The Pyrolysis of Nopinone[1a]

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Vapor-phase pyrolysis of nopinone in the range 460–600° yields 7-methylocta-1,6-dien-3-one (1), 4-isopropenyl-cyclohexanone (3), and cis- and trans-2-methyl-3-isopropenylcyclopentanone (4 and 5). In the same temperature range, dienone 1 gives 4 and 5, and 4 and 5 interconvert. The attempted photocyclization of dienone 1 was not successful. The details and mechanisms of these reactions are discussed.

In the course of studies on photochemical ring closures,[2] we required 7-methylocta-1,6-dien-3-one (1) as a potential precursor of the bicyclo[3.1.1]heptane nucleus with the usual terpene substitution pattern. Since vapor-phase pyrolysis of β-pinene has been reported to yield predominately β-myrcene,[3] the pyrolysis of nopinone (2) was examined as a synthetic route to 1. In fact, vapor-phase thermolysis of bicyclic ketone 2 using a flow unit at 460–600° and reduced pressure did result in the desired acyclic ketone. However, the synthetic utility of this process was diminished by the observation that substantial quantities of three additional materials were found in the pyrolysis product. These were identified as 4-isopropenylcyclohexanone (3), cis-2-methyl-3-isopropenylcyclopentanone (4), and trans-2-methyl-3-isopropenylcyclopentanone (5). The relative proportions of the products was a function of both the temperature and the rate of passage through the thermal zone, but a typical run at 600° gave 39% 1, 27% 3, 14% 4, 8% 5, and 11% total of a number of unidentified minor products. Conditions were not achieved which caused substantial conversion of 1 to 2 without the concurrent formation of large amounts of the other products.

The mass spectra of each of the pyrolysis products display a molecular ion at m/e 138 demonstrating their isomeric relationship to nopinone. The spectral properties of these compounds which are detailed in the Experimental Section fully support the assigned structures. Carbonyl absorption in the ir was particularly instructive in differentiating among cyclopentanone, cyclohexanone, and conjugated acyclic ketone functions. Distinction between epimeric cylcopentanones 4 and 5 was based on the chemical shifts of the methyl group attached to C₂. These values are δ 0.82 and 0.95 for 4 and 5, respectively, and reveal a significant high field shift for 4. This is in accord with the molecular geometry of 4 which positions the saturated methyl group in the shielding zone above the plane of the isopropenyl double bond.[4] Chemical confirmation of this assignment is provided by base isomerization which generates a mixture from either epimer in which the *trans* compound predominates.

Examination of the behavior of the pyrolysis products to the reaction conditions afforded insight into the nature of the thermal transformations of 2. At 570° acyclic dienone 1 was substantially (70%) converted to the isomeric cyclopentanones 4 and 5 along with a

small amount of cyclohexanone 3. At this temperature 3 underwent only 10% transformation mainly to the isomeric cyclopentanones. Even at 740° less than half of 3 was converted to products. The major reaction of 4 and 5 was interconversion, and at 740° the same 1:6 ratio of 4 and 5 was obtained from either isomer.
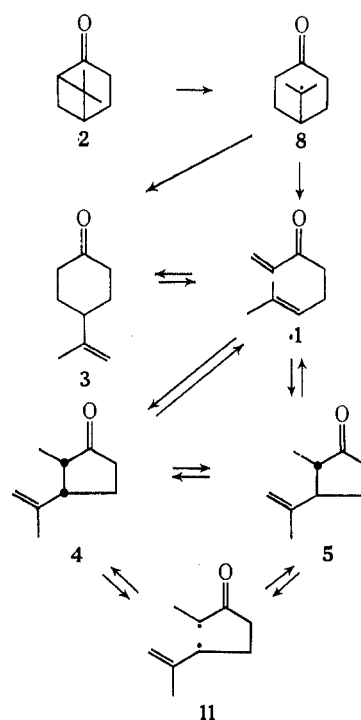
The thermal isomerization of nopinone finds close analogy in the pyrolytic behavior of the related hydrocarbon β-pinene which is converted to β-myrcene and lesser quantities of limonene and 4-isopropenylmethyl-enecyclohexane.[3] A diradical mechanism has been suggested for the hydrocarbon isomerization, and the appropriate modification is an attractive explanation for the origin of acyclic dienone 1 and cyclohexanone 3 in the pyrolysis of 2. This description is also in accord with other observations on the thermal reaction of cyclo-butanes.[5] The pyrolysis of tricyclic compound 6 which gives bicyclic ketone 7 is especially relevant as an example in which hydrogen atom abstraction interrupts the cyclobutane fission process.[6]

(1) (a) Supported by the Public Health Service (Grant GM 12860). (b) Alfred P. Sloan Research Fellow, 1968–1970.

(2) J. K. Crandall and C. F. Mayer, *J. Amer. Chem. Soc.*, **89**, 4374 (1967).

(3) D. V. Banthrope and D. Whittaker, *Quart. Rev.* (London), **20**, 373 (1966).

(4) D. W. Mathieson, "Nuclear Magnetic Resonance for Organic Chemists," Academic Press, New York, N. Y., 1967, p 110.

(5) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

(6) C. H. Heathcock and B. E. Ratcliffe, *J. Org. Chem.*, **33**, 3650 (1968).

Cleavage of the indicated cyclobutane bond of nopinone yields diradical **8**, the most stable such species derivable from **2**. Other modes of bond homolysis must sacrifice either the α-keto radical[7] or the tertiary radical site, and this fact is apparently reflected in the transition state energies for the alternate reaction pathways. Diradical **8** can subsequently cleave the central bond of the 1,4-diradical moiety to yield **1**, or it can undergo intramolecular disporportionation by a 1,5-hydrogen atom transfer to produce cyclohexanone **3**. The latter could also arise by a 1,7-hydrogen shift to give the enol of **3** as an intermediate. Such a 1,7 transfer apparently operates in the case of β-pinene.[3]

The conversion of **1** to cyclopentanones is closely analogous to the known thermal rearrangement of 3,7-dimethyl-1,6-octadiene (**9**) to the isomeric 1,2-di-methyl-3-isopropenylcyclopentanes (**10**) and related examples.[8] These transformations are intramolecular versions of the ene reaction which appears to occur by a concerted cycloaddition mechanism in those instances where this point has been examined.[9]

9 → 10
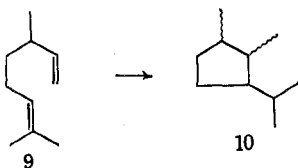
The interconversion of cyclopentanones **4** and **5** may involve homolytic cleavage of the C_2–C_3 bond of the cyclopentane ring to give diradical **11**, which can undergo reclosure to either epimer. On the other hand, the presence of a trace of dienone **1** among the pyrolysis products from each of these suggests the alternate, and perhaps more likely, possibility of interconversion through **1** by a combination of ene and reverse ene reactions.

Attempts to reverse photochemically the **2** to **1** conversion were without success. A variety of direct or sensitized irradiation experiments did not yield volatile products, although transformation of **1** to polymer was observed. Similar resistance to photocyclization has been found for the parent 1,6-heptadien-3-one and for 1,3,6-heptatriene.[10] Recent evidence suggests that 1,6-dienes should preferentially cyclize to bicyclo[3.2.0]heptane skeletons rather than the desired bicyclo[3.1.1]heptanes,[11] although the latter has been observed when the 1,6-diene is restricted in geometry by a medium-ring environment.[12] Nonetheless, neither mode of cyclization has been observed in the present studies, suggesting that 1,6-dienes are, in general, less prone to cycloaddition than 1,5-dienes.[13]

(7) There appears to be some question about the amount of stabilization offered by a carbonyl group adjacent to a radical center, but an acyl group is probably equivalent to an alkyl substituent at the minimum. See ref 5, p 176.

(8) W. D. Huntsman, V. C. Solomon, and D. Eros, *J. Amer. Chem. Soc.*, **80**, 5455 (1958), and references therein.

(9) For example, see J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966); R. K. Hill and M. Rabinovitz, *ibid.*, **86**, 965 (1964); H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

(10) Unpublished results, J. K. Crandall.

(11) R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967); M. Brown, *J. Org. Chem.*, **33**, 162 (1968); L. Crombie, R. Ponsford, A. Shani, B. Yagnitinsky, and R. Mechoulam, *Tetrahedron Lett.*, 5771 (1968); J. R. Scheffer and M. C. Lungle, *ibid.*, 845 (1969); J. W. Stankorb and K. Conrow, *ibid.*, 2395 (1969).

(12) C. H. Heathcock and R. A. Badger, *Chem. Commun.*, 1510 (1968).

(13) F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Lett.*, 4685 (1965). See also W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969); **66**, 373 (1966).

Experimental Section

General.—Nuclear magnetic resonance spectra (nmr) were recorded on a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard. Mass spectra were determined using an AEI MS-9 mass spectrometer at 70 eV. Gas-liquid partition chromatography (glpc) was carried out on a Varian-Aerograph Series 1200 chromatograph (analytical, flame ionization detector) using an 8 ft × ¹/₈ in. 15% Carbowax 20M on 60–80 Chromosorb W column and on an Aerograph A-90P-3 chromatograph (preparative) using a 10 ft × ³/₈ in. 30% XF-1150 on 45–60 Chromosorb W or a 10 ft × ³/₈ in. 30% FFAP on 60–80 Chromosorb W column. Percentage composition data were estimated by integrated peak areas. Analyses were performed by Midwest Microlab, Inc.

General Pyrolysis Procedure.—The vapor-phase pyrolysis apparatus consisted of a horizontal Pyrex or fused-quartz tube, 10-mm i.d., inserted through an E. H. Sargent and Co. tube furnace 170 mm in length. The Pyrex tube was packed with Pyrex helices, 0.25-in. o.d. The quartz tube was used unpacked or was packed with quartz chips 1 mm thick, other dimensions variant. Samples were placed in a flask attached at one end of the tube and the vapors were condensed in a Dry Ice trap at the other end. A pressure of less than 1 mm was maintained by a vacuum pump attached at the trap. The throughput could be increased by heating the sample with an infrared lamp.

Nopinone (2).—A modification of the ozonolysis method of Conia and Leriverend[14] was used. The output from a Welsbach Model T-408 ozonator was bubbled through a solution of 25 g of β-pinene and 30 ml of pyridine in 150 ml of methylene chloride at −78° for 6 hr. The brown solution was purged with oxygen for 30 min, allowed to warm to room temperature, and washed with four 50-ml portions of 10% hydrochloric acid. After washing with water, the solution was dried and concentrated, and the residue was distilled to give 11.2 g (44%) of **2**: bp 55–60° (2 mm); ir 5.83 μ; nmr δ 2.2 (m, 8), 1.31 (s, 3), and 0.81 (s, 3).

Pyrolysis of Nopinone.—A 5-g sample of nopinone was passed through the packed quartz tube at 600° in 4 hr with the aid of the infrared lamp. Glpc assay indicated that the 4.53 g (90%) of yellow liquid collected in the trap consisted of 39% 7-methyl-octa-1,6-dien-3-one (**1**), 27% 4-isopropenylcyclohexanone (**3**), 14% *cis*- and 8% *trans*-2-methyl-3-isopropenylcyclopentanone (**4** and **5**), and 11% total of other products. The four major products were isolated by preparative glpc (XF-1150).

Octadienone **1** displayed ir (CCl₄) 5.94, 6.18, 10.1, and 10.4 μ; nmr δ 6.2 (m, 2, CH=CH₂), 5.7 (m, 1, CH=CH₂), 5.07 (m, 1, C=CH), 2.3 (m, 4), and 1.60 (broad s, 6); mass spectrum *m/e* (relative intensity) 138 (14), 83 (85), 70 (35), 69 (35), 68 (33), 67 (33), 55 (100), 41 (75), 27 (54).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.14; H, 10.18.

Cyclohexanone **3** showed ir 5.82, 6.07, and 11.2 μ; nmr δ 4.74 (m, 2, CH_3C=CH₂), 2.1 (m, 9), and 1.74 (t, 3, J = 1 Hz, CH_3C=CH₂); mass spectrum *m/e* 138 (34), 110 (20), 81 (43), 68 (100), 55 (54), 41 (48).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.86; H, 10.10.

trans-2-Methyl-3-isopropenylcyclopentanone (**5**) had ir (CCl₄) 5.75, 6.07, and 11.2 μ; nmr δ 4.80 (m, 2, CH₃C=CH₂), 2.1 (m, 6), 1.73 (t, 3, J = 1 Hz, CH₃C=CH₂), and 0.95 (d, 3, J = 6 Hz); mass spectrum *m/e* 138 (84), 123 (22), 96 (53), 82 (79), 81 (86), 67 (100), 55 (43), 41 (65).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.04; H, 10.14.

cis-2-Methyl-3-isopropenylcyclopentanone (**4**) was obtained in 85% purity as a mixture with **5**: ir 5.74, 6.06, and 11.2 μ; nmr δ 4.82 (m, 1, CH₃C=CH₂), 4.70 (m, 1, CH₃C=CH₂), 2.82 (broad quartet, 1, J = 7 Hz, CHCH₃), 2.1 (m, 5), 1.69 (m, 3, CH₃C=CH₂), and 0.82 (d, 3, J = 7 Hz, CHCH₃). Further purification could not be effected by glpc, apparently because of conversion of **4** to **5** on the glpc column.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.01; H, 10.08.

Pyrolysis of 1, 3, 4, and 5.—Approximately 15-mg samples of octadienone **1** (95%), cyclohexanone **3**, and cyclopentanones **4** (85% purity) and **5** were passed through the unpacked quartz tube at 570, 660, and 740°. The product mixtures were ex-

(14) J. M. Conia and P. Leriverend, *C. R. Acad. Sci., Paris*, **250**, 1078 (1960).

amined by glpc analysis. The significant data are summarized below. At 570° these four compounds were essentially the only constituents of the product mixtures. At 740° as much as 50% of the product mixtures consisted of unidentified materials. Pyrolysis of dienone 1 at 570° gave 70% conversion to a 3:2:1 mixture of 5:4:3. At the same temperature, 3 gave only 10% conversion, mainly to 4 and 5. Even at 740° less than half of 3 was rearranged (unidentified components taken into account), primarily to 4 and 5. About 30% of the *cis*-cyclopentanone (4) was converted to the *trans*-cyclopentanone (5) at 570°. At the same temperature, about 15% conversion of 5 to 4 was obtained. These were essentially the only products at this temperature. At 740°, both 4 and 5 led to a mixture containing a 6:1 ratio of 5:4 as about 75% of the mixture. There were traces of dienone 1 and cyclohexanone 3 in these products.

Base-Catalyzed Interconversion of Cyclopentanones 4 and 5.—About 10 mg of sodium metal was dissolved in 5 ml of dry methanol and 20 mg of the *trans*-cyclopentanone was added. The solution was heated to reflux for 17 hr, diluted with water, and extracted with pentane. The product was shown by glpc to be 92% *trans*- and 8% *cis*-cyclopentanone. Similar treatment of an 85% pure sample of 4 led to a product mixture indicated to be 83% 5 and 17% 4.

Irradiation of 7-Methylocta-1,6-dien-3-one (1).—A solution of 11 mg of 1 in 1.0 ml of purified hexane in a quartz test tube was degassed by bubbling prepurified nitrogen through the solution for 1 min with a pipet and sealed with a rubber serum cap. This solution was irradiated in a Rayonet reactor with a bank of sixteen 2537-Å bulbs for 1 hr. Glpc analysis indicated no change in the sample. Further irradiation with 3000-Å lamps for 4 hr caused formation of a white solid on the wall of the tube, but glpc assay failed to reveal any volatile products.

Another 10-mg sample of 1 in 5 ml of purified benzene in a 10-ml Pyrex flask was degassed as above. Acetone (2 drops) was added and the solution was irradiated at 3000 Å for 17 hr. Glpc examination again disclosed no volatile products.

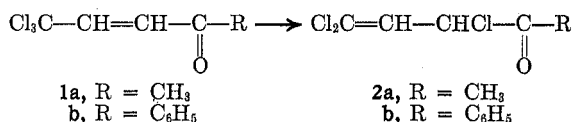# The Allylic Rearrangement of 3,3,3-Trichloro-1-propenyl Ketones

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The anionotropic allylic rearrangement of 3,3,3-trichloro-1-propenyl methyl ketone (1a) and 3,3,3-trichloro-1-propenyl phenyl ketone (1b) has been investigated. It afforded 1,3,3-trichloro-2-propenyl methyl ketone (2a) and 1,3,3-trichloro-2-propenyl phenyl ketone (2b), respectively. The isomerization was catalyzed by various solids, *e.g.*, silica gel, alumina, acid clay, cobaltous oxide, cupric oxide, ferric oxide, and iron and copper powder but not by metal oxides of more ionic character, *e.g.* calcium oxide, magnesium oxide. The rearranged products primarily reacted with nucleophiles as α-chloro ketones. Diethylamine and triethylamine, however, catalyzed the prototropic rearrangement of 2a and 2b to give 1,3,3-trichloro-1-propenyl methyl ketone (10a) and 1,3,3-trichloro-1-propenyl phenyl ketone (10b). The intermediate diethylamine salt of 2b (12) was isolated as a white powder and characterized. The transformation of 12 to 10b was complete within a few days when kept at room temperature.
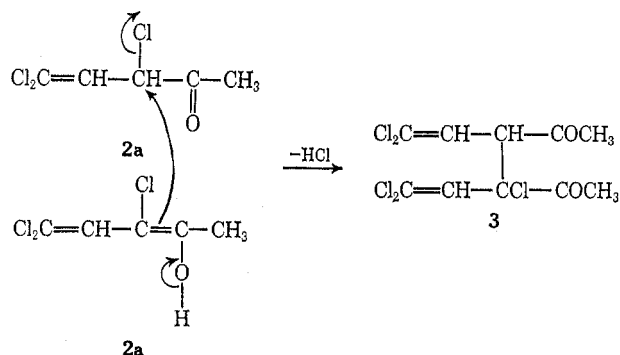
Allylic rearrangements of 1,1,1-trichloro-2-propenes have been reported by several authors. The isomerization of 1,1,1-trichloro-2-methyl-2-propene to 1,1,3-trichloro-2-methyl-1-propene has been studied by Kundiger, *et al.*[1] The reaction might be catalyzed by such materials as silica gel, thionyl chloride, antimony pentachloride, and alkaline soft glass powder, or proceed pyrolitically. Hexachloropropene-1-^{14}C was isomerized by heating at 120° for several hours and by the chromatographical treatment on silica gel.[2] We have recently found that 1-acyl-3,3,3-trichloro-1-propenes (1) also undergo the allylic rearrangement by the action of solid supports of glpc to form 1-acyl-1,3,3-trichloro-2-propenes (2). The α hydrogen in 2 is highly activated by the influence of adjacent groups so that they are subject to further chemical change.

Cl₃C—CH=CH—C—R ⟶ Cl₂C=CH—CHCl—C—R (displayed with carbonyl O below each C)

$$Cl_3C-CH=CH-\underset{\underset{O}{\|}}{C}-R \longrightarrow Cl_2C=CH-CHCl-\underset{\underset{O}{\|}}{C}-R$$

1a, R = CH₃   2a, R = CH₃
 b, R = C₆H₅   b, R = C₆H₅

This paper describes the catalytic transformation of 3,3,3-trichloro-1-propenyl methyl ketone (1a) and 3,3,3-trichloro-1-propenyl phenyl ketone (1b) to 1,3,3-trichloro-2-propenyl methyl ketone (2a) and 1,3,3-trichloro-2-propenyl phenyl ketone (2b) and discusses their structures and chemical properties.

The substrate 1a was heated on a bath at 120–180° in the presence of solid materials as catalyst and distilled under a reduced pressure (20–30 mm) in order to investigate their effect on the present transformation. Strongly ionic substances such as calcium oxide, magnesium oxide, and sodium chloride did not catalyze the reaction. On the other hand, the presence of less ionic materials such as cobaltous oxide, cupric oxide, and ferric oxide catalyzed the reaction considerably with the partial formation of resinous products. Silica gel was most eminent in the catalytic action among solid supports used. A small amount of 3,4-bis(2',2'-dichlorovinyl)-3-chloro-2,5-hexanedione (3) was usually produced as a by-product. A possible mechanism of the formation of 3 is tentatively given as shown in eq 1.

$$Cl_2C=CH-\underset{\underset{O}{\|}}{\underset{|}{\overset{\overset{Cl}{|}}{CH}}}-C-CH_3$$

2a

$$Cl_2C=CH-\overset{\overset{Cl}{|}}{\underset{\underset{\overset{|}{O}}{|}}{C}}=C-CH_3$$

$$\underset{H}{\overset{|}{\overset{|}{}}}$$

2a

—HCl ⟶

$$Cl_2C=CH-CH-COCH_3$$
$$Cl_2C=CH-CCl-COCH_3$$

3

(1) (a) D. G. Kundiger and K. H. Groman, *J. Amer. Chem. Soc.*, **75**, 1744 (1953); (b) D. G. Kundiger and H. N. Haney, *ibid.*, **76**, 615 (1954).
(2) C. H. Shuford, Jr., D. L. West, and H. W. Davis, *ibid.*, **76**, 5803 (1954).

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