.2% of unsaturation calculated for  $C_{18}H_{20}$ , were dissolved in 50 ml. of *n*-hexane and selectively hydrogenated at 200° for 6 hr. in the presence of 3.0 g. of copper chromite catalyst<sup>18</sup> and under an initial hydrogen pressure of 140 atm. The hydrogenated material was distilled on a Podbielniak<sup>19</sup> whirling band column and the following fractions were collected: (a) b.p. 110–117° at 2 mm., 7% vol.,  $n_D^{20}$  1.5512; (b) 117–133.4°, 15%, 1.5540; (c) 133.4–135.4°, 11%, 1.5690; (d) 135.5°, 27%, 1.5717; (e–h) 135.5–136.3°, 38%, 1.5720.

Cuts d–h were composed, according to infrared and ultraviolet spectral analysis, of 1-methyl-1,3-diphenylcyclopentane (VII), while cut c contained about 95% of VII.

*Anal.* of (f–h). Calcd. for  $C_{18}H_{20}$ : C, 91.47; H, 8.53; *M*<sub>R</sub>D, 75.90. Found: C, 91.41; H, 8.47;  $d_4^{20}$ , 1.0244; *M*<sub>R</sub>D, 75.80.

Cuts 6 and 7 (residue) of the original distillation were diluted with *n*-pentane; 0.4 g. of *p*-terphenyl precipitated out which was separated by filtration. The filtrate, after the removal of the solvent, was distilled under 1 mm. of pressure: (7a) <200°, 46%; (7b) 200–210°, 25%, yellow oil; (7c) residue, black oil. Cut 7a contained 30% of unsaturation, according to the bromine number, and was assumed to be composed of  $C_{27}H_{30}$  (trimers of VIII).

**Experiment 2.  $\alpha$ -Methylstyrene (VIII)- $\delta$ -Limonene.**—A solution consisting of 17.7 g. (0.15 mole) of VIII and 30.6

g. (0.22 mole) of  $\delta$ -limonene was refluxed for 24 hr. in the presence of a catalyst prepared from 2 g. of sodium as described in expt. 1. During the refluxing the temperature of the liquid rose from 174 to 182° and 3,500 cc. of hydrogen was produced. The content of the flask was flash distilled under 15 mm. of pressure. The hydrocarbon thus recovered, 27.8 g., consisted of 68% *p*-cymene and 32% cumene (V). The yield of V amounted to 50% based on  $\alpha$ -methylstyrene charged. The volume of hydrogen produced corresponded to the hydrogen formed from the dehydrogenation of  $\delta$ -limonene but which did not undergo a transfer reaction to  $\alpha$ -methylstyrene.

The high boiling hydrocarbons which remained in the reaction flask were not investigated; they were derived, according to calculation, from 0.08 mole of VIII and 0.07 mole of  $\delta$ -limonene.

**Experiment 3.  $\alpha$ -Methylstyrene (VIII)-*p*-Cymene.**—Compound VIII (16.7 g., 0.14 mole) and 28.6 g. (0.21 mole) of *p*-cymene were refluxed for 24 hr. in the presence of a catalyst prepared from 2 g. of sodium (expt. 1). During the refluxing the liquid temperature rose from 174 to 183°. The content of the flask which was flash distilled under reduced pressure yielded 27.7 g. of hydrocarbons which consisted of 10% cumene (V) and 90% *p*-cymene. The yield of V based on VIII reacted was 16.5%.

**Experiment 4.  $\alpha$ -Methylstyrene (VII)-Sodium.**—Compound VIII, 118 g., was heated at 125° for 6 hr. with stirring in the presence of 4 g. of sodium. No evolution of gas was observed. After cooling, *n*-pentane was added to the flask and the solution was filtered. The black solid residue was then treated with benzene and filtered again. From the benzene solution 0.15 g. of *p*-terphenyl, m.p. 211–212°, was separated.

The pentane solution was distilled and from the crude distillation the following fractions were separated: (1) b.p. 55–58° at 15 mm., 13 g.,  $n_D^{20}$  1.5283; (2) 130–140°, 9.6 g., 1.5585; (3) 140–160°, 19 g., 1.5705; (4) 160–205°, 10.0 g.; (5) 205–220°, 37.1 g., 1.5845; (6) 220–260°, 7 g.; (7) residue 21.7 g. (black oil).

Fraction 1 contained 77% of the starting material VIII and 23% cumene.

Fractions 2 and 3.—From these fractions 0.1 g. of *p*-terphenyl was separated by filtration. Fractions 2 and 3, 28 g., were dissolved in 40 ml. of *n*-hexane and selectively hydrogenated in the presence of 0.6 g. of 10% palladium-on-charcoal catalyst. From the hydrogen absorbed it was calculated that the extent of unsaturation based on  $C_{18}H_{18}$  was 15.5%. 1-Methyl-1,3-diphenylcyclopentane (VII), 22.2 g., b.p. 129–130° at 2 mm., was separated by fractional distillation from the selectively hydrogenated product.

Fractions 4 and 5, 45.7 g., were selectively hydrogenated according to the procedure described above; they contained 73% of unsaturation based on  $C_{27}H_{30}$  (trimer of VIII). The selectively hydrogenated material was distilled on a spinning band column and the following fractions were collected: (a) b.p. 103–165° at 2 mm., 5%,  $n_D^{20}$  1.5635; (b) 165–168.6°, 24%, 1.5677; (c) 168.6–168.8°, 27%, 1.5677; (d) 168.8–170°, 28%, 1.5700; (e) 170–172°, 12%, 1.5785; (f) residue, thick gummy material.

Fraction c. *Anal.* Calcd. for  $C_{27}H_{30}$ : C, 91.47; H, 8.53; mol. wt., 354. Found: C, 91.32; H, 8.21; mol. wt., 364 (in camphor).

The infrared spectra of fractions b and c, with the exception of a few minor peaks, were identical.

**Experiment 5. 2,5-Diphenyl-1,5-hexadiene (XII)-Sodium-Benzylo-sodium.**—To a catalyst prepared from 1 g. of sodium and 0.75 ml. of *o*-chlorotoluene in 7 ml. of toluene was added a solution of 3.5 g. of XII in 15 ml. of *p*-cymene. The mixture was refluxed (liquid temperature 182°) for 40 hr. during which time 470 ml. of hydrogen was produced. *p*-Cymene was then removed by distillation under reduced pressure, and the residue was extracted with benzene. After the removal of the solvent, the extract, which consisted of a solid and an oil, was treated with *n*-pentane. A white solid separated out, 1.4 g., which melted at 211° and which corresponded to *p*-terphenyl (VI). It did not depress the melting point of a known sample of *p*-terphenyl.

**Experiment 6. 2,5-Diphenyl-1,5-hexadiene (XII).**—This experiment was made under identical condition as experiment 5 with the exception that no catalyst was used. About 80% of the starting material, m.p. 47–48°, was recovered. The presence of *p*-terphenyl could not be detected in the reaction mixture.

(15) D. Currell and A. Fry, *THIS JOURNAL*, **78**, 4377 (1957), cites numerous references pertaining to the conversion of methallyl alcohol to isobutyraldehyde in the presence of acids.

(16) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

(17) R. E. Byrne, Jr., and J. B. Johnson, *Anal. Chem.*, **28**, 126 (1956).

(18) W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943.

(19) Podbielniak, Inc., Chicago, Illinois.

Synthesis of 1-Methyl-1,3-diphenylcyclopentane (VII). 3-Phenyl-2-cyclopentene-1-one (XXVII) was prepared from ethyl phenylacetylacetate according to the method described previously.<sup>20</sup> The ketone melted at 80–82° and its ultraviolet spectrum in 95% ethanol was  $\lambda_{\max}$  282.5  $\mu$ ,  $\epsilon$  23,000.

3-Phenylcyclopentanone (XVI) was prepared by selective hydrogenation of 20 g. of XXVII in 150 ml. of ethanol in the presence of 10% palladium-on-charcoal catalyst. The ketone XVI distilled at 120–122° at 1 mm.,  $n_D^{20}$  1.5452; literature<sup>20</sup> b.p. 90–95° at 0.05 mm.

1-Methyl-3-phenylcyclopentanol (XVII).—Ketone XVI, 25 g., was treated with methylmagnesium bromide which was prepared from 5 g. of magnesium and a 10% excess of methyl bromide. The alcohol XVII, which was obtained in 95% yield, distilled at 121–124° at 2 mm.,  $n_D^{20}$  1.5365,  $d_4^{20}$  1.0235, ultraviolet spectra (in ethanol)  $\lambda_{\max}$  262  $\mu$ ,  $\epsilon$  286.

*Anal.* Calcd. for  $C_{12}H_{16}O$ : C, 81.77; H, 9.15; *M*<sub>R</sub>D, 53.40. Found: C, 81.22; H, 8.85; *M*<sub>R</sub>D, 53.73.

1-Methyl-3 and/or -4-phenylcyclopentene (XVIII).—Alcohol XVII, 25 g., was dissolved in 50 ml. of toluene and 25 ml. of *p*-xylene and the solution refluxed in the presence of 5 g. of potassium acid sulfate. After 18 hr. of refluxing 2.5 ml. of water was collected. Olefin XVIII, which was obtained in 87% yield, distilled at 88–90° at 2 mm.,  $n_D^{20}$  1.5332. The infrared absorption bands of 6.00  $\mu$  (strong), 11.88  $\mu$  (medium) and 12.45  $\mu$  (medium) are characteristic of the structure  $RR_1C=CHR_2$ . The ultraviolet spectra of XVIII in ethanol showed  $\lambda_{\max}$  262  $\mu$ ,  $\epsilon$  286.

*Anal.* Calcd. for  $C_{12}H_{14}$ : C, 91.08; H, 8.92. Found: C, 91.48; H, 8.72.

1-Methyl-3-phenylcyclopentane (XIX) was prepared by hydrogenating 0.7 g. of XVIII in 10 ml. of *n*-hexane in the presence of 0.1 g. of 10% palladium-on-charcoal catalyst. The theoretical amount of hydrogen was absorbed. Compound XIX thus obtained was chromatographed over silica gel; its refractive index was  $n_D^{20}$  1.5160,<sup>21</sup> and its ultraviolet spectrum in ethanol gave  $\lambda_{\max}$  261  $\mu$ ,  $\epsilon$  242.

1-Methyl-1,3-diphenylcyclopentane (VII).—Into a copper flask containing 40 ml. of anhydrous hydrogen fluoride was introduced slowly with stirring a solution of 15 g. of XVIII in 25 ml. of benzene. The reaction was made at 0–5°. The contents of the flask were then poured onto ice, washed successively with water, 5% aq. potassium hydroxide, water and dried. After the removal of benzene the product was distilled and the following fractions were separated: (1) b.p. 66–72° at 1.5 mm., 5.2 g.,  $n_D^{20}$  1.5175; (2) 72–155°, 1.2, 1.5565; (3) 155–158°, 3.5, 1.5720. Near the end of the distillation the vapor temperature dropped to 95° and 2.8 g. of a solid hydrocarbon was collected in the receiver. The solid, which was identified as 1-methyl-3-phenylcyclopentadiene (XX), distilled at 95–95° at 3 mm. and melted at 57–62°; it quickly became discolored on exposure to air. The presence of XX can be explained by the depolymerization of its Diels–Alder dimer, which was present in the reaction mixture. This type of depolymerization was reported previously.<sup>22</sup>

The ultraviolet spectrum of XX showed the following absorption bands in chloroform:  $\lambda_{\max}$  256  $\mu$ ,  $\epsilon$  6300;  $\lambda_{\max}$  307  $\mu$ ,  $\epsilon$  3700.

Compound XX on selective hydrogenation in the presence of Pt-charcoal catalyst absorbed 2 mole equivalents of hydrogen and yielded compound XIX, which had an infrared spectrum identical with that of synthetically prepared hydrocarbon.

Fractions 1 and 2 from the original distillation contained, according to ultraviolet spectral analysis, from 10–20% of the diene XX. These fractions were chromatographed over silica gel and the following cuts were separated: (a) 0.2 g.,  $n_D^{20}$  1.5140; (b) 2.1 g., 1.5160; (c) 1.6 g.,  $n_D^{20}$  1.5163. The infrared spectrum of cut c was identical with that of the synthetically prepared XIX.

(20) F. Winternitz, M. Mousseron and G. Rouzier, *Bull. soc. chim.*, 190 (1953).

(21) Inasmuch as two isomers are possible, various constants were reported in the literature: (a) W. Borsche and W. Menz, *Ber.*, 41, 190 (1908):  $n_D^{20}$  1.5716. (b) G. Gustavson, *Compt. rend.*, 146, 640 (1908):  $n_D^{20}$  1.5210. (c) Von J. Braun and M. Kuhn, *Ber.*, 60, 2557 (1927);  $n_D^{20}$  1.5136.

(22) K. Alder and H. Holzricher, *Ann.*, 524, 145 (1936).

*Anal.* Calcd. for  $C_{12}H_{16}$ : C, 89.94; H, 10.06. Found: C, 89.80; H, 9.90.

Fraction 3, 3 g., was dissolved in 100 cc. of *n*-hexane and chromatographed on 100 g. of activated silica gel. By elution with 3 l. of *n*-hexane, 2.6 g. of a viscous liquid was collected. By redistillation, 2.0 g. of pure 1-methyl-1,3-diphenylcyclopentane (VII) was obtained; b.p. 145° at 3 mm.,  $n_D^{20}$  1.5720.

*Anal.* Calcd. for  $C_{18}H_{20}$ : C, 91.47; H, 8.53. Found: C, 91.74; H, 8.43.

Its infrared and ultraviolet spectra were superposable with the spectra of the hydrocarbon VII, which was obtained from the dimerization of  $\alpha$ -methylstyrene.

Hydrogenolysis of VII.—Compound VII, 11.2 g., which was obtained from expt. 4 and which according to physical constants and infrared spectral analysis was identical with the synthetically prepared compound VII, was heated at 350° for 3 hr. in the presence of 1.2 g. of nickel-kieselguhr catalyst (65% nickel), 0.28 g. of thiophene and under an initial hydrogen pressure of 74 atmospheres. The reaction was made in a 450-cc. capacity rotating autoclave. The final pressure was 55 atm. The hydrogenolyzed product was distilled and chromatographed over silica gel; it was composed of 5% by wt. cyclohexane, 25% benzene and 43% of 1-methyl-3-phenylcyclopentane (XIX),  $n_D^{20}$  1.5163. The infrared spectrum of the latter is identical with that of the synthetically prepared compound XIX.

Synthesis of 2,5-Diphenyl-1,5-hexadiene (XII).—To a reaction flask containing 5.6 g. (0.23 g. at.) of magnesium turnings and 30 ml. of ether were added dropwise with stirring 42 g. (0.21 mole) of bromides XXIII–XXIV,  $n_D^{20}$  1.5890, dissolved in 70 ml. of dry ether. The bromides were prepared by the bromination of  $\alpha$ -methylstyrene with *N*-bromosuccinimide.<sup>14</sup> To the reaction flask was then added 1 g. of anhydrous cuprous chloride, followed by a second portion of 42 g. of bromides dissolved in 70 ml. of ether. The mixture was refluxed and stirred for 10 hr. After cooling the content of the flask was poured onto ice containing ammonium chloride. After the usual washings and drying the product was distilled: (1) 30–50° at 2 mm., 8.5 g.,  $n_D^{20}$  1.5430; (2) 50–80°, 9.0 g., 1.5758; (3) 80–145°, 2.5, 1.5730; (4) 145–150°, 16.8 (solid); (5) 150–160°, 2.1 (solid); (6) residue, 15.0 (oil and solid).

Cut 1 contained mainly  $\alpha$ -methylstyrene.

Cuts 2 and 3 were composed of a mixture of the vinylic bromide (XXIV) and of 2-phenylpropionaldehyde (hydro-tropic aldehyde). The 2,4-dinitrophenylhydrazone obtained melted at 131–132° and showed no depression in melting when admixed with an authentic sample of the aldehyde.

Cut 4 on filtration yielded crystals of 2,5-diphenyl-1,5-hexadiene (XII), m.p. 47–48°. Its ultraviolet spectrum in isoöctane showed  $\lambda_{\max}$  239  $\mu$ ,  $\epsilon$  20,000.

*Anal.* Calcd. for  $C_{18}H_{18}$ : C, 92.26; H, 7.74. Found: C, 91.98; H, 7.55.

Cut 5 on recrystallization from *n*-hexane yielded a product corresponding to 2,5-diphenyl-2,4-hexadiene (XXV), m.p. 138–139°. Its ultraviolet spectrum in isoöctane had  $\lambda_{\max}$  315–316  $\mu$ ,  $\epsilon$  38,000. Found: C, 91.86; H, 7.61.

Ozonolysis of XII.—Hydrocarbon XII, 1.2 g., was dissolved in 25 ml. of methylene chloride and ozonized at –70°. The ozonide was decomposed reductively with 5 ml. of acetic acid and 5 g. of zinc powder at 40°. The formaldehyde formed from the reaction was trapped in dimedone; 1.8 g. of solid was found, m.p. 188–189°. It did not depress the melting point of an authentic sample produced from the condensation of formaldehyde with dimedone. The yield of formaldehyde was 60%.

The acetic acid solution yielded 1.12 g. of 1,4-diphenyl-1,4-butanedione, which on recrystallization from ethanol melted at 144–145°; ultraviolet spectra in isoöctane:  $\lambda_{\max}$  240  $\mu$ ,  $\epsilon$  20,200.

*Anal.* Calcd. for  $C_{16}H_{14}O_2$ : C, 80.64; H, 5.92. Found: C, 80.74; H, 5.84.

Hydrogenation of XII.—One gram of XII was dissolved in 10 ml. of *n*-hexane and hydrogenated at room temperature and at atmospheric pressure in the presence of 0.2 g. of 10% palladium-on-charcoal catalyst. Two mole equivalents of hydrogen per mole of hydrocarbon were absorbed. The hydrogenated compound was chromatographed over

silica gel; 0.7 g. of 2,5-diphenylhexane was obtained,  $n_D^{20}$  1.5385 (literature<sup>23</sup>  $n_D^{20}$  1.5440).

*Anal.* Calcd. for  $C_{18}H_{22}$ : C, 90.70; H, 9.30. Found: C, 90.36; H, 9.10.

(23) G. Dupont, *Compt. rend.*, **156**, 1623 (1913).

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## COMMUNICATIONS TO THE EDITOR

### EVIDENCE FOR QUADRIVALENT CURIUM. II. CURIUM TETRAFLUORIDE<sup>1</sup>

Sir:

We wish to report the preparation and some properties of a new compound of curium, the tetrafluoride, in which curium has unequivocally the valence of four. Curium tetrafluoride was made by treatment of curium trifluoride with gaseous fluorine at elevated temperatures, and lattice constants have been measured for the monoclinic structure obtained.

$Cm^{244}$ , an alpha emitter of 18.4 years<sup>2</sup> half-life, was used in this investigation and was a fraction of the same curium stock previously employed to prepare  $CmO_2$ .<sup>3</sup> The  $Cm^{242}$  content was only  $\sim 0.004$  mass per cent.

TABLE I (Å. UNITS)

	$a_0$	$b_0$	$c_0$	$\beta$	Ionic radius (IV)
$UF_4^5$	$12.82 \pm 0.06$	$10.74 \pm 0.05$	$8.41 \pm 0.05$	$126^\circ 10' \pm 30'$	0.93 <sup>6</sup>
$NpF_4^5$	$12.70 \pm .06$	$10.64 \pm .05$	$8.33 \pm .05$	$126^\circ 10' \pm 30'$	.92 <sup>6</sup>
$PuF_4^5$	$12.62 \pm .06$	$10.57 \pm .05$	$8.28 \pm .05$	$126^\circ 10' \pm 30'$	.90 <sup>6</sup>
$AmF_4^4$	$12.49 \pm .06$	$10.47 \pm .05$	$8.20 \pm .05$	$126^\circ \pm 1^\circ$	.89 <sup>6</sup>
$CmF_4$	$12.45 \pm .06$	$10.45 \pm .05$	$8.16 \pm .05$	$126^\circ \pm 30'$	.88

A 20–30 microgram pellet of air-dried curium trifluoride, precipitated from aqueous solution, was transferred into a sintered pre-fluorinated calcium fluoride crucible. The crucible was inserted into a nickel fluorinator<sup>4</sup> and the fluorinator evacuated. Tank  $F_2$ , which had been through a NaF trap to remove HF, was then used to fill the fluorinator to 1 atmosphere pressure. The fluorinator was heated to  $400^\circ$  over a one-half hour period, held at  $400^\circ$  for one hour, then at  $300^\circ$  for one hour, and finally cooled down to room temperature. A slow stream of fluorine was passed through the apparatus during this cycle. After the fluorine was displaced by helium gas, the curium compound was transferred to a Pyrex X-ray capillary and sealed off in air.

Initially, an exposure of 2 hours was made, using 114.6 mm. diameter camera with no-screen film and unfiltered copper radiation. This gave a good quality powder pattern of monoclinic  $CmF_4$ . A 20-hour exposure of the same sample was made

subsequently using the same camera, Eastman Type A film, and filtered copper radiation. The longer exposure gave a picture of generally poorer quality, due probably to radiation damage to the crystals.

In Table I are listed X-ray data for several tetrafluorides and their lattice constants in Å. units. All of these show the same monoclinic structure found for  $CmF_4$ .

Under microscopic examination by Eugene Staritzky of this Laboratory, the curium tetrafluoride appeared as light greenish-tan aggregates with a crystal size of a few tenths of a micron. The mean refractive index was 1.62. The absorption spectrum, as viewed through a Zeiss prism spectrometer eyepiece, showed a single very

strong, narrow band at 452 millimicrons, which is not shown by  $Cm(III)$ .

The existence of the compound  $CmF_4$  illustrates the difficulties of deriving chemical conclusions from the electronic configurations assigned to the "actinide elements."<sup>7</sup> It is clear, and perhaps surprisingly so, that the stability of the  $5f^7$  half-filled shell in curium is markedly less than the stability of the corresponding  $4f^7$  half-filled shell in gadolinium. The present results re-enforce earlier observations that detailed predictions of the valence states of these elements may not be properly made on the basis of analogy to the lanthanide series.<sup>8</sup>

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