has been established[9] that the hydrogen, and not the chlorine, of this compound reacts with free-radicals in solution. The very sluggish reactivity of trichlorofluoromethane compared to carbon tetrachloride is another example of the over-all bond strengthening effect exhibited by fluorine.[10] The other observed fact that bromine, in polyhalomethanes, is more reactive than chlorine is so general to the reactions of halogen compounds that it needs no further comment.

While hydrogen–halogen exchange reactions have been known for some time,[4–6,11–13] the reactions with ethanolic silver nitrate or ethanol are believed to be the first observed under such mild conditions.

Experimental[14]

The halomethanes were all purified by distillation and gave negative tests for free halogen or hydrogen halide when shaken with 10% aqueous silver nitrate. Mass spectrometric analysis indicated that the reagents were pure. The alcohols gave negative tests for free carbonyl with 2,4-dinitrophenylhydrazine reagent.

Reaction of Polyhalomethanes with Ethanolic Silver Nitrate.—A mixture of 25 ml. (0.270 mole) of I and 25 ml. of 2% (w./w.) ethanolic silver nitrate solution was allowed to stand for 24 hr. at room temperature. The solution became opalescent almost immediately. At the end of this period, the solids were collected, dried and weighed. They were identified as silver bromide by their behavior with aqueous ammonia.[15] The filtrate was diluted to 100 ml. with ethanol and an aliquot was withdrawn and titrated for free acid with standard alkali. Another aliquot was treated with 2,4-dinitrophenylhydrazine reagent,[16] giving the 2,4-dinitrophenylhydrazone of acetaldehyde, m.p. 150–151°. A mixed melting point with an authentic specimen showed no depression. Bromodifluoromethane was isolated from the remainder of the filtrate by distillation and identified by infrared analysis. The results are shown in Table I. Light, or its absence, has no effect on the course and velocity of the reaction.

Under conditions identical to the experiment described above, carbon tetrachloride, chloroform, methylene chloride, fluorotrichloromethane, difluorodichloromethane, chlorobromomethane, bromoform and bromotrichloromethane were allowed to react separately with 2% ethanolic silver nitrate. The halogen-containing products were isolated by drowning the alcoholic solutions with water and were identified by analysis with the mass spectrometer. The other products were isolated and identified as before. The results are given in Table I.

Reaction of I with Silver Nitrate in Isopropyl Alcohol and *t*-Butyl Alcohol.—A mixture of 25 ml. of I and 25 ml. of saturated isopropanolic silver nitrate, which became opalescent in 15 minutes, was allowed to stand for 23 hr. at room temperature. The reaction mixture then contained 0.264 g. (1.40 millimoles) of silver bromide and 1.60 millimoles of acid and gave 0.205 g. (0.863 millimole) of acetone 2,4-dinitrophenylhydrazone, m.p. 124–126°, which showed no depression of melting point with an authentic specimen.

A mixture of 25 ml. of I and 25 ml. of saturated *t*-butanolic silver nitrate remained clear after standing for 4 hr. at room temperature.

Attempted Reaction of I with Silver Nitrate in Acetone and in Water.—A mixture of 25 ml. of I and 25 ml. of 2% (w./w.) solution of silver nitrate in acetone (containing a trace of water to increase the solubility of silver nitrate) remained clear after standing for 6 hr. at room temperature.

A mixture of 31 g. of I and 250 g. of 10% (w./w.) aqueous silver nitrate remained clear after stirring rapidly under a condenser cooled with Dry Ice–acetone mixture for 23 hr.

Reaction of Polyhalomethanes with Ethanol.—A mixture of 25 ml. of 95% ethanol and 25 ml. of polyhalomethane was allowed to stand at room temperature for approximately 24 hr. The polyhalomethanes used were carbon tetrachloride, chlorobromomethane, bromoform, bromotrichloromethane and difluorodibromomethane. The products were then isolated and identified in the same manner as previously described. The results are reported in Table II.

Azonitrile-catalyzed Reaction of Polyhalomethanes with Ethanol.—A solution of the halogen compound, α,α'-azobisisobutyronitrile (2 mole % based on the halogen compound) and ethanol was heated for a number of hours. The products were determined as described previously. The results are given in Table III.

WILMINGTON 39, DELAWARE

---

(9) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945); see also F. A. Raal and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 578 (1952), and W. E. Hanford and R. M. Joyce, U. S. Patent 2,440,800.

(10) For example, see L. O. Brockway, *J. Phys. Chem.*, **41**, 158 (1937).

(11) J. P. West and L. Schmerling, U. S. Patents 2,553,799, 2,553,800.

(12) P. Savary and P. Desnuelle, *Bull. soc. chim. France*, 213 (1952).

(13) J. Banus, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 3041 (1950).

(14) All temperatures reported are uncorrected.

(15) J. H. Reedy, "Theoretical Qualitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 322, 325 and 326.

(16) G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reactions of Triphenylgermane with Some Organometallic Compounds. A New Method for the Preparation of Triphenylgermyllithium

BY HENRY GILMAN AND CLARE W. GEROW

RECEIVED MAY 18, 1956

Triphenylgermane has been found to react with organolithium reagents to give triphenylgermyllithium in good yields together with some of the tetrasubstituted germane. The reaction of *n*-butyllithium with triphenylgermane has been found to be of value in the preparation of triphenylgermyllithium. These reactions are compatible with the concept of a higher electronegativity for germanium as compared with silicon. The reaction of triphenylgermyllithium with triphenylgermane was found to give hexaphenyldigermane in small yield. Triphenylgermane gave no reaction with certain Grignard reagents under comparable conditions.

Generally speaking, organogermanium compounds undergo the same reactions as the analogous organosilicon compounds. There have been reported some exceptions to this generality, such as the difference in reactions of triphenylsilylpotassium[1] and triphenylgermyllithium[2] with benzophenone, and the difference in the reductions of triphenylhalogermanes and triphenylhalosilanes with tin and hydrochloric acid.[3] Perhaps one of the most pronounced differences has been found in the reactions of Si–H and Ge–H compounds with organolithium compounds. It has been reported

---

(1) H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2935 (1953).

(2) H. Gilman and C. W. Gerow, *ibid.*, **77**, 5740 (1955).

(3) R. West, *ibid.*, **75**, 6080 (1953).

that both triphenylsilane[4] and triethylsilane[5,6] react with RLi compounds to give the tetrasubstituted silane and lithium hydride.

$$R_3SiH + R'Li \longrightarrow R_3SiR' + LiH$$

With triphenylsilane, phenyllithium and methyllithium gave over 90% yields of tetraphenylsilane and triphenylmethylsilane, respectively, and butyllithium gave about 60% of triphenyl-*n*-butylsilane.

Johnson and Harris[7] reported that when triphenylgermane was added to a refluxing ether solution of an excess of phenyllithium, followed by refluxing for 12 hours, there was isolated tetraphenylgermane in 70% yield. The reverse addition of an excess of phenyllithium to refluxing triphenylgermane gave 50–60% yields of hexaphenyldigermane along with some tetraphenylgermane. The latter reaction has been successfully repeated in this Laboratory. Johnson and Harris postulated the formation of hexaphenyldigermane from the reaction of

$$(C_6H_5)_3GeLi + (C_6H_5)_3GeH \longrightarrow (C_6H_5)_3GeGe(C_6H_5)_3 + LiH$$

triphenylgermyllithium with triphenylgermane. The triphenylgermyllithium was suggested as being formed from the reaction of phenyllithium with triphenylgermane.

$$(C_6H_5)_3GeH + C_6H_5Li \longrightarrow (C_6H_5)_3GeLi + C_6H_6$$

We have found that triphenylgermane reacts with organolithium compounds to give triphenylgermyllithium in good yield along with some of the tetrasubstituted germane. When an equivalent amount of phenyllithium was added dropwise to an ether solution of triphenylgermane, the mixture refluxed and a yellow solution was formed. On carbonation there was found an 86% yield of triphenylgermanecarboxylic acid and a small amount of tetraphenylgermane.

$$(C_6H_5)_3GeH + RLi \longrightarrow RH + (C_6H_5)_3GeLi \xrightarrow[2,\ H_2O]{1,\ CO_2} (C_6H_5)_3GeCOOH$$

Under the same conditions butyllithium gave a quantitative yield of triphenylgermanecarboxylic acid. Methyllithium gave little reaction at room temperature; however, after refluxing 24 hours 70–80% yields of triphenylgermanecarboxylic acid were obtained along with 16% of triphenylmethylgermane. The reaction of methyllithium with triphenylgermane at room temperature for three days gave a 10% yield of hexaphenyldigermane, which probably resulted from the reaction of triphenylgermane, with the triphenylgermyllithium which was formed.

We have confirmed the postulate of Johnson and Harris that hexaphenyldigermane is formed by the reaction of triphenylgermyllithium with triphenylgermane. When triphenylgermyllithium was allowed to react with triphenylgermane in ethylene glycol dimethyl ether at room temperature, there was isolated only 1% of hexaphenyldigermane; however, when a mixture of diethyl ether and ethylene glycol dimethyl ether was used as the solvent, and the solution was refluxed 24 hours, a 12% yield of hexaphenyldigermane was isolated. Likewise, when a diethyl ether solution of triphenylgermane and triphenylgermyllithium was refluxed for 40 hours there was obtained a 12% yield of hexaphenyldigermane. In view of these experiments it does not seem probable that the 50–60% yields of hexaphenyldigermane obtained from the reaction of an excess of phenyllithium with triphenylgermane were a result of the reaction of triphenylgermyllithium with triphenylgermane alone. The mechanism of the formation of hexaphenyldigermane is unknown; however, it may involve the phenyllithium which is present in excess. Triphenylsilane has been reported to react with triphenylsilyllithium in ethylene glycol dimethyl ether to give a 14% yield of hexaphenyldisilane along with 11% of tetraphenylsilane.[8]

In its reactions with organolithium reagents triphenylgermane is acting more like triphenylmethane which is known to react with RLi compounds to give triphenylmethyllithium.[9]

The reaction of triphenylgermane with RLi compounds to give triphenylgermyllithium is consistent with the concept of a higher electronegativity for germanium as compared to silicon. Sanderson[10] places the electronegativity of germanium considerably above that of silicon and even slightly higher than that of hydrogen. Rochow and Allred[11] and West[3] have given chemical evidence to support this concept of high electronegativity for germanium. If one assumes, therefore, that germanium has an electronegativity higher than that of hydrogen, then in Ge–H compounds the electrons would be displaced more toward the germanium. Thus the germanium atom would be more likely to couple with the positive portion of the RLi compound, the lithium atom. Because there would be such a small difference in electronegativity between germanium and hydrogen one might expect the formation of a mixture of triphenylgermyllithium and the tetrasubstituted germane. Indeed, this was found to be the case in the reactions of methyllithium and phenyllithium with triphenylgermane.

The reaction of triphenylgermane with an equivalent amount of *n*-butyllithium affords an excellent method for the preparation of triphenylgermyllithium. The advantages of this method over others previously reported[2,12] for the preparation of triphenylgermylmetallic reagent are many. First, the reaction proceeds quantitatively and instantaneously; second, there are no bothersome side reactions or side products; third, the triphenylgermyllithium reagent is soluble in the ether; fourth, the reagent apparently does not react with the solvent; fifth, there is no metal excess to dispose of and reactions may be carried out in the flask in which the reagent is prepared.

Attempts to prepare triphenylgermylmagnesium

---

[4] H. Gilman and H. W. Melvin, THIS JOURNAL, **71**, 4050 (1949).

[5] H. Gilman and S. P. Massie, *ibid.*, **68**, 1128 (1946).

[6] R. N. Meals, *ibid.*, **68**, 1880 (1946).

[7] O. H. Johnson and D. M. Harris, *ibid.*, **72**, 5566 (1950).

[8] A. G. Brook and H. Gilman, *ibid.*, **76**, 2333 (1954); **76**, 2338 (1954).

[9] H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

[10] R. T. Sanderson, *J. Chem. Ed.*, **32**, 140 (1955).

[11] E. G. Rochow and A. L. Allred, THIS JOURNAL, **77**, 4489 (1955).

[12] H. Gilman and C. W. Gerow, *ibid.*, **77**, 4675 (1955); **77**, 5509 (1955).

bromide by the reaction of a Grignard reagent with triphenylgermane have as yet been unsuccessful. Both phenylmagnesium bromide and allylmagnesium bromide[13] gave no apparent reaction with triphenylgermane.

Experimental[14]

Reaction of Methyllithium with Triphenylgermane. At Room Temperature.—To 6.1 g. (0.02 mole) of triphenylgermane dissolved in 20 ml. of ether there was added 0.02 mole of methyllithium prepared from methyl iodide. After stirring 3 days the mixture was filtered and the ether filtrate was poured into an ether–Dry Ice slurry. The ether-insoluble solid was washed with water and dried to give 0.63 g. (10.3%) of hexaphenyldigermane melting over the range 338–341°. After the ether–Dry Ice mixture had warmed to room temperature water was added and the alkaline layer was separated. After washing the ether layer with 50-ml. portions of 5% sodium hydroxide solution the combined alkaline portions were acidified by means of concentrated hydrochloric acid; however, no solid material precipitated. The ether layer was dried over anhydrous sodium sulfate and the solvent was removed by distillation to leave a residue which was dissolved in chloroform, then diluted with methanol until the solution became cloudy. Cooling gave 0.85 g. of solid melting over the range 170–185°. Recrystallization from petroleum ether gave 0.75 g. (12%) of hexaphenyldigermoxane melting at 183–184°.

In Refluxing Ether.—The methyllithium from 6.4 g. (0.045 mole) of methyl iodide was added rapidly to 6.1 g. (0.02 mole) of triphenylgermane dissolved in 25 ml. of ether. When addition was complete the mixture was refluxed 24 hours and then carbonated by pouring it into an ether–Dry Ice slurry. After warming to room temperature the mixture was hydrolyzed by the addition of water. The alkaline layer was separated and the ether layer was extracted twice with 50-ml. portions of 5% sodium hydroxide solution. The combined alkaline portions were acidified by the addition of concentrated hydrochloric acid and there precipitated 5.1 g. (77%) of triphenylgermanecarboxylic acid melting at 186° with the evolution of carbon monoxide.[15] The infrared spectrum of this compound was identical with that of an authentic sample of triphenylgermanecarboxylic acid. The ether layer was dried over anhydrous sodium sulfate and the solvent removed by distillation to leave a residue which was dissolved in methanol and cooled to give 1.05 g. (16.5%) of triphenylmethylgermane melting at 68.5–69.5°. A mixed melting point with an authentic sample of triphenylmethylgermane showed no depression and their infrared spectra were identical.

A second run using an equivalent amount of methyllithium gave 4.6 g. (70%) of triphenylgermanecarboxylic acid and 0.55 g. (8.6%) of triphenylmethylgermane.

Reaction of Phenyllithium with Triphenylgermane.—To 6.1 g. (0.02 mole) of triphenylgermane dissolved in 25 ml. of ether there was added dropwise 23 ml. (0.02 mole) of 0.87 *N* phenyllithium. During the addition enough heat was evolved to cause refluxing of the solution and the color changed to light yellow. After stirring about 5 minutes the mixture was carbonated and worked-up as previously mentioned to give 5.5 g. (83%) of triphenylgermanecarboxylic acid melting at 186° with the evolution of carbon monoxide. This acid was crystallized from ethanol in an attempt to isolate any benzoic acid which might have been present; however, only triphenylgermanecarboxylic acid was recovered. The ether layer from the above reaction was dried and the solvent distilled to leave a residue which was crystallized from petroleum ether to give 0.2 g. of tetraphenylgermane melting over the range 229–232°. No hexaphenyldigermane was found.

The only difference between the above reaction of phenyllithium with triphenylgermane and that as carried out by Johnson and Harris (and repeated successfully in this Laboratory) is that in the above reaction an equivalent amount of phenyllithium was used and the mixture was not refluxed after the addition of the phenyllithium.

Reaction of *n*-Butyllithium with Triphenylgermane.—To a stirred solution of 6.1 g. (0.02 mole) of triphenylgermane in 25 ml. of ether there was added dropwise 22 ml. (0.03 mole) of a 1.384 *N* solution of butyllithium.[16] Enough heat was generated during the addition to cause refluxing of the solution and when about two-thirds of the butyllithium had been added refluxing ceased; during the addition of the remainder of the butyllithium no heat was evolved. Immediately after addition was complete the mixture was carbonated and worked-up as previously mentioned to give 6.4 g. (97%) of triphenylgermanecarboxylic acid melting at 189°. The ether layer was dried and the solvent removed by distillation to leave a negligible amount of residue.

A second run using an equivalent amount of butyllithium gave an quantitative yield of triphenylgermanecarboxylic acid. A third run using an equivalent amount of butyllithium but adding the triphenylgermane to the stirred butyllithium gave the same results.

Reaction of Triphenylgermyllithium with Triphenylgermane. In Ethylene Glycol Dimethyl Ether (GDME).—Triphenylgermyllithium was prepared in GDME by the cleavage of 6.0 g. (0.01 mole) of hexaphenyldigermane according to recent directions.[2,12] This was added dropwise to 6.1 g. (0.02 mole) of triphenylgermane dissolved in 25 ml. of GDME. After stirring overnight water was added and the mixture was filtered to give 0.15 g. (1.3%) of hexaphenyldigermane melting at 340–342°. The filtrate was extracted with diethyl ether, then the ether was dried and the solvents distilled to leave a residue which was dissolved in warm petroleum ether and cooled to yield 1.6 g. (12.5%) of triphenylgermanol (mixed melting point) melting at 132–134°. The petroleum ether was removed from the filtrate by distillation and the residue was crystallized from methanol to give 5.4 g. (44% of the total germanium) of triphenylgermane melting at 45–46.5°.

In a Mixture of GDME and Diethyl Ether.—To the triphenylgermyllithium from 6.0 g. (0.01 mole) of hexaphenyldigermane in 25 ml. of GDME there was added 6.1 g. (0.02 mole) of triphenylgermane dissolved in 25 ml. of diethyl ether. When the addition was complete the mixture was refluxed for 24 hours and stirred for 72 hours at room temperature. At the end of this time water was added and the mixture was filtered to give 1.4 g. (11.5%) of hexaphenyldigermane melting at 340–342°. The filtrate was extracted with diethyl ether, the ether solution was dried and the solvents were distilled to leave a residue which was dissolved in warm petroleum ether and cooled to give 0.4 g. (3.1%) of triphenylgermanol (mixed melting point) melting over the range 129–132°. The petroleum ether was distilled from the filtrate and the residue was seeded with triphenylgermane and set aside to yield 5.6 g. (46% of the total germanium) of triphenylgermane melting over the range 40–43°.

In Diethyl Ether.—An ether solution of triphenylgermyllithium was prepared by the reaction of 0.02 mole of butyllithium with 6.1 g. (0.02 mole) of triphenylgermane. To this stirred solution there was added 6.1 g. (0.02 mole) of triphenylgermane dissolved in 20 ml. of ether. After addition was complete the mixture was refluxed 40 hours and then was hydrolyzed by the addition of water. Filtration gave 1.4 g. (11.5%) of hexaphenyldigermane melting at 342–345°. The ether layer was dried and the solvent was removed by distillation to leave a residue which was dissolved in warm petroleum ether and cooled to yield 1.4 g. (11%) of triphenylgermanol melting at 125–128°. The petroleum ether was removed from the filtrate by distillation and the residue was vacuum distilled at 120–125° (0.07 mm.) to give 7.1 g. (58% of the total germanium) of triphenylgermane melting over the range 43.5–46°.

Reaction of Triphenylgermane with *n*-Butylmagnesium Bromide.—To 0.03 mole of butylmagnesium bromide there was added 6.1 g. (0.02 mole) of triphenylgermane dissolved in 35 ml. of ether. After refluxing overnight the mixture was carbonated and worked-up as previously mentioned; however, no triphenylgermanecarboxylic acid was found. Working-up the ether layer gave 1.0 g. (15.7%) of triphenyl-

---

[13] Studies in this Laboratory by J. Eisch and T. Soddy indicate that allylmagnesium bromide and related Grignard reagents have a reactivity close to organolithium reagents.

[14] All melting points are uncorrected. Reactions involving reactive organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. The petroleum ether used throughout the experimental procedure boiled over the range 60–70°.

[15] A. G. Brook and H. Gilman, This Journal, **76**, 77 (1954).

[16] Prepared according to the directions of H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *ibid.*, **71**, 1499 (1949).

germanol melting at 132–134° and 4.1 g. (67%) of triphenylgermane melting at 46–47°.

Reaction of Triphenylgermane with Allylmagnesium Bromide.—To 6.1 g. (0.02 mole) of triphenylgermane dissolved in 25 ml. of ether there was added 0.02 mole of allylmagnesium bromide.[17] After refluxing 68 hours the mixture was carbonated; however no triphenylgermanecarboxylic acid was found. Working-up the ether layer gave 4.55 g. (75%) of triphenylgermane melting at 43–46°.

---

[17] Prepared according to the directions of H. Gilman and J. H. McGlumphy, *Bull. soc. chim.*, **43**, 132 (1928).

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for their financial support of this work. They are also grateful to the Institute for Atomic Research, Iowa State College, Ames, Iowa, for assistance in the infrared determinations.

AMES, IOWA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

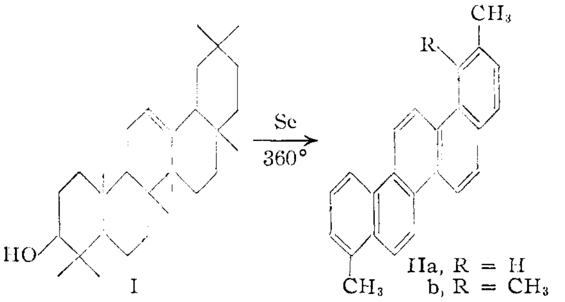
Polynuclear Aromatic Hydrocarbons. VII.[1] The Synthesis of 1,2,9-Trimethylpicene

BY DONALD D. PHILLIPS AND DONALD E. TUITES[2]

RECEIVED JUNE 26, 1956

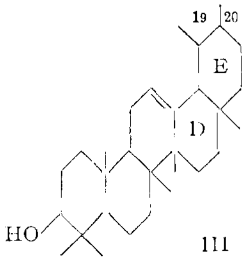
1,2,9-Trimethylpicene (IIb) has been synthesized from methyl γ-(9,10-dihydro-2-phenanthryl)-valerate (V) by a series of reactions illustrated in Chart 1. The hydrocarbon is different from the polymethylpicene isolated from the dehydrogenation products of several triterpenes and the significance of this result on the Jeger–Ruzicka structure III for α-amyrin is discussed.

Selenium dehydrogenation has been an invaluable tool in the elucidation of the complex structures often associated with natural products. Examples of its application to the structure determination of steroids now form a classical part of organic chemistry.[3] The reaction has also been of great assistance in the field of triterpene chemistry where the dehydrogenation products have often retained the complete skeleton of the starting material. An excellent example is afforded by β-amyrin (I) which yields, among other aromatic hydrocarbons, 2,9-dimethylpicene (IIa).[4]

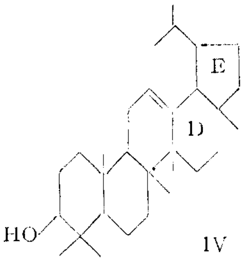


I
IIa, R = H
b, R = CH_3

Until recently, the most widely accepted structure for the triterpene α-amyrin was that proposed by Meisels, Jeger and Ruzicka[5] (III). This formulation has been questioned by Spring and his collaborators, however, and they have presented evidence in favor of IV as the correct structure.[6]



III



IV

The Glasgow group contends that the five-membered ring E more satisfactorily accounts for the stability of the D/E fusion which appears to be *cis*.[7]

Jeger himself[5] has pointed out a discrepancy in structure III for α-amyrin in that the dehydrogenation products from III are the *same* as those from β-amyrin (I) and seem to include 2,9-dimethylpicene (IIa) rather than the expected 1,2,9-trimethylpicene (IIb). Because of the inherent difficulty in making comparisons among these high melting picene derivatives, Jeger has suggested[8] that the 306° hydrocarbon obtained[9] in the dehydrogenation of α-amyrin might well be the trimethyl derivative IIb which was unknown at the time. If this were true, the validity of structure III would be greatly strengthened.

We have now prepared 1,2,9-trimethylpicene (IIb, m.p. 252–254°) and have established that it is *different in all respects* from the 306° hydrocarbon

---

[1] A preliminary account of this work has appeared as paper VI in *Chemistry & Industry*, R29 (1956); paper V, D. D. Phillips, *ibid.*, 54 (1956).

[2] From the Ph.D. thesis of Donald E. Tuites, Cornell University, February 1956.

[3] O. Diels and W. Gädke, *Ber.*, **60**, 140 (1927); O. Diels, W. Gädke and P. Kording, *Ann.*, **459**, 1 (1927); O. Diels and A. Karstens, *ibid.*, **478**, 129 (1930); L. Ruzicka, *et al.*, *Helv. Chim. Acta*, **16**, 216, 812 (1933); **17**, 200 (1934); **18**, 434 (1935).

[4] A comprehensive summary of the various dehydrogenation products is given by D. H. R. Barton in "Chemistry of Carbon Compounds," E. H. Rodd, Editor, Vol. IIB, Elsevier Publishing Co., Houston, Texas, 1953, p. 742.

[5] (a) A. Meisels, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1075 (1949); A. Meisels, R. Rüegg, O. Jeger and L. Ruzicka, *ibid.*, **38**, 1298 (1955); A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger and L. Ruzicka, *ibid.*, **39**, 441 (1956); (b) For excellent reviews on the subject see O. Jeger in L. Zechmeister's "Forschritte der Chemie organischer Naturstoffe," Vol. **7**, 1950, p. 1 and D. H. R. Barton in "Progress in Organic Chemistry," J. W. Cook, Editor, Butterworths, London, 1953, pp. 67–104.

[6] (a) J. M. Beaton, F. S. Spring, R. Stevenson and W. S. Strachan, *J. Chem. Soc.*, 2610 (1955); (b) G. D. Meakins, *Chemistry & Industry*, 1353 (1955).

[7] E. J. Corey and J. J. Ursprung, *ibid.*, 1387 (1954); THIS JOURNAL, **78**, 183 (1956); A. Eschenmoser, L. Ruzicka, O. Jeger and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955).

[8] Reference 5b, p. 54.

[9] (a) L. Ruzicka and E. Morgeli, *Helv. Chim. Acta*, **19**, 377 (1936); (b) F. S. Spring and T. Vickerstaff, *J. Chem. Soc.*, 249 (1937).