[CONTRIBUTION FROM THE BASIC RESEARCH DIVISION, SUN OIL COMPANY]

Formation of Hydronaphthalenes from Cyclopentyl Rings in Acid-catalyzed Reactions[1]

BY W. K. CONN AND A. SCHNEIDER

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Methylcyclopentane gives a mixture of dimethyldecahydronaphthalenes on treatment with *t*-butyl chloride and aluminum chloride; 2,6-dimethylnaphthalene was isolated from this mixture on dehydrogenation. Cyclopentene was dimerized over silica–alumina polymerization catalyst and yielded octahydronaphthalenes; here dehydrogenation gave naphthalene. A mechanism for the acid-catalyzed formation of hydronaphthalenes from cyclopentyl rings is proposed.

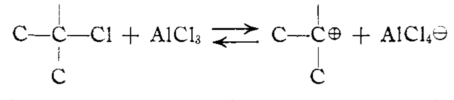
The dimerization of cyclic olefins containing five- and six-membered rings in acid-catalyzed reactions has been the subject of a number of investigations.[2–5] Bloch and Thomas[2] found that by subjecting cyclohexene to the action of a silica–alumina–thoria catalyst at 400°, a small yield of a mixture of dimethylnaphthalenes resulted from polymerization and hydrogen transfer. Criegee and Riebel[5] obtained high yields of $\Delta^{9:10}$-octahydronaphthalene by treating cyclopentene with phosphorus pentoxide and suggested carbonium ion intermediates in the formation of this olefin.

Several investigators have reported saturated dicyclic products in acid-catalyzed reaction involving monocyclic naphthenes containing five- and six-membered rings.[6–8] Nenitzescu[6] was the first to observe the "dimerization" of cyclohexane by its reaction with cyclohexyl chloride and aluminum chloride. His product was characterized as possibly containing 2,2′-dimethyldicyclopentyl. Doering[7] also obtained cyclohexane "dimers" when cyclohexane was used as solvent in the reaction of 4-chlorocamphane with aluminum bromide. Pines and Ipatieff[8] obtained the naphthene "dimer" as a by-product in acid-catalyzed alkylations of olefins with methylcyclopentane. These authors assumed the dicyclic product was a mixture of methylcyclopentylcyclohexanes. Identification involved dehydrogenation over platinum on asbestos at 265° to give, presumably by simultaneous rearrangement and dehydrogenation, a mixture of dimethylnaphthalenes. However, we have shown[9] that a rearrangement of this type does not occur since methylcyclopentylbenzene (an intermediate in dehydrogenation assumed by Pines and Ipatieff) showed no reactivity when passed over platinum under conditions even more severe than those employed by Pines and Ipatieff.

In the present work, methylcyclopentane was caused to self-alkylate (a so-called "dimerization") by the action of *t*-butyl chloride and aluminum chloride. The product was a mixture of dimethyldecalins which on dehydrogenation yielded the corresponding dimethylnaphthalenes. The 2,6-isomer was positively identified as one of the components.

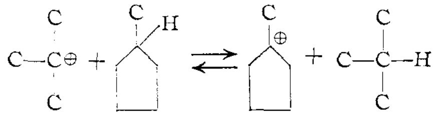
To study the acid-catalyzed reaction of a cyclic olefin, cyclopentene was treated with a silica–alumina catalyst at 200°. Dehydrogenation of the dimeric product gave naphthalene.

With the catalyst employed in the present work it is believed the following steps are operative in the self-alkylation of methylcyclopentane

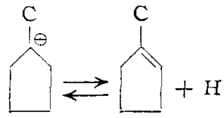

(I)

$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}Cl} + \mathrm{AlCl_3} \rightleftarrows \mathrm{C{-}\underset{C}{\overset{C}{C}}}^{\oplus} + \mathrm{AlCl_4}^{\ominus} \quad \text{(I)}$$

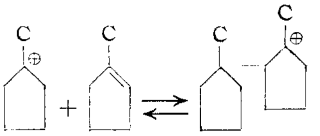
The trimethylcarbonium ion formed in I then abstracts the tertiary hydrogen from a molecule of methylcyclopentane to yield the methylcyclopentyl positive ion. In the case of cyclohexane, prior isomerization to methylcyclopentane is assumed to occur.[6]


(II)

The naphthenic ion enters into equilibrium with methylcyclopentene-1 by loss of a proton.


(III)

The following steps of the mechanism are applicable to both olefin dimerization and naphthene self-alkylation. The methylcyclopentyl positive ion then adds to methylcyclopentene according to Markownikov's rule.


(IV)

This addition is analogous to the well established mode of addition of a proton or an aliphatic carbonium ion to the olefin.[10] At this point direct comparison may be made of the ensuing rearrangements in the system under discussion with the thoroughly studied acid-catalyzed dehydration of 2-cyclopentylcyclopentanol. Two researches[11] have demonstrated that this dehydration yields a mixture of

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[1] Presented before the Organic Section, Meeting in Miniature of the Philadelphia Section of the American Chemical Society, Jan. 29, 1953, and before the Petroleum Division of the American Chemical Society, Los Angeles, California, March 15, 1953.

[2] H. S. Bloch and C. L. Thomas, THIS JOURNAL, **66**, 1589 (1944).

[3] (a) A. E. Bearse and J. E. Leonard, U. S. Patent 2,419,668 (1947); (b) G. A. Lutz, A. E. Bearse, J. E. Leonard and F. D. Croxton, THIS JOURNAL, **70**, 4141 (1948).

[4] B. S. Greensfelder and H. H. Voge, *Ind. Eng. Chem.*, **37**, 983 (1945).

[5] R. Criegee and A. Riebel, *Angew. Chem.*, **65**, 136 (1953).

[6] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **491**, 189 (1931).

[7] W. von E. Doering and E. F. Schoenewaldt, THIS JOURNAL, **73**, 2333 (1951).

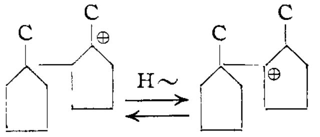
[8] H. Pines and V. N. Ipatieff, *ibid.*, **67**, 1631 (1945).

[9] Unpublished results of this Laboratory.

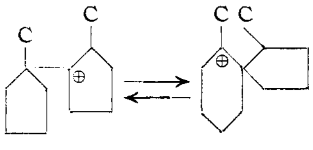
[10] F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[11] (a) N. D. Zelinski, I. Titz and M. Gaverdovskaya, *Ber.*, **59**, 2590 (1926); (b) W. Huckel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 131 (1930).

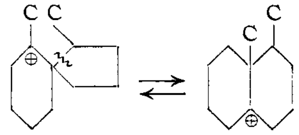
$\Delta^{9:10}$- and $\Delta^{1:9}$-octalin with the former in preponderance. The charge on the tertiary carbonium carbon of the adduct shifts to the adjacent tertiary carbon atom by a Wagner-Meerwein rearrangement.


(V)

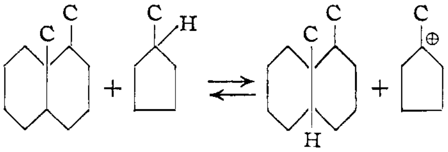
Ring expansion occurs in the cyclopentane ring which has the extracyclic α-carbonium carbon atom.


(VI)

Isomerization of the second cyclopentyl ring gives the decalin structure.

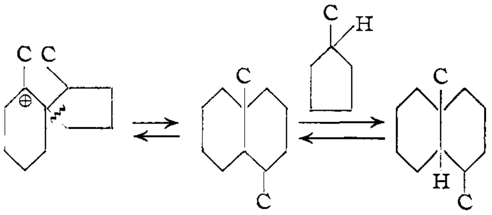

(VII)

Saturation of the decahydronaphthalene positive ion by extraction of a tertiary hydrogen atom from the solvent takes place, thus starting a new cycle.

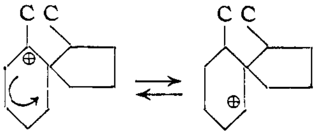

(VIII)

In case of olefin dimerization, the dicyclic ion presumably becomes stabilized by loss of a proton to form the corresponding olefin.

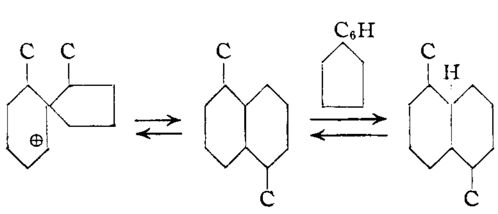
The occurrence of two consecutive ring expansions explains the formation of more than one isomer when the original cyclopentane is substituted. The following variation in step VII gives rise to another angularly substituted product.


(VIIIa)

The charge in the cyclohexane ring is capable of shifting around the ring by a series of Wagner–Meerwein rearrangements with a degree of ease which appears to be a characteristic reaction of cyclohexyl systems.[12]


(IX)

Ring expansion in two possible ways gives rise to dimethyldecalins with no angular side chains.


(X)

Isomerization of methylcyclopentene-1 to either of the two other methylcyclopentenes and subsequent alkylation of these isomers by the methylcyclopentyl ion forms dimethyldecalins substituted in the 2,6- or 2,7-positions. Finally, dimethyldecalins in which both substituents are in the same ring can result from rearrangements involving the methyl groups within the dimethyldecalyl positive ion. Thus, a mixture of all the possible isomers of dimethyldecalin might be expected to be formed in this type of reaction.

Experimental

Dimerization of Cyclopentene.—Cyclopentene (100 g.) was passed over 45 cc. of activated, M-46 Houdry silica-alumina polymerization catalyst in a glass tube at 200° over a period of two hours. Catalyst activation was effected by blowing with nitrogen at 400°. The catalyst did not appear to be badly carbonized after reaction. Blowing the catalyst bed with air at 450° removed adsorbed product and 3 cc. of a very viscous yellow liquid (n^{25}D 1.5425). This material was not investigated further. Distillation of the product gave 79 g. of cyclopentene, b.p. 42–43°, and 8 g. of residue. The following data were obtained on distillation of the residue.

Cut	B.p., °C.	Vol., cc.	n^{25}D
1	175–183	0.5	1.4515
2	183–187	1.0	1.4660
3	187–196	5.0	1.4819
4	196–210	0.5	1.4886
	Residue	1.0	1.5011

Dehydrogenation of cut 3 over platinum on charcoal[13] at 315° yielded naphthalene, m.p. 80–81°; mixed m.p. with an authentic sample showed no depression; picrate, m.p. 151–152.5°.

Self-alkylation of Methylcyclopentane.—To a mixture of 300 g. (3.57 mole) of methylcyclopentane and 30 g. (0.22 mole) of anhydrous aluminum chloride in a 1-liter, 3-necked flask equipped with a stirrer, dropping funnel, condenser, water scrubbing tower and Dry Ice–acetone trap was added 70 g. (0.76 mole) of distilled *t*-butyl chloride. The addition was made at room temperature over a period of one hour. After stirring an additional hour the organic layer was separated, washed with dilute sodium hydroxide and water and then dried over potassium carbonate. A total of 36 g. (0.62 mole) of isobutane was collected during the reaction.

Distillation of the product resulted in 193 g. (2.30 moles) of unreacted methylcyclopentane and cyclohexane and 60 g. of residue. Distillation of the residue afforded the following data

Cut	B.p., °C.	Vol., cc.	Wt., g	n^{25}D
1	140–214	6.5	5.4	
2	214–219	41	34.4	1.4642–1.4668
3	219–222	3	3	
4	222–309	5	5	

The following properties have been reported for the self-alkylate

Source	B.p., °C.	n^{25}D
Nenitzescu[6]	213–215	1.46453 (21°)
Doering[7]	216–220	1.4641
Pines[8]	214–219	1.4638

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(12) C. D. Nenitzescu and D. V. Curcaneanu, *C. A.*, **37**, 3740 (1943).

(13) H. C. Rampton, *Anal. Chem.*, **21**, 1377 (1949).

A sample of cut 2 (12.5 g.) was dehydrogenated over platinum on charcoal at 350° and yielded 8.45 l. of hydrogen (theoretical = 8.5 l. assuming 5 moles per mole of sample). The dehydrogenated material (9.7 g.) was then distilled.

Cut	B.p., °C.	Vol., cc.	$n^{25}D$
1	210–236	0.8	1.5381
2	236–258	2.4	1.5934
3	258–263	2.2	1.6045
4	263–268	1.8	1.6053
	Residue	2.3	1.6072

The boiling point and refractive index values agree with the literature[14] values for the liquid dimethylnaphthalene isomers (b.p. 263–266°, $n^{20}D$ 1.6072–1.6164).

White crystals separated from cuts 3, 4 and residue. Cut 4 was filtered and the solid recrystallized from ethanol yielding white plates, m.p. 110–110.5°. The picrate was prepared and found to melt at 141–142°. These values check the literature[14] values of 2,6-dimethylnaphthalene.

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(14) A. S. Bailey, K. C. Bryant, R. A. Hancock, S. H. Morrell and J. C. Smith, *J. Inst. Pet.*, **33**, 503 (1947).

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Utilization of *n*-Alkyl Methyl Ketones in the Pfitzinger Reaction[1]

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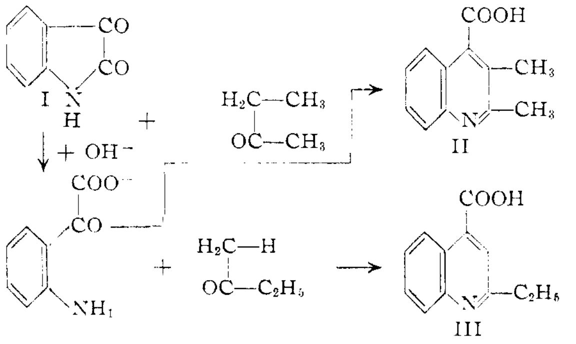
A series of Pfitzinger condensations, utilizing *n*-alkyl methyl ketones (alkyl = methyl through hexyl), has been accomplished. The unsymmetrical ketones produce two isomeric cinchoninic acids, a 2-monosubstituted acid and a 2,3-disubstituted acid, the monosubstituted compound usually being formed in the larger amount. A new sequence of syntheses has been developed in order to establish the structure of one series of these isomeric cinchoninic acids.

Although the Pfitzinger reaction[3] is one of the more commonly used procedures for preparation of quinoline derivatives,[4-6] surprisingly little attention has been given to the study of the structure of the products resulting from the utilization in this synthesis of mixed aliphatic ketones of the type RCH_2COCH_2R'. Since this synthesis in part involves condensation of the β-carbonyl group in isatin with a methylene group adjacent to the carbonyl group of the ketone, obviously two isomeric products should be capable of formation from this unsymmetrical ketone type, RCH_2COCH_2R'. From the initial condensation of ethyl methyl ketone with isatin (I), Pfitzinger[3] reported only the isolation of 2,3-dimethylcinchoninic acid (II). However, subsequently v. Braun, *et al.*,[7] showed that a smaller amount of the isomeric 2-ethylcinchoninic acid (III) was produced also.



From the meager experimental data then available, Hollins[8] stated that the course of reaction in the Pfitzinger synthesis is such that "as in the Friedländer synthesis, the quinolines from unsymmetrical ketones usually contain the *smaller* group in the α-position." A survey of the literature fails to disclose a sufficient number of condensations either to substantiate or to refute Hollins' statement.

More recently, Buu-Hoï, *et al.*,[9] have made a partial study of this condensation, utilizing the ethyl, propyl, hexyl and nonyl homologs of acetone; data reflecting these and a few other pertinent condensations have been collected in Table I. Buu-Hoï concluded that the condensation of isatin with *n*-alkyl methyl ketones, excluding ethyl methyl ketone, yielded primarily 2-monosubstituted cinchoninic acids. However, this conclusion was not based upon isolation of two products from each of the condensations studied.

In the present investigation, isatin has been condensed, under the condition typical for the Pfitzinger reaction, with five members of the *n*-alkyl methyl ketone series, namely, ethyl through hexyl. In each instance, evidence was obtained of the production of two reaction products. After separation of the products, through fractional crystallization of the reaction product, the isomeric compounds were mixed in known amounts and melting point studies made of the known mixtures in an effort to evaluate the relative amounts formed of the two isomers in a given condensation.

In the case of the condensation of isatin with ethyl methyl ketone, the two isomers were obtained; in all probability, five-sixths of the mixture of isomers was made up of the 2,3-disubstituted cinchoninic acid. The identity of the lesser prod-

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(1) From the Ph.D. dissertation of Donald Wesley Carroll, The University of Texas, June, 1952.

(2) Research Scientist I, University of Texas Research Institute, 1952 Summer Session.

(3) W. Pfitzinger, *J. prakt. Chem.*, [2] **33**, 100 (1886); **38**, 583 (1888); **56**, 283 (1897).

(4) C. Hollins, "The Synthesis of Nitrogen Ring Compounds," E. Benn, Ltd., London, 1924, Chapter VIII.

(5) A. A. Morton, "The Chemistry of Heterocyclic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 273.

(6) R. C. Elderfield, "Heterocyclic Compounds," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 54.

(7) J. v. Braun, W. Gmelin and A. Schultheiss, *Ber.*, **56**, 1338 (1923).

(8) J. Hollins, ref. 4, p. 287; with regard to the Friedländer synthesis Hollins wrote (p. 284) "In the case of ketones of the type MeCO·CH₂R, the methyl group takes the α-position in the resulting quinoline."

(9) Ng. Ph. Buu-Hoï, *J. Chem. Soc.*, 795 (1946); Buu-Hoï and P. Cagniant, *Bull. soc. chim.*, 13 (1946); Buu-Hoï and R. Royer, *ibid.*, 374 (1948). See also Ng. Ph. Buu-Hoï, R. Royer, Ng. D. Xuong and P. Jacquignon, *J. Org. Chem.*, **18**, 1209 (1953).