tallized from ethanol to give 0.8 g. of pale yellow needles, m.p. 117–118°.

Anal. Calcd. for $C_{17}H_{15}NO_4$: N, 4.71. Found: N, 4.58.

It is soluble in ethanol, acetic acid, ethyl acetate, and acetone. It gives a reddish brown color with an ethanolic ferric chloride. It is soluble in dilute alkali, but insoluble in dilute mineral acids.

6-Acetamino-flavone (III: R = Ph). 2-Hydroxy-5-acetamino-ω-benzoylacetophenone (0.5 g.) in a mixture of acetic acid (15 ml.) and concentrated hydrochloric acid (3 ml.) was heated at 118–120° for 0.5 hr. On diluting with ice cold water, a brown solid separated; it was collected, washed with dilute alkali (5%) and crystallized from ethanol to give yellowish brown needles, m.p. 174°; the mixed melting point with an authentic sample was undepressed.

The *diacetyl derivative* prepared by the acetic anhydride–pyridine method, crystallized from ethanol in form of brown granules, m.p. 256–258°, mixed melting point with an authentic sample remaining undepressed.

6-Aminoflavone (IV: R = Ph). 2-Hydroxy-5-acetamino-ω-benzoylacetophenone (0.5 g.) and concentrated hydriodic acid (10 ml.) were refluxed on an oil bath at 140° for 3 hr. The reaction mixture was poured into ice cold water containing sodium bisulfite. The clear solution on treatment with ammonia gave a pale brown solid; it was collected and washed with dilute alkali and crystallized from ethanol to give brown needles, m.p. 192°, mixed melting point with an authentic sample remaining undepressed.

The *diacetyl derivative*, prepared as before, crystallized from ethanol in form of brown granules, m.p. 256–258°; the mixed melting point with the sample obtained earlier was undepressed.

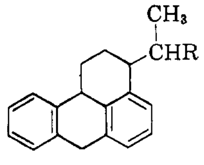
CHEMISTRY DEPARTMENT
M. R. SCIENCE INSTITUTE
GUJARAT COLLEGE AND ST. XAVIER'S COLLEGE
AHMEDABAD-6, INDIA

9,10-Dimethyl-3,4-benzpyrene[1,2]

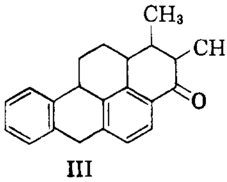
JULES L. ADELFANG[3] AND GUIDO H. DAUB

Received October 18, 1957

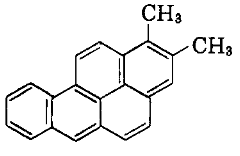
The synthesis of 9,10-dimethyl-3,4-benzpyrene (IV) has been accomplished *via* α-(1,2,3,11b-tetrahydro-7*H*-*meso*-benzanthrenyl-3)propionic acid (I), an intermediate available from previously reported research.[4] The Wilds modification of the Arndt-Eistert synthesis with diazoethane[5] converted α-(1,2,3,11b-tetrahydro-7*H*-*meso*-benzanthrenyl-3)propionyl chloride to α-methyl-β-(1,2,3,-11b-tetrahydro-7*H*-*meso*-benzanthrenyl-3)butyric acid (II) in 80% yield. Cyclization of II with anhydrous hydrogen fluoride produced 8-keto-9,10-dimethyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (III). Reduction of the ketone III with aluminum isopropoxide in toluene gave a carbinol which was directly dehydrated and dehydrogenated over palladium-charcoal to provide 9,10-dimethyl-3,4-benzpyrene (IV) in 20% yield from III.



I, R = COOH
II, R = CH(CH₃)COOH



III



IV

The acid II, the ketone III, and its *p*-nitrophenylhydrazone were isolated as oily mixtures of diastereoisomers which could not be crystallized. Precedence for this reaction sequence was established by the synthesis of 9-methyl-3,4-benzpyrene described previously.[6]

The hydrocarbon IV formed an unstable purple picrate derivative and gave an ultraviolet absorption spectrum characteristic of 3,4-benzpyrene. The hydrocarbon has been submitted to Northwestern University Medical School for carcinogenic testing.

EXPERIMENTAL[7]

8-Keto-9,10-dimethyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (III). This ketone (3.5 g.) was obtained as a viscous yellow oily mixture of isomers from 5.8 g. (0.020 mole) of α-(1,2,3,11b-tetrahydro-7*H*-*meso*-benzanthrenyl-3)propionic acid (I) via the acid II using previously published procedures.[6]

9,10-Dimethyl-3,4-benzpyrene (IV). Reduction of 3.15 g. (0.0104 mole) of the oily ketone III was carried out with 5.0 g. (0.0245 mole) of aluminum isopropoxide and 50 ml. of C.P. toluene. After 50 hr. of intermittent distillation using a Hahn condenser, the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent. The reaction mixture was worked up in the usual manner[6] and the crude alcohol thus obtained was directly dehydrated and dehydrogenated at 240–345° over 0.5 g. of 10% palladium-charcoal for 1.5 hr. After cooling, the hard cake was dissolved in benzene and the solution was filtered. This solution was chromatographed over alumina to give an initial fraction containing an oil which did not give a darkly colored solution with picric acid. Further elution of the column with benzene yielded fractions containing an orange solid which was decolorized with Norit and crystallized twice from ethyl acetate producing 0.57 g. (11% over-all yield from I) of 9,10-dimethyl-3,4-benzpyrene (IV) as small yellow needles, m.p. 174–175.5°.

---

[1] From the dissertation presented by Jules L. Adelfang to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This investigation was supported in part by a research grant (C-1595) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

[3] Graduate Research Assistant, February 1956 to August 1957.

[4] J. L. Adelfang and G. H. Daub, *J. Am. Chem. Soc.*, **77**, 3297 (1955).

[5] A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).

[6] J. L. Adelfang and G. H. Daub, *J. Am. Chem. Soc.*, **79**, 1751 (1957).

[7] All melting points are uncorrected.

An analytical sample, m.p. 174.5–175.5°, was prepared by crystallization from ethyl acetate.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.45; H, 5.64.

The hydrocarbon IV gave an unstable, purple picrate, m.p. 182–184°.

Ultraviolet absorption spectrum. The ultraviolet absorption spectrum of 9,10-dimethyl-3,4-benzpyrene in 95% ethanol was measured with a Model DU Beckman spectrophotometer. Maxima and (log ϵ) values are: 260 mμ (4.59), 268 mμ (4.70), 288 mμ (4.63), 300 mμ (4.70), 372 mμ (4.40), and 392 mμ (4.48).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, N. M.

Vinyl-Alkali Metal Compounds[1]

R. G. ANDERSON, M. B. SILVERMAN AND D. M. RITTER

Received October 11, 1957

Reaction of vinyl chloride with alkali metals in tetrahydrofuran has yielded the vinyl-alkali metal compounds, as might be expected from recent success in making the vinyl-Grignard reagent in that solvent.[2] The simplicity of the procedure makes it preferable to the exchange reaction through which vinylsodium was first made.[3] Propenyllithium and several other alkenyllithium compounds have been made directly from the bromides in diethyl ether or petroleum ether,[4] but all attempts to similarly prepare vinyl compounds have failed.

The example given below concerns vinylpotassium prepared from liquid 90% potassium-sodium alloy,[5] but small-scale qualitative observations have shown that potassium, sodium, and lithium will each react.

Though the Grignard reagent is as easily made, vinylsodium or vinylpotassium may offer advantage on those occasions where the solid organometallic compound is needed, since they have little solubility and can be made solvent-free without decomposition by removal of solvent under reduced pressure. This operation leads to decomposition of the vinyl Grignard reagent.[2]

As an example the reaction of vinyl Grignard solution with diethyl bromoborane gave only triethylborane, no trivinylborane, and evidence of polymers was seen. In contrast reaction of solid vinylpotassium gave some polymer, but trivinylborane and a mixture of ethylvinylboranes were obtained also.

The solvent should be removed from vinylpotassium (and presumably vinylsodium) as soon as possible because the solid reacts with the tetrahydrofuran. Were the solvent removed at once, the yield would probably be comparable with the best obtained by the exchange method.

EXPERIMENTAL

The vinyl chloride solution (95 g. in 405 g. tetrahydrofuran) was prepared by passing the gas through sodium hydroxide solution and a drying train into the solvent cooled to 0°. This was added slowly to 50 g. 90% potassium-sodium alloy covered with 350 g. tetrahydrofuran cooled to 0° C. in a 3-neck flask fitted with a Hershberg stirrer. A blue precipitate formed which reached a viscous gel-like consistency as the reaction proceeded.

A day after completion the preparation was assayed using a 3/808 g. aliquot from the well stirred slurry. Treatment with isopropyl alcohol in the vacuum apparatus gave 1.8 mmoles of ethylene with the correct vapor pressure, corresponding to a total vinylpotassium content of 485 mmoles or a yield of 32%. Five days later the solvent was removed under reduced pressure, and a similar assay of a 1.81/90 g. aliquot of dry powder gave a yield of 7.4%. Apparently reaction with the solvent had occurred.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASH.

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1541. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] H. Normant, *Compt. rend.*, **239**, 1510 (1954). Ramsden *et al.* Abstracts, 130th Meeting, ACS, September 1956, p. 80-O.

[3] A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

[4] E. A. Braude, J. A. Coles, and C. J. Timmons, *J. Chem. Soc.*, 2000, 2007, 2012, 2014 (1950).

[5] M. Sittig, Sodium, *ACS Monograph No. 133*, Reinhold, N. Y., 1956, p. 61.

Reaction of Isocyanates with Tris(hydroxymethyl)aminomethane

ROY G. NEVILLE[1]

Received October 16, 1957

During the course of an investigation of certain urea derivatives it was necessary to prepare a series of 1-substituted-3-tris(hydroxymethyl)methylureas. Pierce *et al.*[2] described aromatic compounds of this type in which the substituents were phenyl, *o*- and *p*-tolyl, and 1- and 2-naphthyl. These compounds were prepared by reaction of equimolar quantities of isocyanate with tris(hydroxymethyl)aminomethane (I) in chloroform solution, but this method was disadvantageous in that I was insoluble in chloroform.

In addition to the phenyl and 1-naphthyl derivatives, made by the method of Pierce, a series of new derivatives has been prepared. It was found

---

[1] For reprints: 3267 57th Avenue S. W., Seattle 16, Wash.

[2] J. S. Pierce, C. D. Lunsford, R. W. Raiford, J. L. Rush, and D. W. Riley, *J. Am. Chem. Soc.*, **73**, 2595 (1951).