melting points of copolymers are ill-defined.[3] It is difficult to understand, however, why the lowering of T_m with reduction in degree of polymerization[2] does not appear to be subject to a corresponding error.

According to the results shown in Fig. 2, dimethylformamide is a far more potent solvent for the polyester than is diphenyl ether. Values of B' estimated from the slopes of the lines are +8.0 cal./cc. and −1.8 cal./cc., respectively.

TABLE I

MELTING TEMPERATURE OF POLYMER–DILUENT MIXTURES

Dimethylformamide		Diphenyl ether	
v_1	T_m, °C.	v_1	T_m, °C.
0.078	72.5 ± 0.5	0.123	74.5 ± 0.5
.202	66.5 ± .5	.180	71.5 ± .5
.422	61.5 ± .5	.410	59.5 ± .5
.603	57.5 ± .5	.594	50.5 ± .5

Experimental.—Decamethylene glycol and adipic acid, both carefully purified, were polymerized by heating without added catalysts at 160 to 217° under a reduced pressure of pure nitrogen for a total of 33 hours. A 2% excess of glycol over the amount required stoichiometrically was used in order to compensate loss of glycol by volatilization. The final viscosity at 109° was 1800 poises, corresponding to a number average molecular weight of 11,500.[8]

The solvents, dimethylformamide and diphenyl ether, were of reagent grade. The former was redistilled. Polymer–diluent mixtures were prepared by heating the ingredients with stirring as previously described.[3] The dilatometric procedures have been described elsewhere also.[3,4]

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[8] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

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Steroids Derived from Bile Acids. XVII. Dehydrobromination of 3-Keto-4-bromosteroids with 2,4-Dinitrophenylhydrazine[1]

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When 3-keto-4-bromosteroids are treated with 2,4-dinitrophenylhydrazine in acetic acid hydrogen bromide is eliminated and a Δ^4-steroidal hydrazone is formed.[3a,b] The probable mechanism of this reaction has been discussed. Djerassi[4] believed that hydrogen bromide was eliminated before formation of the hydrazone. Mattox and Kendall[5] suggested that the hydrazone was formed with the atom of bromine at C-4 still intact and that subsequently hydrogen bromide was lost.

Isolation and identification of the 3-hydrazone of the 4-bromosteroid as an intermediate compound did not appear feasible since at room temperature the organically bound bromine rapidly appeared in solution as bromide ion.

It seemed probable that the bromohydrazone would be stable in relatively non-polar solvents, such as chloroform or benzene, but attempts to prepare this intermediate product in such solvents were unsuccessful. For this reason the postulated compound was prepared indirectly by bromination at C-4 of methyl 3,11-diketo-12α-bromocholanate 3-(2,4-dinitrophenylhydrazone) in chloroform. The 3-hydrazone of the 4-bromosteroid was isolated[5] in crystalline form and its physical characteristics were determined. When this compound was dissolved in acetic acid hydrogen bromide was spontaneously eliminated and the Δ^4-steroidal hydrazone was separated in excellent yield.

It has now been shown that when the 3-keto-4-bromosteroid was added to 2,4-dinitrophenylhydrazine in a 1:1 mixture of acetic acid and chloroform at 0° the 3-hydrazone of the 4-bromosteroid was formed and that at this temperature hydrogen bromide was very slowly eliminated. After the acetic acid had been removed by washing at 0° with water, the compound was obtained in a yield of 80% and was found to be identical with the material previously prepared by bromination of the saturated steroidal hydrazone. The separation of this unstable intermediate product furnishes additional support for the mechanism of the reaction suggested by Mattox and Kendall.

Methyl 3,11-Diketo-4,12α-dibromocholanate 3-(2,4-Dinitrophenylhydrazone).—To a solution of 500 mg. of 2,4-dinitrophenylhydrazine in 150 ml. of chloroform and 150 ml. of acetic acid which was freed of air with a stream of carbon dioxide and cooled to 0°, 559 mg. of methyl 3,11-diketo-4,12α-dibromocholanate was added and the mixture was agitated at intervals to effect complete solution. After 1.5 hours at 0°, 300 ml. of water was added, the chloroform solution was separated, washed quickly with dilute acetic acid, 0.10 N sulfuric acid, dilute sodium bicarbonate solution and water, and was filtered through a pad of sodium sulfate. The solution was concentrated immediately under reduced pressure to about 5 ml., diluted with 25 ml. of absolute ether and cooled in a Dry Ice–acetone-bath. The yellow crystals (591 mg.) which separated melted at 135–137°; $\lambda_{\max}^{\text{chloroform}}$ 361 mμ, ε 26,400; $[\alpha]_D$ −162 ± 2° (chloroform).

The melting point, optical activity and absorption spectra of the compound, in both the ultraviolet and infrared regions, were identical with those of an authentic sample which had been prepared by Dr. V. R. Mattox in this Laboratory by bromination of the saturated hydrazone.

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[1] Abridgment of portion of thesis submitted by Mr. McGuckin to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Fellow in Biochemistry.

[3] (a) V. R. Mattox and E. C. Kendall, THIS JOURNAL, **70**, 882 (1948); (b) V. R. Mattox and E. C. Kendall, *J. Biol. Chem.*, **185**, 601 (1950).

[4] Carl Djerassi, THIS JOURNAL, **71**, 1003 (1949).

[5] V. R. Mattox and E. C. Kendall, *ibid.*, **72**, 2290 (1950).

High Vapor Pressure of *n*-Hexadecafluoroheptane[1]

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Recently the vapor pressure of this compound below two atmospheres was published with other thermodynamic properties.[2] In the course of testing a method to determine critical temperature and pressure, by means of vapor pressure measurements in the region of the critical point, vapor pressure data were measured on *n*-hexadecafluoroheptane from two atmospheres to the critical point.

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[1] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

[2] G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).