The precipitate was collected, washed with ethanol, dried and crystallized twice from glacial acetic acid; m.p. 281° dec. This compound is very slightly soluble in ethanol.

Anal. Calcd. for $C_{29}H_{28}N_{10}O_2$: C, 63.69; H, 4.80; N, 25.63. Found: C, 63.19; H, 4.91; N, 25.71.

Chromatographic Separation of *p*-Phenylazophenylsemicarbazone of Trioses.—All the semicarbazones reported here are very soluble in pyridine hence the latter was useful for the preparation of solutions for chromatographic work. A pyridine solution of a mixture of the semicarbazone of glyceraldehyde, dihydroxyacetone and pyruvaldehyde was applied to a strip of Whatman No. 1 filter paper to make a spot 6–8 mm. in diameter. The paper had been washed with ethanol previously. The paper strip was developed with a methanol:water mixture (2:1), descending technique was employed. When the solvent front had traveled 40 cm. or more three distinct spots were observed. The pyruvaldehyde derivative remained at the origin as in the case when it was developed as a single substance. The glyceraldehyde derivative has moved further down than the dihydroxyacetone derivative. When developed individually these two derivatives have the following R_f values (27°): glyceraldehyde derivative, 0.61; dehydroxyacetone, 0.52.

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DEPARTMENT OF PEDIATRICS AND
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Thiourea Adduct of 1,2,4,5-Tetramethylbenzene

BY J. W. TETER AND W. P. HETTINGER, JR.

RECEIVED JULY 15, 1955

Although benzene itself and most alkyl benzenes do not form adducts with thiourea, we find that durene readily forms a stable adduct. X-ray diffraction patterns of the solid obtained in adduction experiments show the presence of some thiourea but also clearly indicate adduct formation.

We have used this adduct as a means of isolating durene from fractions of high-octane-reforming products boiling in the neighborhood of 196°, the durene content of which can be estimated by cryoscopic means.

The fact that only durene adduction was observed in the presence of other tetramethylbenzene isomers indicates the selectivity of the reaction. Likewise none of the C_8-, C_9- or C_{11}-methyl substituted benzenes appeared to form adducts approaching the stability of durene.

Experimental

A solution of dry methanol, saturated with thiourea at 25° (150 ml.), was mixed with 26.6 ml. of a solution containing 21.9 volume per cent. durene and 78.1 volume per cent. toluene. Almost immediately a voluminous precipitate of white needles was formed. This solution plus precipitate was then cooled to 3°. The remaining mother liquor contained 91.6% toluene and 8.4% durene on a methanol and thiourea free basis.

The precipitate was collected, dried and weighed (12.9 g.) and analyzed.

Anal. Found: C, 37.2; H, 6.3; N, 26.2; S, 30.3.

X-Ray Examination.—Samples of durene, thiourea and the solid complex were analyzed on a North American Phillips X-ray spectrometer employing CuKα radiation. Table I shows the results of these analyses in terms of *d/n*.

TABLE I

X-RAY DIFFRACTION PATTERNS

Durene thiourea add.		Durene		Thiourea	
d/n	Int.	*d/n*	Int.	*d/n*	Int.
7.61	10	....	..	....	..
....	..	6.44	100	....	..
5.80	20	....	..	....	..
....	..	5.29	14	....	..
....	..	5.20	24	....	..
....	..	5.02	10	....	..
4.49	15	....	..	4.60	10
4.43_8	100	....	..	4.43_5	100
....	..	4.38	5	....	..
4.30_8	50	....	..	4.25_2	100
....	..	3.89	15	....	..
3.85	4	3.85	15	3.82	80
3.64	6	....	..	....	..
3.51	50	....	..	3.50	70
3.37	40	....	..	....	..
....	..	3.22	20	....	..
....	..	....	..	3.13	100
2.93	5	....	..	3.08	70

The data show that a new crystalline substance has been formed. Similarity of the cyclohexane and durene adduct patterns further confirms this.

Acknowledgment.—The authors wish to express their appreciation to Sinclair Research Laboratories for permission to publish this information. They also wish to acknowledge the assistance of Mr. R. A. Van Nordstrand who contributed the X-ray data presented here.

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4-Methyl-4-(3,5-Dimethylphenyl)-2-Methylpentene-1. An Intermediate Compound in the Synthesis of 1,1,3,3,4,6-Hexamethylindan

BY PHILIPPE TEYSSIÉ AND GEORGES SMETS

RECEIVED OCTOBER 10, 1955

During the course of an investigation on intramolecular cyclization in polymeric systems,[1] the synthesis of several reference substances has been carried out in order to allow an infrared spectrometric determination of the structure of this new class of polymers. For this purpose, 1,1,3,3,4,6-hexamethylindan has been prepared according to the method of Smith and Spillane[2]: reaction of methyl (3,5-dimethylphenyl)-isovalerate (I) with methylmagnesium iodide, and subsequent dehydration of the crude carbinol II in the presence of sulfuric acid. Owing to its insensitivity to ozone and alkaline permanganate in the cold, a structure of 1,1,3,3,4,6-hexamethylindan (IV) was assigned[2] to the hydrocarbon obtained. However, the same procedure in our laboratory gave a hydrocarbon different from that described by Smith and Spillane; it has been proved to be 4-methyl-4-(3,5-dimethylphenyl)-2-methylpentene-1 (III). Moreover, in the presence of aluminum chloride, internal cyclization occurs and the pentene III is trans-

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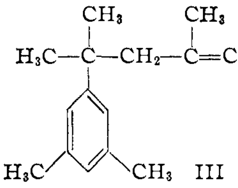
(1) Ph. Teyssié and G. Smets, Friedel-Crafts Reactions on Polyvinyl Chloride, *J. Polymer Sci.*, in press.

(2) L. I. Smith and J. L. Spillane, THIS JOURNAL, **65**, 202 (1943).



III

formed into the corresponding substituted indan IV.

These conclusions are drawn from the infrared spectrometric data and from the different values of the refractive index.

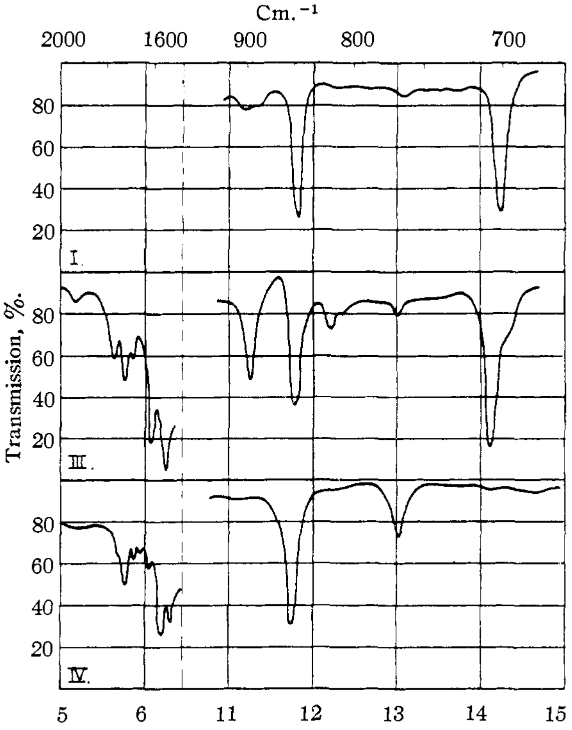
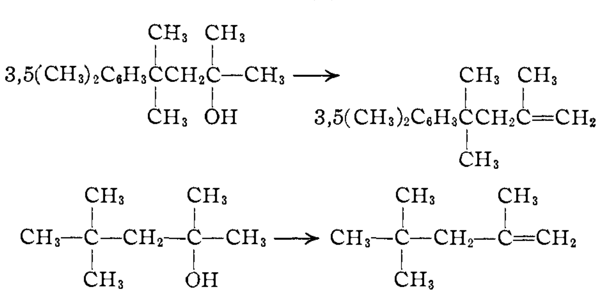


Fig. 1.

In the region of the strong absorption bands due to the aromatic C–H vibrations, compounds I and III show a similar spectrum with two strong bands at 11.80–11.85 and 14.20 μ which are characteristic of a 1,3,5-trisubstituted aromatic ring. Both bands disappear in the spectrum of IV, in which a strong band appears at 11.73 μ, characteristic of a 1,2,3,5-tetrasubstituted ring.[3,4] In the 5–6 μ region a group of sharp overtone bands is present, which are also characteristic of this tetrasubstitution.[5] Only compound III shows a typical olefinic absorption band at 6.09 μ (C=C stretching vibration).[3,6] This olefinic bond is a disubstituted terminal vinyl group RR'C=CH_2, as established by the typical absorption band at 11.25 μ (–CH out-of-plane deformation vibration).[3,7] By cyclization in presence of aluminum chloride, the same absorption band disappears.

The refractive index of compound III ($n^{28.5}D$ 1.5056) is very different from that of compound IV ($n^{28.5}D$ 1.5101), which shows the same value as that given by Smith and Spillane (1.5100).

This type of dehydration of 4-methyl-4-(3,5-dimethylphenyl)-2-methylpentanol-2 is completely analogous to that of dimethylneopentylcarbinol as given by Whitmore,[8] and must be related to the steric influence of the substituents.[9]



$$3,5(CH_3)_2C_6H_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{\underset{OH}{C}}-CH_3 \longrightarrow 3,5(CH_3)_2C_6H_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{C}=CH_2$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2$$

Experimental Part

The infrared spectra were measured with a single-beam Perkin-Elmer spectrometer, model 112; 10% carbon disulfide solutions between 10 and 15 μ, and pure hydrocarbons between 5 and 6.5 μ, were used (cell thickness, 0.1 mm.).

For the cyclization reaction, 1 g. of aluminum chloride was added slowly with stirring and cooling to 10 g. of compound III. The mixture was kept 48 hr. at 20°, poured in ice-water containing hydrochloric acid and extracted with ether. The ethereal solutions were washed, dried on sodium sulfate and evaporated. The residue yielded 8.1 g. (81%) of 1,1,3,3,4,6-hexamethylindan, b.p. 125–127° (20 mm.).

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[9] H. C. Brown and I. Moritani, *ibid.*, **77**, 3623 (1955).

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The Preparation of Substituted Hydrazines. III.[1] A General Method for Preparing N-Substituted Glycines[2]

BY JACK M. TIEN AND I. MOYER HUNSBERGER[3]

RECEIVED AUGUST 26, 1955

Recent papers[1,4,5] from this Laboratory have described the conversion of a variety of primary amines (RNH_2) *via* the corresponding glycine ($RNHCH_2CO_2H$), nitrosoglycine [$RN(NO)CH_2CO_2H$] and sydnone to the corresponding monosubstituted hydrazine ($RNHNH_2$). Our inability to prepare N-(3-pyridyl)-glycine by the conventional condensation of 3-aminopyridine with various halogenated acetic acid derivatives led us to investigate alternate synthetic routes to the N-substituted glycines. The successful preparation of N-(3-pyridyl)-glycine hydrochloride by catalytic

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[1] Paper II, J. M. Tien and I. M. Hunsberger, THIS JOURNAL, **77**, 6604 (1955).

[2] This work was sponsored by the Air Forces under Contract No. AF 33(038)-22909, Supplemental Agreement No. 5(54-1875).

[3] To whom inquiries concerning this article should be sent. Present address: Department of Chemistry, Fordham University, New York 58, N. Y.

[4] J. M. Tien and I. M. Hunsberger, *Chemistry & Industry*, 119 (1955).

[5] J. Fugger, J. M. Tien and I. M. Hunsberger, THIS JOURNAL, **77**, 1843 (1955).