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°.

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

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

[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]

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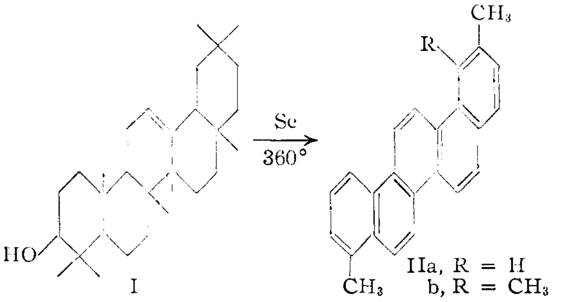
1,2,9-Trimethylpicene (IIb) has been synthesized from methyl γ-(9,10-dihydro-2-phenanthryl)-valerate (V) by a series of reactions illustrated in Chart 1. The hydrocarbon is different from the polymethylpicene isolated from the dehydrogenation products of several triterpenes and the significance of this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

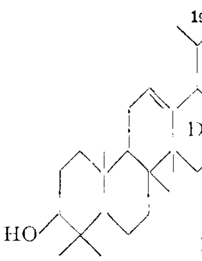
Selenium dehydrogenation has been an invaluable tool in the elucidation of the complex structures often associated with natural products. Examples of its application to the structure determination of steroids now form a classical part of organic chemistry.[3] The reaction has also been of great assistance 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]



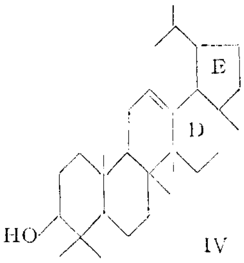
I

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

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[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).

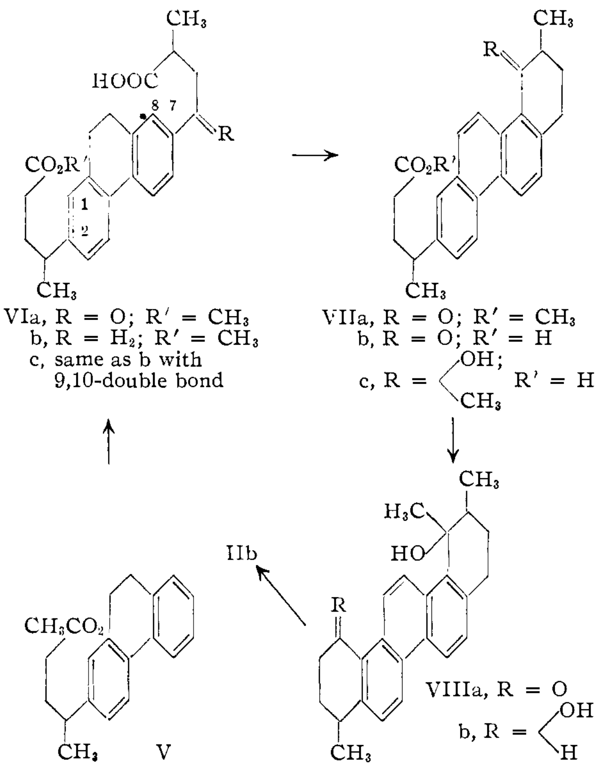
[8] Reference 5b, p. 54.

[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).

isolated in the dehydrogenation of α-amyrin. Although this fact alone does not establish IV as the structure of α-amyrin, it does cast some doubt on the validity of III because well-authenticated examples of the elimination of non-quaternary methyl groups during dehydrogenation do not seem to have been described in the literature.[10] There is no obvious *a priori* reason why the C_{19} methyl in III should be lost during the dehydrogenation even though it occupies a sterically hindered position. A thorough search for IIb in the high boiling dehydrogenation fractions of α-amyrin must be made, however, before definite conclusions can be drawn and work along these lines is in progress in these laboratories.

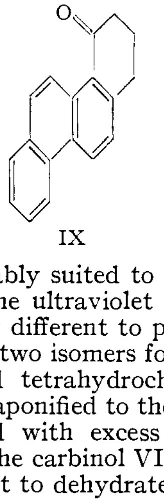
The synthesis of IIb was accomplished by using the general scheme previously reported.[11] Methyl γ-(9,10-dihydro-2-phenanthryl)-valerate (V)[11b] was condensed with methylsuccinic anhydride in the Friedel–Crafts reaction to give the keto acid VIa. Earlier work in this series[11a] has established that acylations of 2-substituted-9,10-dihydrophenanthrenes occur in the 7-position, a result to be expected from classical biphenyl chemistry. Moreover, there is a large body of evidence to support the contention that the methyl group introduced in the methylsuccinic anhydride reaction is α- to the carboxyl group.[12] To verify this assignment, the reduced acid VIb was subjected to the Barbier–Wieland degradation[13] and the resultant product gave high yields of iodoform when treated with iodine–potassium iodide solution. A methyl ketone would be formed in this reaction if the methyl group were α- to the carboxyl but not if it occupied the β-position.

CHART 1

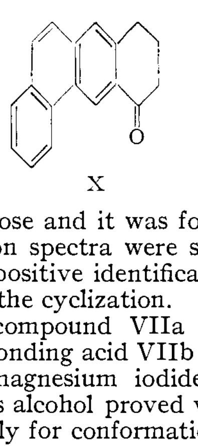


For this particular approach to the synthesis of IIb it was necessary that VIa and VIb retain both the acid *and* the ester groups so that selective cyclizations could be effected later. Infrared analysis of VIa indicated the presence of three sharp peaks at 5.77, 5.87 and 5.96 μ and these could be ascribed to the ester, carboxyl and conjugated carbonyl groups, respectively. To preserve the ester group in VIb, the carbonyl function in VIa was reduced catalytically rather than by the more usual Clemmensen or Wolff–Kishner techniques. The suggested reaction time[14] of two hours or less resulted in the formation of a lactone but on prolonged reduction (24 hours) this material was converted to the desired compound VIb which had the characteristic ester and carboxyl absorption peaks at 5.78 and 5.88 μ, respectively.

Before VIb could be cyclized, the 9,10-double bond had to be restored in order to obtain the correct orientation in the product.[11] This was accomplished by palladium-on-charcoal dehydrogenation in refluxing *p*-cymene. The fully aromatic acid VIc was then cyclized by the inverse Friedel–Crafts procedure[15] to yield the expected tetrahydrochrysene derivative VIIa. An isomeric ketone was also formed in this reaction and model compounds were necessary to identify the desired isomer. The two ketones, IX and X,[16] seemed admirably suited to our purpose and it was found that the ultraviolet absorption spectra were sufficiently different to permit a positive identification of the two isomers formed in the cyclization. The desired tetrahydrochrysene compound VIIa was then saponified to the corresponding acid VIIb and treated with excess methylmagnesium iodide to form the carbinol VIIc. This alcohol proved very difficult to dehydrate, probably for conformational reasons, but no serious attempts to effect the dehydration were made at this point since the final step in the synthesis was to be a combined dehydration–dehydrogenation.



IX



X

To build up the final ring of the picene skeleton, acid VIIc was cyclized to a mixture of two ketones in which VIIIa was the predominant isomer. This ketone was treated with lithium aluminum hydride and the resultant diol VIIIb was dehydrated and dehydrogenated to 1,2,9-trimethyl-

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(10) P. Plattner, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 41.

(11) (a) D. D. Phillips, THIS JOURNAL, **75**, 3223 (1953); (b) D. D. Phillips and E. J. McWhorter, *ibid.*, **76**, 4948 (1954); **77**, 3856 (1955).

(12) E. Berliner, *Org. Reactions*, **5**, 242 (1949).

(13) H. Wieland, O. Schlichting and R. Jacobi, *Z. physiol. Chem.*, **161**, 80 (1926).

(14) E. C. Horning and D. B. Reisner, THIS JOURNAL, **71**, 1036 (1949).

(15) W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949).

(16) L. F. Fieser and W. S. Johnson, *ibid.*, **61**, 1647 (1939). We are grateful to Professor Fieser for generous samples of each ketone.

picene (IIb) by heating to 300° in the presence of 10% palladium-on-charcoal catalyst. The analysis of the hydrocarbon and its 2,4,7-trinitrofluorenone derivative agreed with the formula $C_{25}H_{20}$ and the ultraviolet absorption spectrum (Fig. 1) was that of a typical picene with the characteristic bathochromic shift being observed throughout.

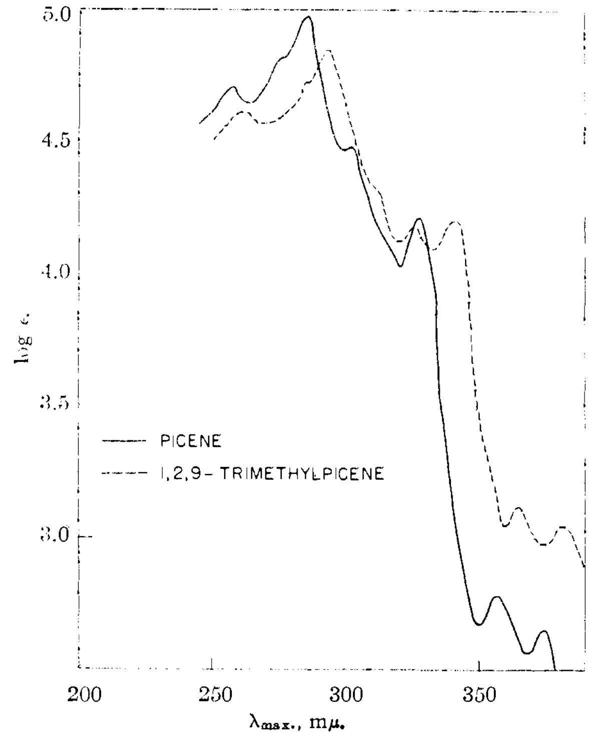

Fig. 1.

The usual comparisons definitely established that the synthetic hydrocarbon was different from 2,9-dimethylpicene (IIa). This means that the hindered methyl group presumably was *not lost* in the dehydrogenation of VIIIb whereas the formation of IIa from III, in which the C_{19} methyl is similarly hindered, requires the loss of the methyl group. This anomalous behavior may be due to the difference in catalysts employed although it should be pointed out that the formation of IIa from the Spring formulation IV would present no problem.

Experimental[17]

2-(1-Carbomethoxy-3-butyl)-7-(3-carboxy-1-butanoyl)-9,10-dihydrophenanthrene (VIa).—To a well-cooled solution of 4.4 g. (0.039 mole) of methylsuccinic anhydride (m.p. 29.5–30.5°), 10 g. (0.034 mole) of methyl γ-(9,10-dihydro-2-phenanthryl)-valerate (V)[11b] and 75 ml. of ethylene chloride was added with stirring over 10 minutes 20 g. (0.15 mole) of anhydrous aluminum chloride. The orange-brown complex was stirred at 0° for three hours and at room temperature for 24 hours. It was then decomposed in the usual fashion and the acidic material was taken up in sodium carbonate solution. This basic solution was acidified, extracted with ether and the solvent evaporated to leave 12.8 g. (93%) of VI as a semi-solid that failed to crystallize from a variety of solvents. The ultraviolet (λ_{max} 299 mμ, log ε 4.28 and 315 mμ, log ε 4.24) and infrared (λ_{max} 5.77, 5.87 and 5.96 μ) absorption spectra were in agreement with the structure assigned to this compound.

Anal. Calcd. for $C_{25}H_{28}O_6$: C, 73.50; H, 6.91, neut. equiv., 408.5. Found: C, 73.17; H, 7.20; neut. equiv., 404.

2-(1-Carbomethoxy-3-butyl)-7-(3-carboxy-1-butyl)-9,10-dihydrophenanthrene (VIb).—In an electrically heated hydrogenation flask were placed 19.0 g. (0.046 mole) of VIa, 4.4 g. of 10% palladium-on-charcoal catalyst and 100 ml. of absolute ethanol. The mixture was shaken for 24 hours at 60° and 3 atmospheres pressure in a Parr apparatus. The catalyst was filtered and the solution was evaporated to 17.1 g. of a colorless, viscous oil. Infrared analysis indicated the presence of lactone (5.65 μ) in this material so that it was taken up in ether, extracted with carbonate solution, reacidified and extracted to yield 16.1 g. (89%) of acid VIb as a viscous oil. The ultraviolet (λ_{max} 268 mμ, log ε 4.16 and 296 mμ, log ε 3.79) and infrared (λ_{max} 5.78 and 5.88 μ) absorption spectra indicated that complete reduction of the carbonyl group had occurred.

Anal. Calcd. for $C_{25}H_{30}O_4$: C, 76.12; H, 7.67. Found: C, 75.88; H, 7.94.

When the reduction was carried out at 60° for two hours there was obtained a 7:3 ratio of lactone and acid VIb. Before it was discovered that the lactone could be reduced under much longer reaction times, an attempt was made to dehydrogenate it to the corresponding phenanthrene derivative. When heated to 250–260° for two hours in the presence of 10% palladium-on-charcoal however, the lactone lost carbon dioxide so that this route was abandoned.

Barbier–Wieland[18] Degradation of VIb.—To a Grignard reagent prepared from 10 g. (0.064 mole) of bromobenzene and 1.07 g. (0.07 mole) of magnesium in 50 ml. of ether was added 1.52 g. (0.0037 mole) of VIb (as the dimethyl ester) dissolved in 15 ml. of benzene. The mixture was heated under reflux for two hours, then decomposed with ice and acid. The organic material was extracted into ether, the solvent was removed and replaced by methanol containing 0.8 g. of sodium hydroxide. This basic solution was heated under reflux for two hours, poured into excess water and the crude carbinol extracted with ether.

The ether was removed by evaporation and the oily residue was heated for one hour with 10 g. of acetic anhydride. Excess anhydride was decomposed in water and the crude olefin was extracted and dissolved in acetic acid to which was added at 17° a solution of 5 g. of chromic anhydride in 15 cc. of 60% acetic acid. The solution was stirred at 16° for one hour and the excess oxidant was decomposed with sodium bisulfite solution. The mixture was poured into 100 ml. of 2 *N* hydrochloric acid, extracted with ether and the organic phase washed well with acid. On evaporation there remained 0.60 g. of an oil. This was esterified with methanol and chromatographed on alumina to remove colored impurities. The material was then treated with iodine–potassium iodide solution as recommended by Shriner and Fuson.[19] A copious precipitate of iodoform, m.p. 116–119°, was formed, which, on recrystallization from dilute dioxane, gave yellow needles, m.p. 118–120°.

2-(1-Carbomethoxy-3-butyl)-7-(3-carboxy-1-butyl)-phenanthrene (VIc).—A solution of 10.6 g. (0.027 mole) of acid VIb in 25 ml. of *p*-cymene containing 1.1 g. of 10% palladium-on-charcoal catalyst was heated under reflux for 4 hours. The catalyst was removed by filtration and the solvent evaporated at reduced pressure to give 10.25 g. (97%) of a pale yellow, viscous oil. This material failed to crystallize and efforts to prepare derivatives were unsuccessful. The appearance in the ultraviolet absorption spectrum of the typical phenanthrene[20] peaks at λ_{max} 265 mμ (log ε 4.83) and 298 mμ (log ε 3.95) indicated that de-

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[17] Melting points and boiling points are both uncorrected unless indicated otherwise. Ultraviolet absorption spectra were measured on a Beckman DK automatic recording spectrophotometer in 95% ethanol as solvent. Infrared spectra were determined on a Perkin-Elmer model 21 spectrophotometer. All solids were pressed in potassium bromide. Analyses were performed by Geller Labs., Hackensack, N. J., and Schwarzkopf Labs., Woodside 77, N. Y.

[18] J. F. Lane and E. S. Wallis, THIS JOURNAL, **63**, 1674 (1941). We are grateful to A. W. Johnson of this Laboratory for performing this experiment.

[19] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 138.

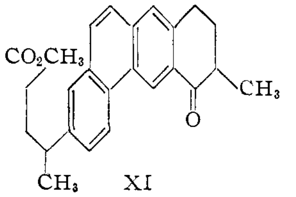
[20] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Charts 341–371.

hydrogenation had been complete. Infrared peaks at 5.78 and 5.88 μ proved that no alteration of the ester or carboxyl groups had occurred.

Anal. Calcd. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.54; H, 7.36.

3-Methyl-4-keto-8-(1-carbomethoxy-3-butyl)-1,2,3,4-tetrahydrochrysene (VIIa).—To 18.6 g. (0.047 mole) of acid VIc in a round-bottom flask protected by a calcium chloride tube was added 10.9 g. (0.052 mole) of phosphorus pentachloride. After the initially vigorous reaction had subsided the mixture was warmed to 70° for 20 minutes. To the cooled solution was added 15 ml. of dry benzene and the volatile material was removed by co-distillation. This process was repeated with two more portions of benzene. The crude acid chloride was finally taken up in 25 ml. of benzene and added at 5°, with stirring, to a suspension of 8.4 g. (0.063 mole) of aluminum chloride in 50 ml. of benzene. The orange complex was stirred for five hours at room temperature (during which time it turned a deep red) and decomposed in the usual fashion to give 16.4 g. (95%) of oily ketonic material.

The crude mixture of ketones was chromatographed on alumina using first benzene and then benzene–chloroform as eluants. In this way it was possible to separate the mixture into 12.7 g. (78%) of semi-crystalline ketone whose ultraviolet absorption spectrum (λ_{max} 255 mμ, log ε 4.52; 293 mμ, log ε 3.99 and 325 mμ, log ε 3.79) was very similar to that of 4-keto-1,2,3,4-tetrahydrochrysene (IX)[16] (λ_{max} 252 mμ, log ε 4.62; 292 mμ, log ε 4.08 and 318 mμ, log ε 3.98) and hence was assigned structure VIIa. The later fractions on evaporation gave 0.44 g. of an oil whose ultraviolet absorption spectrum (λ_{max} 247 mμ, log ε 4.58; 256 mμ, log ε 4.61; 294 mμ, log ε 4.10 and 325 mμ, log 3.98) closely resembled that of 8-keto-5,6,7,8-tetrahydro-1,2-benzanthracene (X)[16] and hence it was assigned the isomeric structure, 7-methyl-8-keto-3′-(1-carbomethoxy-3-butyl)-5,6-7,8-tetrahydro-1,2-benzanthracene (XI).



XI

Ester VIIa was converted directly to the corresponding acid VIIb without analysis in the hope that crystalline material would be obtained.

3-Methyl-4-keto-8-(1-carboxy-3-butyl)-1,2,3,4-tetrahydrochrysene (VIIb).—Ten grams (0.027 mole) of ester VIIa was saponified in the usual manner to give 8.25 g. (86%) of acid VIIb as a semi-crystalline solid, m.p. 70–80°; λ_{max} 256 mμ (log ε 4.47), 294 mμ (log ε 4.26) and 320 mμ (log ε 3.88). Purification attempts on this acid were abortive but the analysis was satisfactory for the mixture of diastereoisomers in which the acid probably exists.

Anal. Calcd. for $C_{24}H_{24}O_3$: C, 79.98; H, 6.71. Found: C, 79.79; H, 6.77.

The **2,4-dinitrophenylhydrazone** was prepared under conditions (ethanol and sulfuric acid) that resulted in the esterification of the acid portion and crystallized from ethanol–ethyl acetate as an orange-red powder, m.p. 114–115°.

Anal. Calcd. for $C_{32}H_{32}N_4O_6$: C, 67.60; H, 5.67. Found: C, 67.72; H, 5.79.

3,4-Dimethyl-4-hydroxy-8-(1-carboxy-3-butyl)-1,2,3,4-tetrahydrochrysene (VIIc).—To a well-stirred solution of 8.0 g. (0.022 mole) of keto acid VIIb in 75 ml. of benzene was added 50 ml. of methylmagnesium iodide solution (from 1.78 g. of magnesium and 9.45 g. (0.067 mole) of methyl iodide) at a rate sufficient to maintain a gentle reflux. After the addition was complete the yellow complex was stirred under reflux for 4 hours and then decomposed in the usual fashion.

Acidic material was extracted with sodium carbonate solution and reacidified to give 5.24 g. (65%) of the hydroxy acid VIIc as a semi-crystalline solid. In view of the failure to crystallize the precursor, no further attempts to purify the acid were made.

Anal. Calcd. for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50. Found: C, 79.63; H, 7.37.

The hydroxy acid VIIc was heated under reflux with anhydrous formic acid for two hours but was not dehydrated under these conditions.

1,2,9-Trimethyl-1-hydroxy-12-keto-1,2,3,4,9,10,11,12-octahydropicene (VIIIa).—The acid chloride from 4.83 g. (0.0135 mole) of acid VIIc was prepared as described above for VIIa and added with stirring to a cooled mixture of 2.53 g. (0.019 mole) of aluminum chloride in 50 ml. of dry benzene. The complex was stirred at room temperature for five hours and then was worked up in the usual manner. The neutral material (3.23 g.) was chromatographed on alumina, and by analogy with the first cyclization, the first fractions were assumed to be the desired isomer VIIIa. This semi-crystalline solid (1.71 g.) had λ_{max} 275 mμ, log ε 4.54 in the ultraviolet absorption spectrum and a strong hydroxyl peak in the infrared spectrum, indicating that the tertiary alcohol had not dehydrated under the conditions of the cyclization. Although not entirely satisfactory, the analysis was in agreement with this contention.

Anal. Calcd. for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Calcd. for $C_{25}H_{24}O$: C, 88.21; H, 7.11. Found: C, 84.93; H, 7.00.

The **2,4-dinitrophenylhydrazone** crystallized from ethanol–ethyl acetate as a reddish-orange powder, m.p. 159–170° (after three crystallizations) and the analysis indicated that it too was probably a mixture of dehydrated and non-dehydrated material.

Anal. Calcd. for $C_{31}H_{30}O_5N_4$: C, 69.10; H, 5.61. Calcd. for $C_{31}H_{28}O_4N_4$: C, 71.54; H, 5.42. Found: C, 70.26; H, 5.42.

Since the main contaminant in this ketone was presumably dehydrated material, no attempt was made to remove it because the final step in the synthesis was a dehydration and both components in the mixture would give 1,2,9-trimethylpicene.

1,2,9-Trimethylpicene (IIb).—A solution of 0.46 g. (0.012 mole) of lithium aluminum hydride in 25 ml. of ether was added to 1.36 g. (0.004 mole) of VIIIa dissolved in 25 ml. of ether. The solution was heated under reflux and worked up in the usual manner to give 1.20 g. (88%) of the diol VIIIb. This crude diol (1.00 g.) was intimately mixed with 0.15 g. of 10% palladium-on-charcoal catalyst and heated to 300° for two hours to effect the dehydration–dehydrogenation.

The melt was taken up in petroleum ether–benzene and chromatographed on alumina to give 0.40 g. of an oily forerun and 0.50 g. of a pale yellow solid. This was recrystallized from ethanol–benzene to give 1,2,9-trimethylpicene (IIb) as very pale yellow microcrystalline needles, m.p. 252–254°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.71; H, 6.29. Found: C, 93.52; H, 6.30.

The ultraviolet absorption spectrum (Fig. 1) showed the following maxima in chloroform (log ε in parentheses): 262 mμ (4.58); 281 (4.68); 293 (4.84); 326 (4.16); 342 (4.21); 365 (3.11) and 384 (3.04). The bathochromic shift expected of a trimethyl derivative is clearly shown in the spectrum.

The mixed m.p. with the 306° hydrocarbon[21] from the dehydrogenation of α-amyrin was 237–248°. The infrared and ultraviolet absorption spectra of the two compounds were also significantly different.

The mixed m.p. with authentic[22] 2,9-dimethylpicene (IIa, m.p. 303–304°) was 238–242°.

The **2,4,7-trinitrofluorenone** complex of IIb crystallized from acetic acid as a reddish-purple powder, m.p. 203–205°.

Anal. Calcd. for $C_{38}H_{25}N_3O_7$: C, 71.81; H, 3.97. Found: C, 71.95; H, 4.01.

ITHACA, NEW YORK

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[21] We have repeated this dehydrogenation[9] and full details will be reported later.

[22] We are grateful to Professor M. S. Newman for a sample of this material.