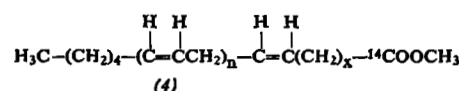
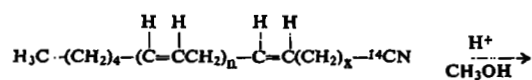
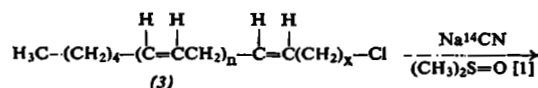
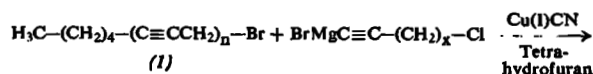


and 1-<sup>14</sup>C-all-*cis*-eicosa-5,8,11,14-tetraenoic acid (arachidonic acid) were synthesized according to the following reaction scheme:



The nitrile synthesis with Na<sup>14</sup>CN and the subsequent acid-catalysed hydrolysis of the nitrile each gave yields of over 90 %. The purity of the intermediates and of the methyl esters of the polyenoic acids (Table 1) was ascertained by gas chromatography, hydrogen number, ultraviolet and infrared spectroscopy, and isomerisation with alkali.

Table 1. Physical properties of the intermediates and of the methyl esters of polyenoic acids synthesized.



$n = 1$ ; b.p. 90–91 °C/12 mm;  $n_D^{20} = 1.4862$   
 $n = 2$ ; b.p. 100–102 °C/0.1 mm;  $n_D^{20} = 1.5115$   
 $n = 3$ ; b.p. 140 °C/0.1 mm;  $n_D^{20} = 1.5252$

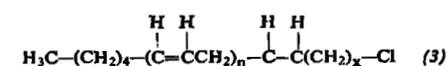


$x = 7$ ; b.p. 94–95 °C/13 mm;  $n_D^{20} = 1.4549$   
 $x = 4$ ; b.p. 144 °C;  $n_D^{20} = 1.4480$   
 $x = 3$ ; b.p. 116 °C;  $n_D^{20} = 1.4448$



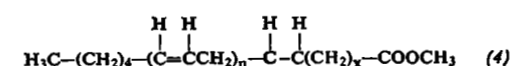
$n = 1$ ;  $x = 7$ ;  $n_D^{20} = 1.4804$  [\*]  
 $n = 2$ ;  $x = 4$ ;  $n_D^{20} = 1.4985$  [\*]  
 $n = 3$ ;  $x = 3$ ; m.p. 18–20 °C; colorless needles.

[\*] Purified by molecular distillation [2] at 80–130 °C (bath temperature)/10<sup>−4</sup> mm.



$n = 1$ ;  $x = 7$ ;  $n_D^{20} = 1.4702$  [\*\*]  
 $n = 2$ ;  $x = 4$ ;  $n_D^{20} = 1.4778$  [\*\*]  
 $n = 3$ ;  $x = 3$ ;  $n_D^{20} = 1.4870$  [\*\*]

[\*\*] Purified by molecular distillation at 70–100 °C (bath temperature)/10<sup>−4</sup> mm or by preparative gas chromatography.



$n = 1$ ;  $x = 7$ ;  $n_D^{20} = 1.4620$ ; linoleic acid [\*]  
 $n = 2$ ;  $x = 4$ ;  $n_D^{20} = 1.4672$ ; γ-linolenic acid [\*]  
 $n = 3$ ;  $x = 3$ ;  $n_D^{20} = 1.4797$ ; arachidonic acid [\*]

[\*] Purified by molecular distillation at 100–130 °C (bath temperature)/10<sup>−4</sup> mm or by preparative gas chromatography.

Received, October 11th, 1962 [Z 369/252 1E]

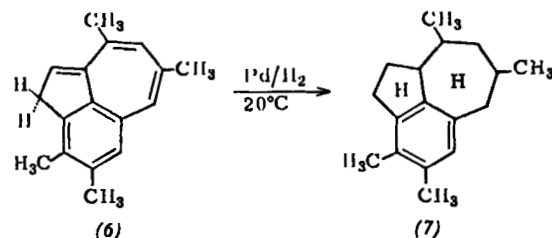
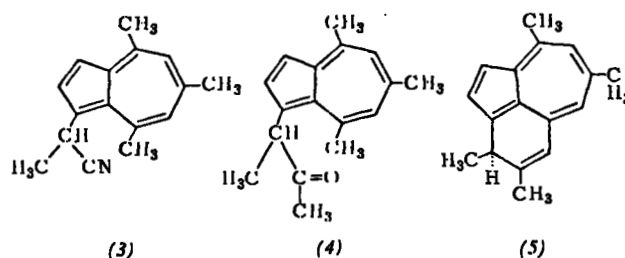
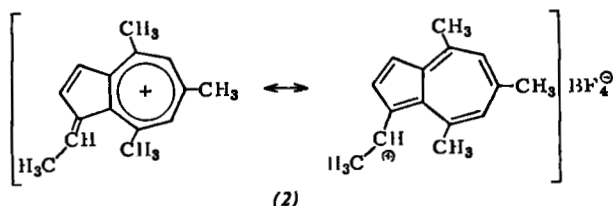
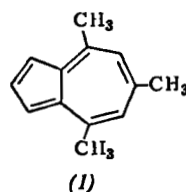
- [1] R. A. Smiley and C. Arnold, J. org. Chemistry 25, 257 (1960).  
 [2] E. Klenk and H. Mohrhauser, Hoppe-Seyler's Z. physiol. Chem. 320, 218 (1960).

## Cycloheptatrieno-Indene

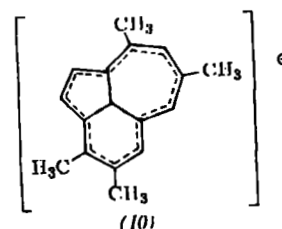
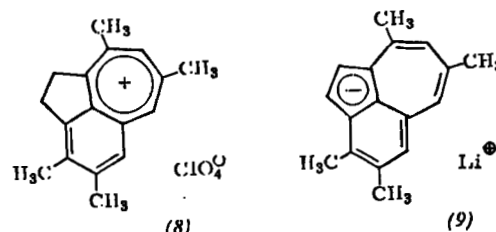
By Prof. Dr. K. Hafner and cand. chem. H. Schaum

Institut für Organische Chemie  
der Universität München (Germany)

Starting from 4,6,8-trimethylazulene (1) [1], we were able to prepare a non-benzenoid isomer of perinaphthalene, viz. cycloheptatrieno-indene or 2H-benz[c,d]azulene (6) [2]. Condensation of (1) with acetaldehyde in the presence of HBF<sub>4</sub> in ether affords (2) [3], which with sodium cyanide yields (3), m.p. 111–112 °C.



This was converted with methylmagnesium bromide into the ketone (4), m.p. 84–85 °C. With sodium *N*-methylaniline [4], (4) reacts immediately to give (6). The intermediate (5), which without doubt is formed first, changes with loss of the



azulenoid system resonance into the energetically more favorable benzenoid system (6). Compound (6) crystallizes in golden-yellow needles of m.p. 116 to 117°C; its ultraviolet spectrum has a strong fine structure:  $\lambda_{\max} = 231 \text{ m}\mu$  ( $\log \epsilon = 4.55$ ); 235 (4.55); 280 (3.91); 291 (3.80); 312 (3.71); 325 (3.69); 340 (3.59); and 406 (3.20).

Compound (6) absorbs 3 moles of  $\text{H}_2$  to form the indane derivative (7). With trityl perchlorate, (6) gives the stable orange carbonium salt (8), m.p. 236 to 238°C with decomposition. With methyl-lithium, (6) forms a green compound (9), which is sensitive to hydrolysis. Compound (9) is an example of a cyclic conjugated 14  $\pi$ -electron system with the general structure (10).

Received, November 19th, 1962 [Z 392/242 IE]

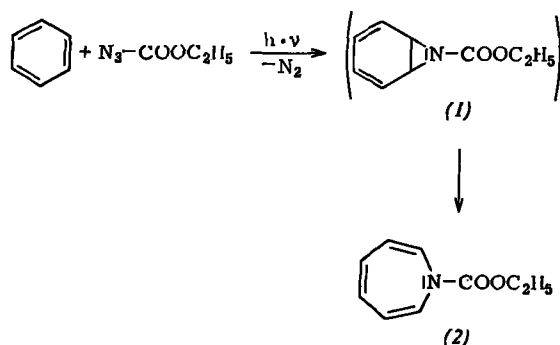
- [1] K. Hafner and H. Kaiser, *Liebigs Ann. Chem.* 618, 140 (1958).  
 [2] A. M. Patterson, L. T. Capell, and D. F. Walker: *The Ring Index*, 2nd Edition, American Chemical Society, Washington, D.C., 1960, p. 409.  
 [3] K. Hafner, H. Pelster, and J. Schneider, *Liebigs Ann. Chem.* 650, 62 (1961).  
 [4] K. Hafner et al., *Liebigs Ann. Chem.* 650, 80 (1961); 624, 37 (1959).

## N-Ethoxycarbonylazepine

By Prof. Dr. K. Hafner and Dr. C. König

Institut für Organische Chemie  
 der Universität München (Germany)

By irradiating a solution of ethyl azidocarbonate in benzene with ultraviolet light, we obtained *N*-ethoxycarbonylazepine (2) in ca. 70 % yield as a stable yellow oil, b.p. 130°C/20 mm ( $\lambda_{\max} = 208 \text{ m}\mu$  ( $\log \epsilon = 4.44$ ) and  $\lambda_{\max} = 330 \text{ m}\mu$  ( $\log \epsilon = 2.72$ ) in *n*-hexane).



This new ring expansion reaction resembles the photolytic reaction of benzene with diazomethane to yield cycloheptatriene. Here, however, instead of the methylene group, the ethoxycarbonylazepine group [1] reacts with the benzene, probably to give first the azanorcaradiene derivative (1), which rearranges at once to its isomeric azepine (2).

Compound (2) is the first monocyclic azepine derivative to have been prepared [2]. Catalytic hydrogenation of (2) with  $\text{Pd}/\text{H}_2$  at 20°C affords *N*-ethoxycarbonyl hexamethylene imine (b.p. 118–120°C/20 mm;  $n_D^{25} = 1.4635$ ), which we also prepared from hexamethylene imine [3] and ethyl chloroformate. The two products proved to be identical, judging from their infrared and nuclear magnetic resonance spectra. The NMR-spectrum of (2) shows a multiplet for the 6 ring protons at 4–4.7  $\tau$ , in addition to the characteristic signals for the protons of the ethyl group (quartet at 5.8  $\tau$ , triplet at 8.7  $\tau$ ).

The stability of the 8  $\pi$ -electron system in (2) appears to be due at least in part to the claim on the free electron pair on the nitrogen made by mesomerism of the urethane system. In the presence of protic acids, (2) resinifies rapidly at 20°C.

Attempts to extend this ring expansion reaction with azides to other aromatic systems are in progress.

Received, November 20th, 1962 [Z 396/243 IE]

- [1] W. Lwowski and Th. W. Mattingly, *Tetrahedron Letters* 1962, 277.  
 [2] K. Dimroth and H. Freyschlag, *Chem. Ber.* 89, 2602 (1956); 90, 1628 (1957); R. Huisgen and M. Appel, *ibid.* 91, 12 (1958); R. Huisgen et al., *ibid.* 93, 392 (1960); *Liebigs Ann. Chem.* 630, 128 (1960), etc.  
 [3] L. Ruzicka et al., *Helv. chim. Acta* 32, 544 (1949).

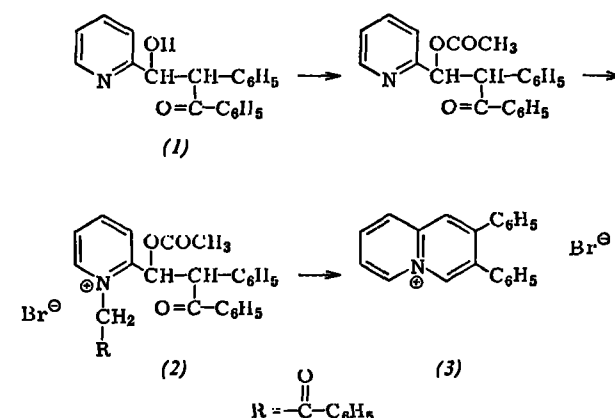
## Synthesis of Dehydroquinolizinium Systems

By Prof. Dr. O. Westphal and Dipl.-Chem. G. Feix

Chemisches Institut der Universität Freiburg/Breisgau  
 (Germany)

It has been shown [1] that 1,2-diketones can be condensed readily with *N*-methylene- $\alpha$ -picolinium salts to give dehydroquinolizinium derivatives. Here the first component supplies the two ketonic groups necessary for cyclization, and the second supplies the two activated methylene groups. We have now gone over to using two reactants, each of which contains both a ketonic group and an activated methylene group, so that monoketonic compounds derived from *N*-methylene-pyridinium-2-aldehyde can be used for the synthesis of dehydroquinolizinium systems.

The 1,3-ketol (1) formed from pyridine-2-aldehyde and deoxybenzoin was esterified and converted into the quaternary ammonium salt (2) using bromoacetophenone; the salt (2) was then cyclized using dibutylamine in boiling acetone to give 2,3-diphenyl-dehydroquinolizinium bromide (3). In this way, as also in the synthesis mentioned above [1], the activating residue R is split off as benzoic acid. The yields of the individual reaction stages are between 65 and 80 %.



Judging from its melting point (284–285°C), mixed melting-point, and infrared spectrum, compound (3) is identical with the compound obtained from benzil and *N*-carbethoxy- $\alpha$ -picolinium bromide [2].

Received, November 19th, 1962 [Z 398/222 IE]

- [1] O. Westphal, K. Jann, and W. Heffe, *Arch. Pharmac.* 294, 37 (1961).  
 [2] K. Jann, Ph. D. thesis, Universität Freiburg/Breisgau, 1958.

## Bis-Silylated Carboxamides

By Prof. Dr. L. Birkofer, Dr. A. Ritter  
 and Dipl.-Chem. W. Giessler [1]

Institut für Organische Chemie  
 der Universität Köln (Germany)

Silylation of 1 mole of acetamide with 1 mole of trimethylchlorosilane in the presence of triethylamine gives *N*-trimethylsilylacetamide [2]. On the other hand, reaction of a