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At the meeting of the Honorary Editorial Advisory Board in Paris, July 1957, *it was decided that the Journal should publish occasionally a résumé of the Life and Work of deceased eminent Organic Chemists.*

I. N. NAZAROV 1906–1957

INTRODUCTION*

I. N. NAZAROV was born of peasant stock in the village of Koshelevo in the heart of the country of the middle Volga region. He received his early education at a village school in which he subsequently became a teacher at the age of 17. He was one of the workers and peasants for whom the Soviet government opened the doors of the Universities, and in 1927 he became a student of the Moscow Agricultural Academy named after Timiryazev. This was one of the main seats of chemistry in Russia and associated with the names Kablukov, Pryanishnikov, Williams and Demyanov which inspired young Nazarov.

After graduating from the Academy he decided to devote himself to Organic Chemistry and began his graduate studentship under A. E. Favorsky, at Leningrad University, who suggested to Nazarov that he should study metal ketyls. Favorsky soon recognised the ability of his student. In 1934 the Academy of Sciences was transferred to Moscow, and here Nazarov worked in the newly founded Institute of Organic Chemistry, becoming head of the Vinyl-acetylene Research Laboratory in 1940. In this laboratory—later named the Laboratory of Fine Organic Chemicals—Nazarov worked until the end of his days, and under his leadership gradually developed a team of 60 workers. In 1949 he was elected to the chair of Organic Chemistry of the Moscow Institute of Fine Chemical Technology. Few were better able to set forth material in a systematic and logical fashion and as he himself put it "to make one feel the very nature of matter."

Nazarov received many academic distinctions. In 1940 he was elected corresponding member of the Academy of Sciences of the U.S.S.R. and member of the Academy of Sciences in 1953. He was awarded the Mendeleyev Prize and two Stalin prizes, and was a member of the German Academy of Naturalists (Leopoldina) in Halle, and a corresponding member of the Berlin Academy of Sciences.

He died suddenly on 30th July 1957 in France, after the Sixteenth Congress of Pure and Applied Chemistry in Paris, at which he read four papers. He is survived by his wife and three daughters.

SCIENTIFIC WORK

In his first papers produced in Favorsky's laboratory, Nazarov made a study of the action of sodium on aliphatic and aliphatic–aromatic ketones.

It was established that the stability of metal ketyls of the aliphatic–aromatic series increases with branching of the alkyl substituent in the series $(CH_3,\ C_2H_5,\ n\text{-}C_3H_7) < (CH_3)_2CH < (C_2H_5)_2CH$, $(CH_3)_3CH < (C_2H_5)(CH_3)_2C < CH(C_2H_5)_2 < (C_2H_5)_3C$.

Closely related to these studies were the investigations of dissociation and isomerisation of olefines of highly branched structure, published by Nazarov in 1933–1936.

A very important stage in Nazarov's scientific work was connected with the study of the derivatives of vinyl acetylene. The simple method which he devised for the condensation of vinylacetylene with ketones in the presence of potassium hydroxide made accessible various vinylethinylcarbinols, the properties of which were subjected to a comprehensive study.

$$CH_2{=}CHC{\equiv}CH + RR'CO \xrightarrow{KOH} CH_2{=}CHC{\equiv}C{-}\underset{\displaystyle R'}{\overset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}{-}OH$$

The principal results of these studies are given in Fig. 1.

* Condensed from the original by L. D. Bergelson.

These investigations, which were stopped by the Second World War when Nazarov and his laboratory were engaged in urgent assignments for the front and the war industry, were resumed with renewed energy after the war.

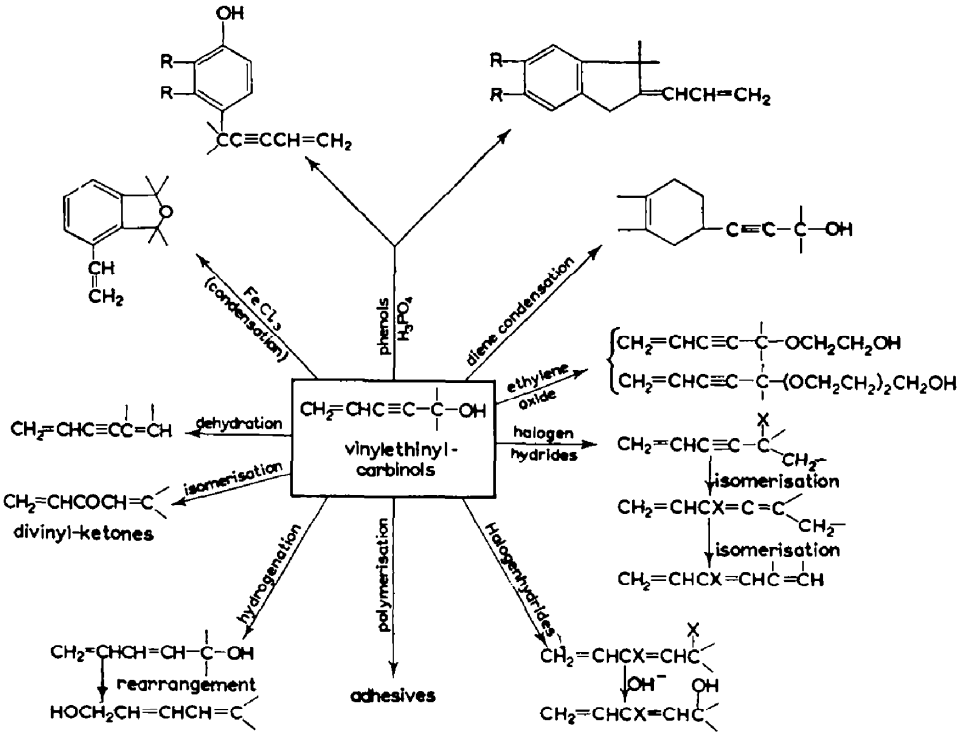
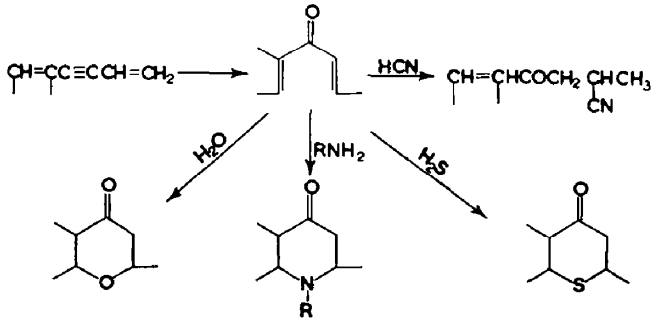


FIG. 1. Reactions of the vinylethinylcarbinols.

Of special interest among the transformations of vinylethinylcarbinols was their isomerisation to reactive divinylketones. A study of the numerous reactions of divinylketones led to a whole range of previously inaccessible compounds (see Fig. 2).

Similar reactions were also carried out with another class of divinylketones synthesised by Nazarov by means of hydration of divinylacetylenes:



Of interest, both theoretically and practically, were the piperidones obtained by reaction of ammonia and amines with divinylketones. The esters of 4-phenyl-piperid-4-ol, synthesised from

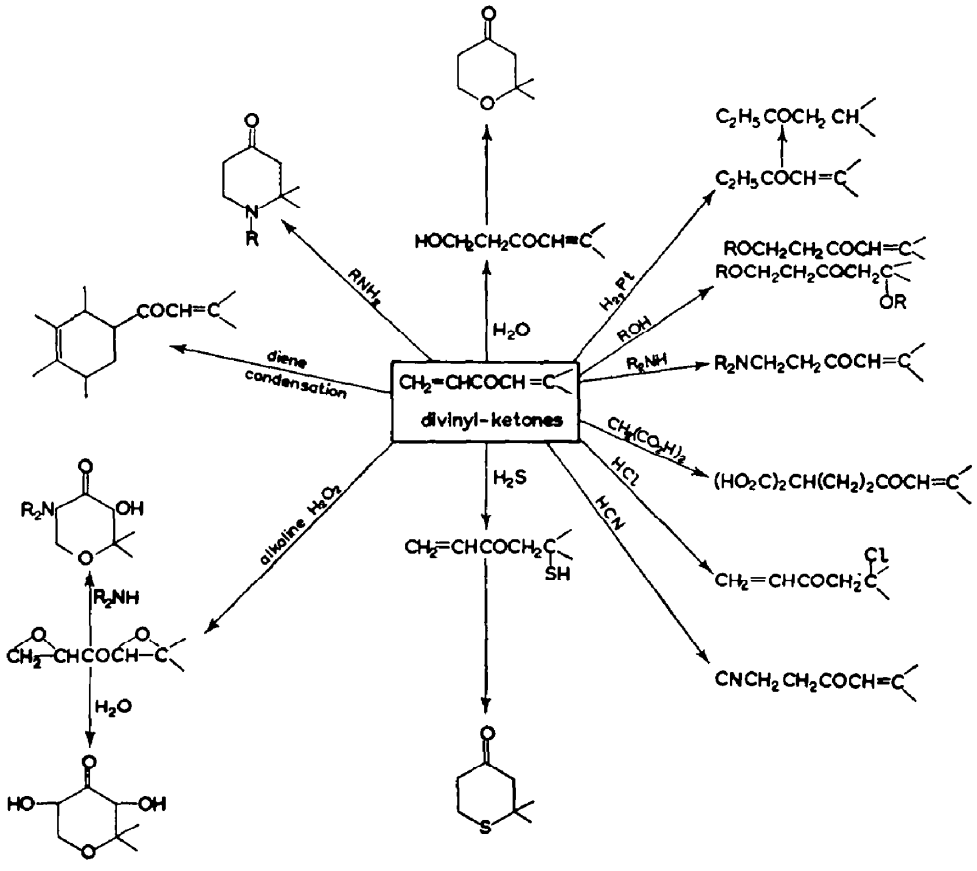
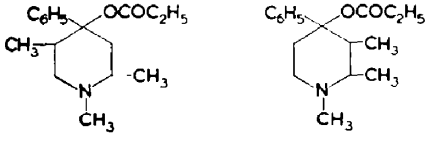


FIG. 2. Transformations of divinylketones.

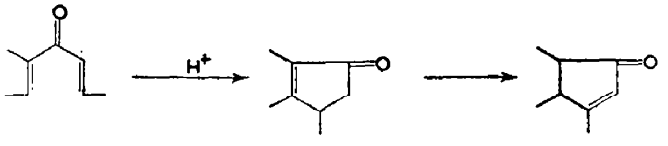
piperidones, possessed analgesic action. One of them, the hydrochloride of 1:2:5-trimethyl-4-phenyl-piperid-4-ol propionate (I), has a number of advantages over morphine and is widely used in clinics of the Soviet Union under the name of "promedol."



I II

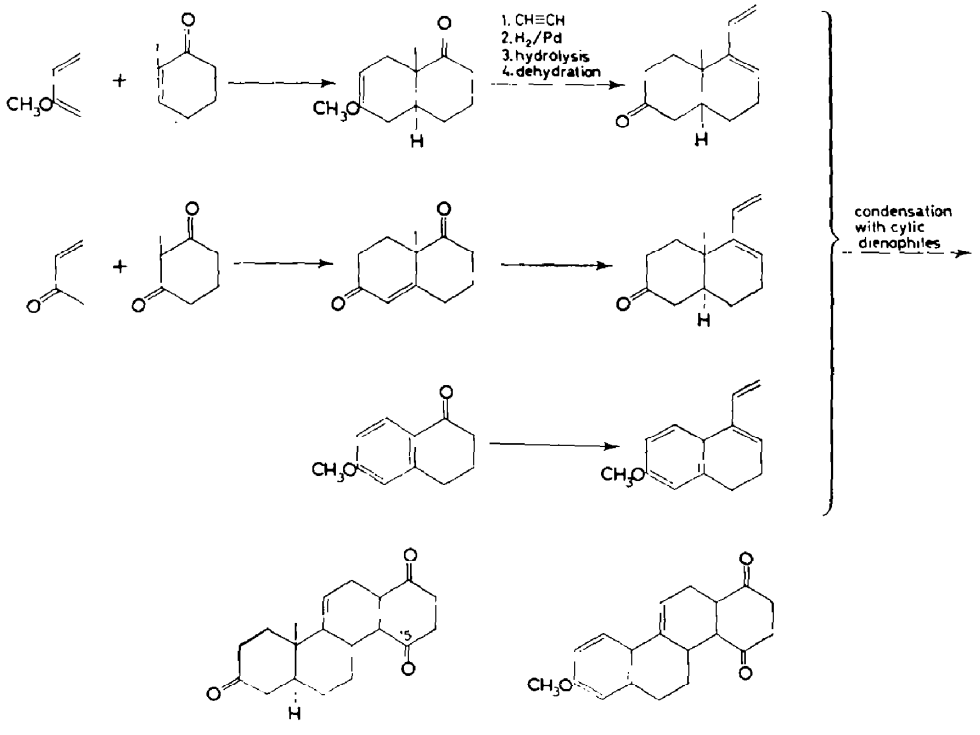
The most active of all presently known analgesics is the hydrochloride of 1:2:3-trimethyl-4-phenyl-piperid-4-ol propionate(II), synthesised by Nazarov. It possesses an activity forty times that of morphine.

Nazarov made a study of the cyclisation of many divinylketones into *cyclo*pentenones and the isomerisation of the latter:



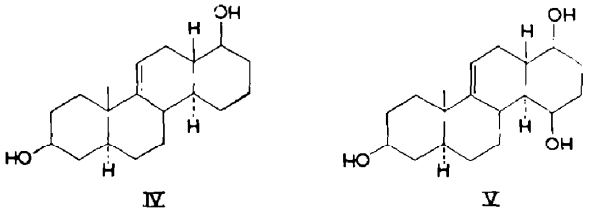
The substituted *cyclo*pentenones entered relatively easily into diene condensation, and this fact served as an impetus to two new independent lines of investigation.

Firstly, certain regularities in diene synthesis and the influence of temperature and other conditions on the reaction, were systematically studied. The quantitative ratio of the isomers formed in a single reaction mixture was shown to be dependent on the structures of the diene and dienophile. Secondly, the polycyclic compounds obtained by means of diene condensation and other reactions were used for the synthesis of substances related to steroids:



III

A detailed study of the condensation of 1-vinyl-Δ^1-octalones and 1-vinyl-6-methoxy-3:4-dihydronaphtalene with unsaturated cyclic ketones showed that the chief products of this reaction were the structural isomers of steroids with "inverted" D rings. For this reason, the condensation of the foregoing dienes with benzo-quinone was used to give tetracyclic compounds related to D-homosteroids.



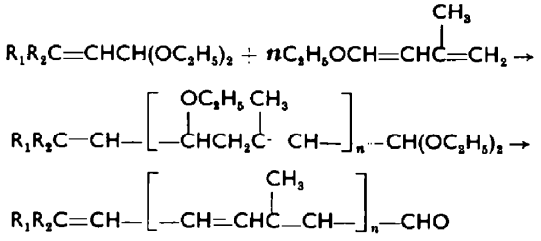
IV V

These tetracyclic ketones were selectively reduced at $C_{(18)}$. In particular, A/B-trans-triketone (III) was converted into the D-homosteroids (IV) and (V), which proved active androgens. In the case of the triol (V), the interesting fact was discovered that the introduction of a hydroxyl group into position 15 increased the androgen activity of the molecule.

New non-steroid estrogens were also obtained, and a study was made of the ways of introducing the dioxyacetone and glycerol side chains of corticosteroids into the polycyclic molecule.

Another part of Nazarov's work was connected with the study of the stereochemistry of certain organic reactions. He investigated the stereochemistry of hydrogenation, oxidation and lactonization of substituted tetrahydrophthalic and octalin-carbonic acids, and the stereochemistry of bromination of acetylenes. A study of the stereochemistry of diene condensations with vinyl*cyclo*hexene and 1(α-acetoxyvinyl)-*cyclo*hexene made possible a stereo-selective synthesis of bicyclic systems.

During the latter years of his life Nazarov was engaged in intensive work on the synthesis of *iso*prenoids. These studies were based on Nazarov's earlier investigations on the anionotropic rearrangement of secondary and tertiary polyene alcohols to primary alcohols, and on the method he discovered of alkali condensation of carbonyl compounds with acetylene under pressure. His work in the field of *iso*prenoids resulted in the synthesis (suitable for industrial production) of the *iso*prenoid alcohols—linalool, geraniol, nerol, nerolidol, farnesol, geranyllinalool, and phytol. A new method was developed of extending the *iso*prenoid chain. It was based on the condensation of acetals with 1-alkoxy*iso*prenes:



Together with his pupils and co-workers Nazarov published over 400 scientific papers. A number of his papers are still unpublished and will appear in the near future. Much of what he had begun was left unfinished and many of his plans were not brought to fruition, for I. N. Nazarov died at the height of his creative work.

L. D. BERGELSON