Isomers of the Spiro[cyclohexane-1,1′-(Δ^9-Tetrahydroindan)]-3-one System

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Structures are reassigned to two isomeric ketones (I and II) on the basis of nuclear magnetic resonance data and the two compounds are shown to have the same skeleton on the basis of lithium in liquid ammonia reduction to a single ketone.

DURING a general study of dienyne cyclization, Marvel and coworkers (*6*) attempted to prepare Δ^{11}-dodecahydro-9-phenanthrone from cyclohexanone and acetylene. The products of this reaction were characterized as two isomeric ketones (*4*), with one melting at 39° and the other at 94° C.

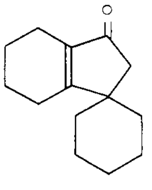
The nature of the cyclization products has been the subject of much work (*5, 7*). Early investigators assigned phenanthrene structures to these isomers, while later studies have led to the assignment of a spirocyclohexaneindanone system (*3*).

Prior evidence favoring identical skeletons for the two isomers (I and II) was obtained under conditions where rearrangement could have occurred—e.g., acidic media and metallic catalysts at high temperatures. In the present reinvestigation of these isomers it has been shown unequivocally that they have the same skeletons. Reduction of the double bond in each of the two pure isomers with lithium in liquid ammonia produced ketones, the derived oximes of which gave identical melting points, and showed no depression in the melting point of the admixture.

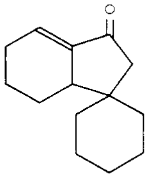
Nuclear magnetic resonance studies now show that previous assignment (*9*) of the position of the double bond in the two isomers is incorrect.

The nuclear magnetic resonance spectrum of the higher melting isomer showed a broad doublet (T = 3.45) in the vinyl hydrogen region, while that of the lower melting isomer showed no olefinic hydrogen resonance. Thus structure I represents the lower melting isomer and II the higher melting ketone.

These assignments are in accordance with Woodward's rules (*1, 8*) on ultraviolet absorption spectra, if a correction —viz., 11 mμ— for the cyclopentenone (*2*) structure is considered in computing the theoretical ultraviolet absorption maxima.



I



II

Structure	M.P., ° C.	$\lambda_{\text{max.}}^{\text{EtOH}}$, Mμ
I	39	241
II	94	247

EXPERIMENTAL

1,1′-Spirocyclohexanehexahydroindan-3-oxime. To a solution of 20 mg. of lithium metal in 25 ml. of liquid ammonia 290 mg. of 1,1′-spirocyclohexane-$\Delta^{4:9'}$-tetrahydroindan-3-one in 50 ml. of a dried 50 to 50 mixture of ethyl ether and dioxane was added. The cooling bath used to liquefy the ammonia was removed, and the solution was stirred with a mechanical stirrer. After 5 minutes the reaction was quenched with dry *tert*-butyl alcohol. After the ammonia had evaporated, the residue was extracted with ether several

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times; the ether extracts were washed with water and dried over anhydrous magnesium sulfate.

The ether was removed and the residue taken up in benzene. The benzene solution was then run through a chromatography column containing Merck acid-washed alumina in benzene. The eluted benzene solution was collected and stripped of solvent. The oxime, 1,1′-spirocyclohexanehexahydroindan-3-oxime, was prepared from this material. The oxime (m.p. 138–40°) was recrystallized from water-ethanol.

Analysis. Calculated for $C_{14}H_{23}NO$: C, 75.96; H, 10.47; N, 6.33. Found: C, 76.09; H, 10.49; N, 6.31.

The same procedure was used for converting 1,1′-spirocyclohexane-$\Delta^{8(9)}$-tetrahydroindan-3-one to 1,1′-spirocyclohexanehexahydroindan-3-oxime. A mixed melting point of the oximes of the reduced products of the two isomeric ketones showed no depression.

The ultraviolet spectra were determined in 1-cm. quartz cells using a Cary Model II spectrophotometer.

Proton magnetic resonance spectra were determined in carbon tetrachloride solution using a Varian A-60 high resolution spectrometer. Spectra were obtained at 60 mc. using tetramethylsilane as an internal standard.

ACKNOWLEDGMENT

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Thermodynamic Properties of Perfluoropropane

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The thermodynamic properties of perfluoropropane (octafluoropropane) have been calculated over a temperature range of −1.00° to 71.9° C. for the saturated region and from −35° to 300° C. and over a pressure range from 1 to 40 atm. in the superheated region. The properties were determined from vapor pressure, heat capacity, and volumetric data using the Martin and Hou equation of state. The calculated results are internally consistent.

EXPERIMENTAL *P-V-T* data and physical properties for perfluoropropane have been published in the literature (*2*). However, the derived thermodynamic properties, enthalpy and entropy, have not been reported previously. This paper presents the calculated values of enthalpies, entropies, densities, and specific volumes for the saturated region from −100° C. to the critical point, and for the superheated region from 1 to 40 atm. and from −35° to 300° C.

The calculations were made based upon rigorous thermodynamic relations using the Martin and Hou equation of state (*5*).

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-kT/T_c}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT/T_c}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{B_5T}{(V-b)^5} \quad (1)$$

SOURCES OF DATA

Critical evaluation of the thermodynamic properties of a compound requires some knowledge of pressure-volume-temperature behavior as well as some measurements of vapor heat capacity over the range of temperatures involved. Limited data for perfluoropropane are available in the literature and were used in the preparation of this paper. A tabulation of these data with sources is presented in Table I.

Experimental gas heat capacities at low pressures and over a range of temperatures were obtained by Masi (*6*). Edgell (*4*) studied the Raman and infrared spectrum of perfluoropropane, and found 22 of the 27 fundamental frequencies of vibration. By using statistical methods, additional specific heat data were calculated (*1*). Data were then fitted to several generalized forms of heat capacity equations. The following equation was developed in the present study as the one most consistent with the data:

$$C_p^0 = 3.0911305 + 0.1485887T - 0.15309 \times 10^{-3}T^2 + 5.7292141 \times 10^{-8}T^3 \quad (2)$$

Since there are no data available for temperatures below −30° C., extrapolation was necessary to cover the temperature range studied. Dobratz's (*7*) equation, a modification of the equation of Meghreblian, Crawford, and Parr (*7*), Crawford and Parr's (*3*) expression, and Equation 2 all yielded values agreeing with one another to within 10% when extrapolated to low temperatures. Equation 2 was chosen to be used throughout the entire temperature range in this study, since none of the other methods are considered reliable below 250° R.

Table I. Physical Properties of Perfluoropropane

Property		Source
Chemical formula	C_3F_8	(*1*)
Molecular weight	188.02	(*1*)
Normal boiling point	−36.7° C.	(2)
Normal freezing point	−160° C.	(*1*)
Critical temperature	71.9° C.	(2)
Critical pressure	26.45 atm.	(2)
Critical volume	0.299 liter/g.-mole	(2)

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