plex melted near 190° then solidified and remelted at 201–202°.

Anal. Calcd. for $C_{30}H_{19}O_{11}N_5{\cdot}CH_3CO_2H$: C, 56.1; H, 3.4. Found: C, 56.2; H, 3.6.

(c) **1-Naphthyl (2-Butyl) Ether.**—A solution containing 0.26 g. of 1-naphthyl 2-butyl ether,[24] m.p. 29.0–31.5°, and 0.13 g. of (±)-III in 3 ml. of acetic acid deposited a gummy red solid. This was triturated with 2 ml. of Skellysolve B and washed with two small portions of Skellysolve B and of Skellysolve F. After drying at room temperature *in vacuo* over phosphorus pentoxide the analytical sample melted at 155–158°.

Anal. Calcd. for $C_{30}H_{25}O_{12}N_5$: C, 55.6; H, 3.9; N, 10.8. Found: C, 55.6; H, 4.1; N, 11.2.

(d) **Methyl α-(1-Anthryl)-propionate.**—Prepared from 0.25 g. of ester and 0.25 g. of (±)-III in 3 ml. of acetic acid this complex weighed 0.34 g. (87%). Recrystallization from acetic acid afforded the complex as dark brown leaflets with metallic luster, m.p. 191.0–192.5°.

Anal. Calcd. for $C_{34}H_{25}O_{13}N_5$: C, 57.4; H, 3.5; N, 9.8. Found: C, 57.3; H, 3.7; N, 9.7.

(e) **Miscellaneous.**—Complexes with benzo[c]phenanthrene, red, m.p. 215–217°, anthracene, green black, m.p. 258°, and acenaphthene, red, m.p. 190–195°, were also formed. These complexes were not analyzed or otherwise examined. No crystalline complex of 1,12-dimethylbenzo[c]phenanthrene[25] could be obtained although evidence of complex formation was provided by the red color of solutions of the components in various solvents.

Resolution of 1-Naphthyl 2-Butyl Ether.—A hot solution of 0.589 g. of ether and 0.994 g. of (−)-III in 1 ml. of acetic acid on cooling solidified to a pasty mass. After trituration with 4 ml. of Skellysolve B the purplish complex was collected and washed with 4 ml. of Skellysolve B. After drying *in vacuo* 0.81 g. (94%) of complex, m.p. 137–141°, was obtained. The comparable complex formed from (±)-III (see above) melted at 155–158°. The 1-naphthyl 2-butyl ether from the complex and from the filtrate was recovered after removing the (−)-III by washing with bicarbonate solution. The crude ether obtained from the solid complex was obtained in two fractions, 0.158 g., $[\alpha]^{31}_{D}$ −7.8 ± 0.2° (*c* 6.4, ethyl acetate) and 0.0508 g., $[\alpha]^{29}_{D}$ −7.4 ± 0.5° (*c* 2.03, ethyl acetate), by evaporative distillation onto a cold finger at low pressure. There was a negligible residue from this vaporization. The infrared spectra of these fractions were identical to that of the racemic ether. The ether recovered from the filtrate was purified in the same way and afforded a product, $[\alpha]^{32}_{D}$ +6.4 ± 0.09° (*c* 11, ethyl acetate). For this determination the entire distillate was used. From the bicarbonate extracts the (−)-III was recovered in 65% yield, $[\alpha]^{26}_{D}$ −92.2 ± 0.3°.

Resolution of Methyl α-(1-Anthryl)-propionate.—A hot acetic acid solution of 0.330 g. of (+)-III, $[\alpha]^{23}_{D}$ +84.1° (or 93° if allowance for solvation with acetic acid is made, see above) and 0.368 g. of ester,[26] m.p. 91–92°, deposited 0.521 g. of complex, m.p. 196–200°. The comparable complex from ester and (±)-III (see above) melted at 191–192.5°. The ester, recovered from the complex after washing out III with bicarbonate solution, was crystallized from 2 ml. of Skellysolve B to yield 0.126 g., $[\alpha]^{29}_{D}$ +36.8 ± 0.1° (*c* 4.3, dioxane). The residue in the filtrate from this ester amounted to 0.0409 g., m.p. 88–91°, $[\alpha]^{24}_{D}$ +101 ± 0.8° (*c* 1.32, dioxane). The ester, recovered from the filtrate from the original solid complex, afforded 0.150 g. of tan solid, m.p. 85–89°, $[\alpha]^{27}_{D}$ −66.0 ± 0.1° (*c* 5, dioxane). On recrystallization of this solid from Skellysolve F containing a little chloroform there was obtained 0.0546 g. of tan solid, m.p. 89–90°, $[\alpha]^{28}_{D}$ −28.0, and from the filtrate, 0.0274 g. of ester, m.p. 88.5–91.0°, $[\alpha]^{19.5}_{D}$ −80.4 ± 0.8°. It is thus apparent that racemic ester is less soluble than the (+)- or (−)-forms.

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[24] V. H. Dermer and O. C. Dermer, *J. Org. Chem.*, **3**, 289 (1938), report the m.p. as >10°. The picrate we prepared from our ether, m.p. 29–31.5°, melted at 100.0–101.2° in agreement with the reported m.p. of 100.5–101.0°.

[25] M. S. Newman and M. Wolf, THIS JOURNAL, **74**, 3225 (1952).

[26] We are indebted to Mrs. T. Miwa for the preparation of this ester.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

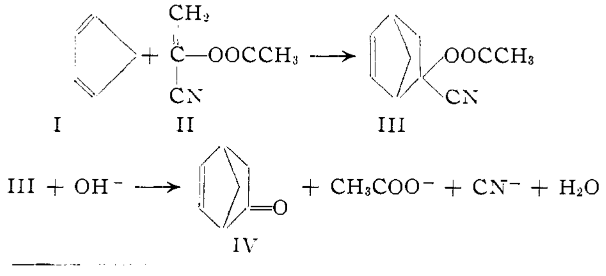
Dehydronorcamphor from α-Acetoxyacrylonitrile

BY PAUL D. BARTLETT AND BRYCE E. TATE

RECEIVED DECEMBER 15, 1955

The addition of α-acetoxyacrylonitrile to cyclopentadiene, followed by alkaline hydrolysis of the adduct, leads to dehydronorcamphor in a two-step preparation with 51% over-all yield. Previous reports on derivatives of this ketone are supplemented by determination of the ultraviolet absorption spectrum of the ketone itself in ethanol and in isoöctane. Compared to norcamphor the absorption maximum is shifted 13.5 mμ to longer wave lengths, with a tenfold increase in intensity.

Dehydronorcamphor (IV) has been prepared previously by the oxidation of dehydronorborneol.[1–3] It does not result from the direct addition of ketene to cyclopentadiene. However, α-acetoxyacrylonitrile (II), which should be an excellent dienophile, is readily obtained as the principal product of ketene with hydrogen cyanide under appropriate conditions.[4–6] Under other conditions,[7] the formation of this product can be very largely suppressed. In view of the availability of α-acetoxyacrylonitrile and its increasing industrial interest,[8,9] we have investigated its use as a dienophile. It appears that the use of this compound represents a superior way of introducing the elements of ketene into a diene synthesis.



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[1] K. Alder and H. F. Rickert, *Ann.*, **543**, 19 (1940).

[2] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[3] C. J. Norton, Thesis, Harvard University, 1955.

[4] S. Deakin and N. T. M. Wilsmore, *J. Chem. Soc.*, **97**, 1971 (1910).

[5] G. C. Roy, U. S. Patent 2,396,201 (1946).

[6] H. J. Hagemeyer, Jr., *Ind. Eng. Chem.*, **41**, 765 (1949).

[7] A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, THIS JOURNAL, **72**, 1305 (1950).

[8] J. B. Dickey, U. S. Patent 2,472,811 (1949); U. S. Patent 2,611,675 (1952).

[9] H. J. Hagemeyer, Jr., U. S. Patent 2,652,390 (1953).

Experimental

2-Cyano-2-acetoxybicyclo[2,2,1]heptene-5 (III) (Acetate of Dehydronorcamphor Cyanohydrin).—A mixture of 13.0 g. (0.197 mole) of cyclopentadiene (I) and 17.0 g. (0.153 mole) of α-acetoxyacrylonitrile (II) (kindly made available by the B. F. Goodrich Co.) was heated at 100° for 3 hr. The mixture stood overnight at room temperature and was then distilled. There was an 8.5-g. forerun up to 132° (18 mm.) consisting mostly of dicyclopentadiene. The adduct, boiling at 132–137° (18 mm.), was obtained in a yield of 16.8 g. (62%). Redistillation yielded material of b.p. 84–85° (1.5 mm.), $n^{25}\text{D}$ 1.4762. The infrared spectrum in chloroform showed a cyanide band at 6.41 μ and a carbonyl band at 5.76 μ.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.76; H, 6.26; N, 7.90. Found: C, 67.66; H, 6.16; N, 8.30.

Dehydronorcamphor (IV).—Seven grams of the cyanhydrin acetate III was added to 20 g. of sodium hydroxide in 200 ml. of water containing a few granules of detergent. The mixture was heated under reflux for 2 hr. and then steam distilled. The distillate was saturated with potassium carbonate and extracted with one 25-ml. portion and two 15-ml. portions of ether. After drying and distillation of the ether extract, dehydronorcamphor, b.p. 59.0–59.3° (18 mm.), $n^{25}\text{D}$ 1.4839, was obtained in a yield of 3.51 g. (82%). This material melted at 22–23°. Alder and Rickert reported a melting point of 0–2° for material obtained by oxidation of the alcohol.

Anal. Calcd. for C_7H_8O: C, 77.75; H, 7.45. Found: C, 77.36; H, 7.42.

The semicarbazone melted at 205.8–206.8° after recrystallization from methanol (Alder and Rickert report 207–208°). The infrared spectrum in carbon disulfide showed a double carbonyl peak at 5.76 and 5.80 μ.

Ultraviolet Absorption Spectrum.—The spectrum of dehydronorcamphor from 230 to 330 mμ was determined on a Cary recording spectrometer. The spectrum in ethanol shows a maximum at 300.5 mμ (ε 292) and a minimum at 247 mμ (ε 6); in 2,2,4-trimethylpentane the maximum is at 308 mμ (ε 266), flanked by two subsidiary peaks at 297 and 320 mμ, and the minimum is at 247 mμ (ε 6). The presence of the double bond thus results in a shift of the absorption maximum to longer wave lengths by 13.5 mμ and a tenfold increase in the intensity, as compared to norcamphor.[3] This effect is reminiscent of those noted by Braude, Jones, Sondheimer and Toogood.[10] Here, however, any explanation involving hyperconjugation is rendered unlikely by the presence of a bridgehead between the functional groups which are interacting. It is more probable that a direct covalent or electrostatic interaction occurs through space between the 5,6-double bond and the carbonyl group, as suggested to explain the mutual influence of the benzene rings in triptycene upon one another.[11] These spectral effects are probably related to the activation toward solvolysis of the corresponding tosylate by the 5,6-double bond.

Infrared Effects.—In dehydronorcamphor a carbonyl doublet at 5.76 and 5.80 μ takes the place of the single peak at 5.72 observed in 2-norcamphor. Curiously enough, the saturated isomer, 7-norcamphor, has a carbonyl doublet at 5.62 and 5.70 which is replaced by a single peak at 5.62 in the related unsaturated compound, 1,2-dehydro-7-norcamphor.[12]

Acknowledgment.—We are indebted to the B. F. Goodrich Co. for support of this research.

[10] E. A. Braude, E. R. H. Jones, F. Sondheimer and J. T. Toogood, *J. Chem. Soc.*, 607 (1949).

[11] P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1007 (1950).

[12] R. B. Woodward and C. J. Norton, *ibid.*, **78**, in press (1956); S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4138 (1955).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

An Unusual Cyclization in the Naphthalene Series. Synthesis of 1-Ethylanthracene and of 4-Ethylphenanthrene

BY HILLEL BENDAS[1] AND CARL DJERASSI

RECEIVED NOVEMBER 9, 1955

Polyphosphoric acid cyclization of 6-(2-naphthyl)-3-hexanone followed by dehydrogenation yielded 1-ethylanthracene rather than 4-ethylphenanthrene. The latter could be obtained from 4-phenanthrylacetic acid *via* the alcohol, mesylate and iodide.

At an early stage of our examination[2] of the dehydrogenation products of the diterpene cafestol, it was desirable to have available for comparison purposes all of the possible ethylphenanthrenes and the synthesis of the missing isomer—4-ethylphenanthrene—was consequently undertaken.

The most obvious approach involved reaction of 4-keto-1,2,3,4-tetrahydrophenanthrene (I) with ethylmagnesium iodide followed by dehydration and dehydrogenation as has been carried out successfully with the corresponding methyl derivative.[3,4] In the present instance, the Grignard reaction yielded a mixture, which could not be resolved readily, and dehydrogenation afforded chiefly phenanthrene and, in one instance, pyrene (II).[5] While the desired 4-ethylphenanthrene (XI)[5a] was probably formed in this reaction sequence, the difficulty in isolation prompted us to investigate an alternate synthesis.

It was felt that introduction of the ethyl group prior to dehydrogenation would be preferable and consequently γ-2-naphthylbutyric acid (III)[3] was transformed *via* its acid chloride IV to 6-(2-naphthyl)-3-hexanone (V) and cyclized with polyphosphoric acid.[6] The crude cyclization product was directly dehydrogenated with palladized charcoal and the hydrocarbon was characterized by means of the crystalline complexes with picric acid, trinitrobenzene and 2,4,7-trinitrofluorenone[7] as well

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[1] General Foods Corporation Postdoctorate Fellow, 1954–1955.

[2] C. Djerassi, H. Bendas and P. Sengupta, *J. Org. Chem.*, **20**, 1046 (1955).

[3] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

[4] W. E. Bachmann and R. O. Edgerton, THIS JOURNAL, **62**, 2219 (1940).

[5] Such cyclodehydrogenations (especially with sulfur) have already been observed by G. Genie, *Ind. Chim. Belg.*, **16**, 576 (1951) (see also D. N. Chatterjee, THIS JOURNAL, **77**, 5131 (1955)). Genie apparently has synthesized 4-ethylphenanthrene without, however, indicating the method or the constants of the compound; his article does not appear to be abstracted in *C. A.*

[5a] NOTE ADDED IN PROOF.—Prof. R. H. Martin (University of Brussels) has informed us that this hydrocarbon is described in the Ph.D. thesis of G. Genie (see ref. 5).

[6] *Cf.* J. Koo, THIS JOURNAL, **75**, 1891 (1953), and F. Uhlig, *Angew. Chem.*, **66**, 435 (1954).

[7] *Cf.* M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946).