cal values of the "A-factors." The experimental ratios of the "A-factors" are given in column two of Table V.

A_1 refers to the dimerization of tetrafluoroethylene, A_3 to trifluorochloroethylene, and A_2 to the interdimerization. The experimental "A-factors" are in the ratio of 4/2/1. If one assumes that octafluorocyclobutane is planar, the symmetry numbers would require ratios of 2/4/1; on the other hand, a puckered ring gives 8/4/1. Although the rotational and vibrational partition functions do not cancel completely in this case, it is doubtful if they can bring about an inversion of the ratios as indicated in column three. The kinetic data, therefore, favor the puckered ring.

BOULDER, COLORADO RECEIVED OCTOBER 10, 1951

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Specific Heat and Degree of Crystallinity of Polychlorotrifluoroethylene

BY JOHN D. HOFFMAN

The specific heats of slow-cooled and air-quenched samples of polychlorotrifluoroethylene (m.p. 210–212°) have been measured between 0 and 250° in a differential calorimeter. The calorimeter is described. By comparison of the experimental heat of fusion with the heat of fusion of the pure crystalline polymer obtained from Flory's theory by Bueche, the degree of crystallinity at 0° was found to be 0.82 ± 0.07 for the slow-cooled sample and 0.35 ± 0.03 for the air-quenched sample. The enthalpies of the pure crystals and supercooled liquid polymer were obtained as functions of temperature by a simple interpolation procedure. Comparison of these enthalpies with the observed enthalpies permitted the degree of crystallinity of both the air-quenched and slow-cooled polymer to be calculated as a function of temperature. The results for the slow-cooled sample were in good agreement with those obtained by Price by a volume method. The quenched sample showed a distinct tendency to crystallize on warming. Reasons were advanced for believing that the glass transformation temperature for this polymer is below −80°.

Introduction

The degree of crystallinity, X, of a polymeric system is usually defined by

$$X = (P_l - P_x)/(P_l - P_c) \qquad (1)$$

where P is an extensive property of the polymer, and the subscripts l, c, and x refer to the liquid, crystalline and mixed liquid + crystal polymer, respectively. In practice, P is most commonly the enthalpy, the volume, or an X-ray line intensity, all expressed on a per unit weight basis. The above definition of crystallinity obviously ignores surface energy and internal disorder effects in the crystals.

The principal difficulty in applying (1) to any practical case is to obtain P_c as a function of temperature. This was done for polyethylene[1] by extrapolating the enthalpies of the n-paraffins to infinite chain length for a series of temperatures, thus obtaining $H_c(T)$. In the case of polychlorotrifluoroethylene, such a scheme could not be used owing to a lack of suitable thermodynamic data on the shorter members of the series, so a somewhat different method was devised.

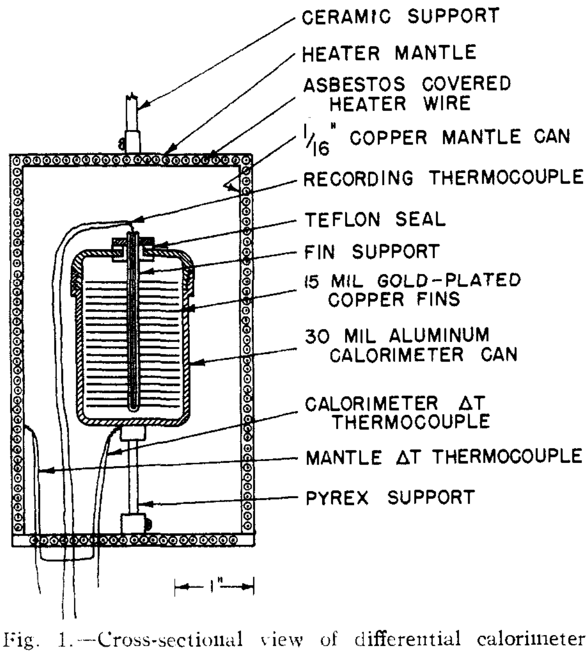

Fig. 1.—Cross-sectional view of differential calorimeter.

Price[2] has recently introduced a new method of obtaining the degree of crystallinity of polymers from volume–temperature plots provided that the glass transformation temperature, T_g, is known. The basis of this method is an ingenious way of fixing $V_c(T)$. If T_g is not known, the degree of crystallinity can still be bracketed. The bracketing procedure was used by Price to obtain the degree of crystallinity of slow-cooled polychlorotrifluoroethylene as a function of temperature, and it is one of the main objectives of this research to check his method with an independent determination of degree of crystallinity.

Apparatus.—The measurements were made in a differential calorimeter (Fig. 1) calibrated between 0° and 250° with diphenyl ether[3,4] and sapphire.[5] The assembly consisted of an outer heater mantle inside of which was supported an aluminum calorimeter. The shell of this calorimeter was made of aluminum instead of copper because polychlorotrifluoroethylene attacks copper at elevated temperatures. Special care was taken to design an efficient fin system so that fusion points and transition points would not be unduly smeared out, as is often the case with this type of calorimeter. It should be mentioned in this connection that the fusion of a purified sample of diphenyl ether occurred over less than 0.4°. The fins were made of 15 mil gold-plated oxygen-free copper spaced 1.6 mm. apart. Care was also taken to provide materials of high thermal

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(1) H. C. Raine, R. B. Richards and H. Ryder, *Trans. Faraday Soc.*, **41**, 56 (1945).

(2) F. P. Price, *J. Chem. Phys.*, **19**, 973 (1951).

(3) G. F. Furukawa, D. C. Ginnings, R. E. McCoskey and R. A. Nelson, *J. Res. Natl. Bur. Stds.*, **46**, 195 (1951).

(4) The author is indebted to Dr. Defoe C. Ginnings for use of these data prior to its publication.

(5) D. C. Ginnings and R. J. Corruccini, *J. Res. Natl. Bur. Stds.*, **38**, 593 (1947).

conductivity for the inner side of the mantle can and in the calorimeter can. The ΔT thermocouples were inserted in holes drilled in the appropriate place and covered with annealed gold and tamped in place.

In operation, the copper–copnic thermocouples on the mantle can and the aluminum calorimeter can were opposed, and the current in the heater coil controlled so that the net voltage difference was always a 0.600 ± 0.002 millivolt. This corresponded to a temperature difference (ΔT) of 15.40° at 0° and 10.83° at 250°. In this research, the mantle was the warmer of the two. The resultant voltage of 0.600 millivolt was bucked out by a 0.600 millivolt standard source. Consequently, when a sensitive galvanometer was connected in series in this circuit its deflection was zero when the ΔT was correct. This scheme had an advantage over using a galvanometer 0.600 millivolt off the true null, because changes in ΔT due to changes in the galvanometer suspension were avoided. The time–temperature data were obtained by connecting the copper–copnic thermocouple situated in the center of the fin system to a recording potentiometer.

If Φ is the heat input to the calorimeter in cal./min., S_e the rate of warming in °C./min. of the empty calorimeter, and S_f the rate of warming of the full calorimeter, it is easily shown that

$$M_x c_p = \Phi(1/S_f - 1/S_e) \qquad (2)$$

where M_x is the weight of sample and c_p its specific heat. The calorimeter was run empty to obtain S_e as a function of temperature, and then run with sapphire or diphenyl ether. In this way Φ was evaluated as a function of temperature.

The heat of fusion of diphenyl ether was also used to find Φ at 26.8°. In the case of latent heats, Φ is given by

$$\Phi = M_x \Delta h_f / t \qquad (3)$$

Δh_f is the heat of fusion in cal./g. and t the time required for fusion. Φ increased from 8.44 at 0° to 12.40 at 250° because the thermal conductivity of air increases more rapidly with rising temperature than was compensated for by the concomitant drop of ΔT. Knowing Φ and $1/S_e$ as a function of temperature, it was a simple matter to insert the values of $1/S_f$ obtained from the recorded time–temperature curves and find c_p for an unknown. Using the values of $1/S_e$ and Φ obtained with diphenyl ether, the specific heat of sapphire was obtained to within ±0.8% over the entire range. The average rate of rise with a normal load was ~ 0.4°/min.

Materials.—Powdered Kel-F high molecular weight polychlorotrifluoroethylene was pressed at about 250° into sheets 1 mm. thick and quenched by cooling in air at room temperature. These sheets had a clear appearance. After being melted and then cooled slowly in the calorimeter to obtain a more crystalline polymer, the sheets appeared to be cloudy.

Procedure.—25.91 g. of the air-quenched polymer sheets cut in semicircular shapes was inserted between the fins in the calorimeter, and heat capacity measurements made from 0° to 100° (Run 1). The sample was then cooled down and a run made to 250° (Run 2). The results of Runs 1 and 2 were very similar, so the data were combined and listed as "air-quenched." The material was then cooled at a rate of ~9°/min. from 250° to room temperature and another run made to 250° (Run No. 3). This slow-cooling procedure was then repeated again, but at a rate of 5°/min., and another run made (Run No. 4). Runs 3 and 4 gave nearly identical results and were combined to give the data listed as "slow-cooled."

Results

The specific heats of air-quenched and slow-cooled samples of polychlorotrifluoroethylene are given in Table I.

Calculation of Enthalpies and Degree of Crystallinity.—The heat of fusion, Δh_f, of "pure" crystalline polychlorotrifluoroethylene obtained by Bueche[6] was 10.3 ± 0.6 cal./g. The deviation given is the mean deviation of the results for the three solvents used. Some confidence may be placed in this value, particularly since it has been shown that Flory's method[7] gives good agreement between the known heats of fusion of *n*-paraffins and polyethylene and the melting points of crystals of these materials in the presence of small amounts of solvents.[4] It should be mentioned that Bueche's experiments were carried out in a concentration range where Flory's theory is applicable, *i.e.*, for a high ratio of polymer to solvent.

TABLE I

SPECIFIC HEAT OF POLYCHLOROTRIFLUOROETHYLENE BETWEEN 0° AND 250°

T, °C.	Air-quenched c_p, cal./g./°C.	T, °C.	Slow-cooled c_p, cal./g./°C.
0.0	0.211[a]	0.0	0.200[a]
17.0	.218	10.0	.204
37.4	.225	25.0	.209
63.1	.235	42.0	.214
70.0	.238	72.1	.231
72.3	.236	115.3	.259
83.3	.242	156.0	.291
115.4	.257	190.0	.337
156.0	.272	206.0	.608
184.0	.305	211.1	1.09
197.5	.398	212.0	0.98
202.0	.50	213.0	.38
206.8	.690	220.0	.340
209.4	.702	240.8	.340
211.5	.371	$\Delta h_f' = 8.40 \pm 0.2$ cal./g.	
222.4	.339		
240.8	.340		
$\Delta h_f'' = 3.6 \pm 0.1$ cal./g.			

[a] Extrapolated values.

The experimental value of the heat of fusion of the slow-cooled sample was 8.40 ± 0.20 cal./g.; the value for the air-quenched sample was 3.60 ± 0.1 cal./g. These values were obtained by graphical integration under the specific heat maxima using the extrapolated specific heat of the specimen at low temperatures as a base line.[8]

The degree of crystallinity at 0°, where it may safely be stated that $\mathrm{d}X/\mathrm{d}T = 0$, is thus (3.6 ± 0.1)/(10.3 ± 0.6) or 0.35 ± 0.03 for the air-quenched sample and (8.40 ± 0.20)/(10.3 ± 0.6) or 0.816 ± 0.07 for the slow-cooled sample. The principal uncertainty in these results is in the estimated heat of fusion of the pure crystals.

In order to find the degree of crystallinity of the polymer at higher temperatures, it will be necessary to insert the appropriate enthalpy data in (1). The raw enthalpies (not given) were calculated from the usual formula

$$(H_x - H_0{}^{\prime,\prime\prime})\Big|_0^T = \int_0^T c_p \mathrm{d}T \qquad (4)$$

where H_0' was the enthalpy of the slow-cooled material at 0° and H_0'' the enthalpy of the air-quenched material. The enthalpy of the liquid polymer must be the same in each case, and it was found that when 1.50 cal./g. was added to the data for the air-quenched sample, the liquid values coincided exactly; thus, $H_0' + 1.50 = H_0''$.

Assuming $\mathrm{d}X/\mathrm{d}T = 0$, the enthalpy of the pure

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(6) A. M. Bueche, THIS JOURNAL, **74**, 65 (1952).

(7) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949); R. D. Evans, H. P. Mighton and P. J. Flory, THIS JOURNAL, **72**, 2018 (1950).

(8) This may make $\Delta h_{f(x)}$ somewhat high, but not enough to change the results more than a few per cent.

liquid and pure crystalline polymer may now be found at 0° from the following simultaneous equations based on equation (1).

$$0.816 = [(H_l - H_0') - 0]/(H_l - H_c) \qquad (5)$$

for the slow-cooled material, and

$$0.350 = [(H_l - H_0') - 1.50]/(H_l - H_c) \qquad (6)$$

for the air-quenched polymer. $(H_l - H_0')$ turns out to be 2.63 cal./g. and $(H_c - H_0')$ comes to −0.60 cal./g.

For convenience, the calculated enthalpy of the pure crystals at 0°, H_0, will be taken as the reference point for all the enthalpies. Hence, $H_0' = H_0 + 0.60$ and $H_0'' = H_0 + 2.10$ transposed to the new zero. Thus, the corrected enthalpy of the liquid, $H_l - H_0$, at 0° is 0.60 + 2.63 or 3.23 cal./g. ($H_0''' = H_0 + 3.23$), and that of the crystals, $H_c - H_0$, is zero. For the air-quenched sample at 0° $(H_x - H_0)$ is 2.10 cal./g. and $(H_x - H_0)$ is 0.60 for the slow-cooled material. The enthalpies of the air-quenched and slow-cooled material based on the same standard state are given in the first two columns of Table II.

TABLE II

ENTHALPY OF POLYCHLOROTRIFLUOROETHYLENE

H_0 = Enthalpy of Crystals at 0°

T°	$(H_x - H_0)$ Air-quenched	$(H_x - H_0)$ Slow-cooled	$(H_c - H_0)$ Liquid	$(H_c - H_0$ Crystal
0	2.10	0.60	3.23[a]	0.0[a]
50	13.00	11.03	14.45	10.25
100	25.10	22.67	27.01	21.42
150	38.10	36.03	40.93	33.50
190	49.60	48.33	52.99	43.80
200	53.30	52.20	56.15	46.48
210	59.05	58.10	59.35	49.19
212	60.05	60.00	60.00[a]	49.70[a]
215	61.10	61.10	...	...
230	66.20	66.20	...	...
250	73.00	73.00	72.73	...

[a] Calculated values used for interpolation.

The next step is that of finding the enthalpy of the pure liquid and pure crystal as a function of temperature so the degree of crystallinity may be found from (1). At 212° $(H_l - H_0)$ is 60.00 cal./g. It then follows that $(H_c - H_0)^{212°} = (H_l - H_0)_0^{212°} - \Delta h_f$ or 49.70 cal./g. Consequently, $(H_l - H_0)$ and $(H_c - H_0)$ are known at both 0° and 212°, and all that need be done to obtain $(H_l - H_0)$ and $(H_c - H_0)$ as functions of temperature for use in (1) is to find a reasonable basis for interpolation.

The best assumption is that the specific heat of the pure liquid or pure crystal is linear with temperature. Away from the vicinity of melting or lambda points, and in the absence of quantal phenomena, this assumption is remarkably good for many substances. For diphenyl ether,[3] for example, the specific heat of the liquid does not vary more than 0.04% from linearity between 26.8° and 226.8°, and the specific heat of the solid between −73.2° and 26.8° varies no more than 1% from linearity. In order to make the desired interpolation it is required to know the specific heat of the liquid and crystal at 0°. At 0° the specific heats may be regarded as additive since $dX/dT = 0$. The specific heat of the air-quenched sample at 0° is 0.211, and that of the slow-cooled, 0.200 cal./g. Thus, using the notation c_{p^0} (l) and c_{p^0}(c) to denote the specific heat of the pure liquid and pure crystals at 0°

$$0.350 = [c_{p0}(l) - 0.211]/[c_{p0}(l) - c_{p0}(c)] \qquad (7)$$

$$0.816 = [c_{p0}(l) - 0.200]/[c_{p0}(l) - c_{p0}(c)] \qquad (8)$$

whence $c_{p^0}(l) = 0.219$ and $c_{p^0}(c) = 0.196$ cal./g./° C. Using these data with the assumption that $c_p(T)$ is linear with temperature, *i.e.*, $c_p(T) = c_{p^0} + BT$, it is readily seen that for the pure crystals

$$(H_c - H_0)_0^{212} = 49.70 = \int_0^{212} (c_{p0(c)} + BT)dT \quad (9)$$

and for the pure liquid

$$(H_l - H_0''')_0^{212} = 56.77 = \int_0^{212} (c_{p0(l)} + B'T)dT \qquad (10)$$

where $H_0''' = H_0 + 3.23$ cal./g.

It is found from (9) and (10) that $B = 1.82 \times 10^{-4}$ and $B' = 2.68 \times 10^{-4}$ so that

$$(H_c - H_0)\Big|_0^T = 0.196T + 1.82 \times 10^{-4}T^2 \qquad (11)$$

and

$$(H_l - H_0)\Big|_0^T = 3.23 + 0.211T + 2.68 \times 10^{-4}T^2 \quad (12)$$

Enthalpy values calculated from (11) and (12) have been entered in Table II and plotted in Fig. 4. The interpolated values of the basal specific heats are plotted in Figs. 2 and 3 with dashed lines. It is satisfactory that the liquid enthalpy forms a smooth continuation of the observed liquid values at 212° and higher.

The degree of crystallinity of the polymer between 0° and 212° may now be calculated from the data in Table II by use of the appropriate form of equation (1)

$$X = [(H_l - H_0) - (H_x - H_0)]/[(H_l - H_0) - (H_c - H_0)] \qquad (13)$$

The results of these calculations are shown in Table III and plotted in Fig. 5.

TABLE III

DEGREE OF CRYSTALLINITY OF POLYCHLOROTRIFLUOROETHYLENE AS A FUNCTION OF TEMPERATURE

T, °C.	Air-quenched	Slow-cooled
0	0.350	0.816
50	.345	.815
100	.342	.778
150	.380	.660
190	.370	.507
200	.295	.410
210	.030	.124
212	.0	.00

Discussion

The degree of crystallinity of polychlorotrifluoroethylene obtained by the present method and that obtained by Price[2] agree to within about ±6% which may be regarded as satisfactory.

The slow-cooled sample apparently contains a few small crystallites which melt as low as 80 to 100°. This may be seen in Fig. 5, or by inspection of the specific heat data in Fig. 2. The air-

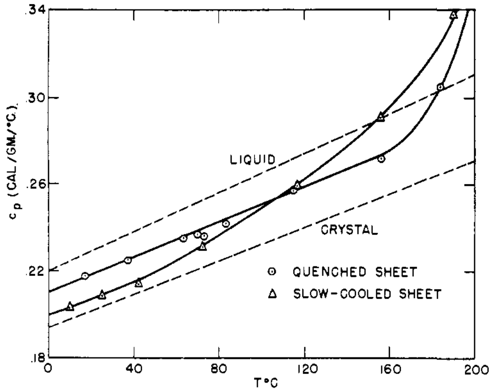

Fig. 2.—Specific heat of polychlorotrifluoroethylene between 0° and 200°. Dashed lines are computed pure liquid and crystal curves.

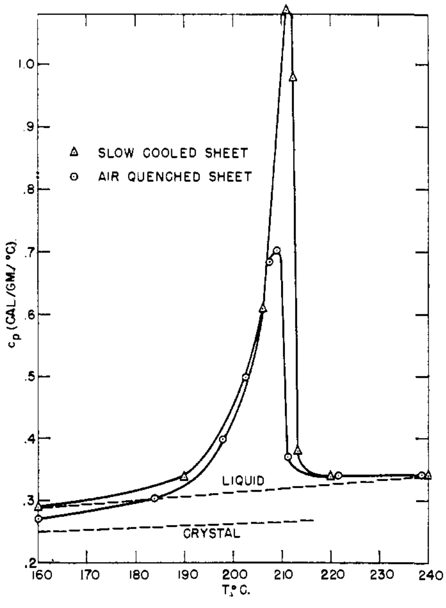

Fig. 3.—Specific heat of polychlorotrifluoroethylene near the fusion point.

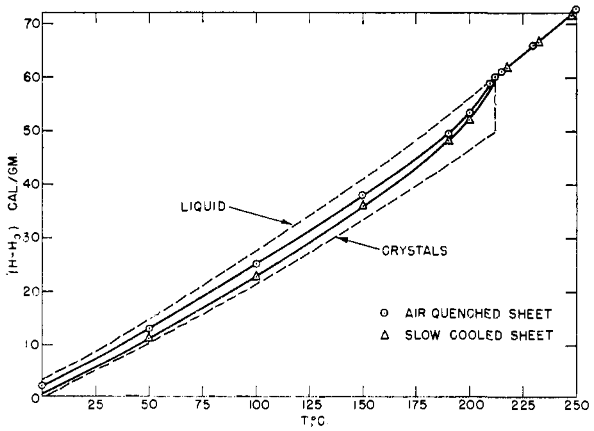

Fig. 4.—Enthalpy of polychlorotrifluoroethylene as a function of temperature. Dashed lines are calculated liquid and crystal values.

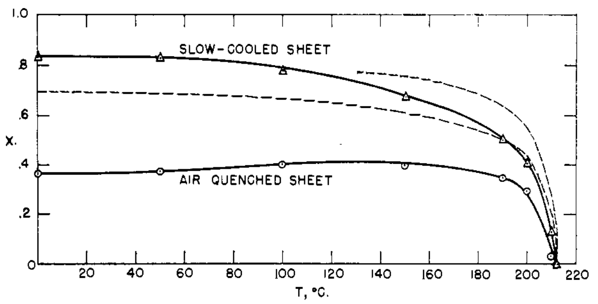

Fig. 5.—Degree of crystallinity of polychlorotrifluoroethylene as a function of temperature. The dashed lines show the limits set by Price's volume method.

quenched sample shows a definite increase in crystallinity as it is warmed. This must be due to sub-cooled liquid forming crystallites as the viscosity decreases sufficiently to permit diffusion to the crystallite surface. Price noted that the volume of a quenched sample actually decreased even at 100° as the sample stood overnight, and the explanation of this must be the same as that given for the presence of the maximum in the degree of crystallinity curve of the quenched sample.

A slight "tail" in the specific heat of the slow-cooled sample above 212° indicates that a few very large crystallites still exist above what appears as the macroscopic melting point, but this must account for less than 0.3% of the crystals, and they have been ignored in the calculations. Inspection of the specific heat data suggests a wider distribution of crystallite sizes in the slow-cooled sample than in the air-quenched material.

No glass transformation has appeared in the supercooled liquid phase down to 0°. If a plot[9] is made of the temperature at which the dielectric loss, ϵ'', is a maximum *vs.* seconds/cycle for this polymer using data of Reynolds,[10] an extrapolation[11] to 10 seconds/cycle (or "experiment") leads to −90° and an extrapolation to 100 seconds/cycle leads to −120°. This should be in the vicinity of $T_{g(\text{thermal})}$. The brittle point for a high molecular weight polymer is usually 5 to 20° above T_g. A crude experiment wherein polychlorotrifluoroethylene was bent rapidly at −90° showed the polymer was not brittle. The above evidence would tend to indicate that T_g is well below −80° for this polymer. This does not agree with the estimate of T_g made by Price by extrapolation of the volume of the liquid polymer to low temperatures, but this does not invalidate his method of obtaining degree of crystallinity. A relatively large error in T_g does not necessarily mean $X(T)$ by the volume method will be greatly in error because his method is quite insensitive to the exact value of T_g.

If the calculated specific heat data for the pure liquid and pure crystal are extrapolated until they coincide, it is found that they do so at −93 ± 20°. If this extrapolation is valid and T_g is below −90°, it would mean that T_g would be difficult, if not impossible, to observe thermally because the increase of c_p would be very small in this temperature region.

Finally, it is worth pointing out that the results

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(9) W. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

(10) Unpublished data of S. I. Reynolds.

(11) Both the liquid and crystalline portions show dipole rotation. Care was taken to use the lower temperature (liquid) peaks for the calculations.

of this work could be viewed in another way. If the degree of crystallinity obtained by Price's volume method were accepted and combined with the observed heat of fusion for the slow-cooled sample, the calculated heat of fusion of the pure crystals would be (8.40 ± 0.2)/(0.75 ± 0.05) or 11.2 ± 1.0 cal./g., which is in good agreement with the value 10.3 ± 0.6 obtained by Bueche by application of Flory's theory.

Acknowledgment.—The author is indebted to Dr. A. M. Bueche of this Laboratory for use of data prior to publication and for suggesting the present application of Flory's theory as a basis for crystallinity measurements. Thanks are also due Dr. Defoe C. Ginnings of the Bureau of Standards, and Mr. S. I. Reynolds of the laboratory, for use of data prior to publication.

SCHENECTADY, NEW YORK RECEIVED AUGUST 1, 1951

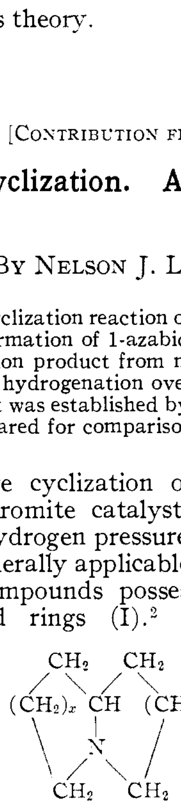
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reductive Cyclization. A Route to 6-Methyl-1-azabicyclo[5.3.0]decane from Methyl Sorbate[1]

BY NELSON J. LEONARD, DONALD L. FELLEY AND ERNEST D. NICOLAIDES

The reductive cyclization reaction of nitro α,ω-diesters, recognized as general for the preparation of pyrrolizidines, has been extended to the formation of 1-azabicyclo compounds containing one five- and one seven-membered ring. As an example, the Michael addition product from methyl γ-nitrobutyrate with methyl sorbate gives 6-methyl-1-azabicyclo[5.3.0]decane when subjected to hydrogenation over copper chromite at high temperature and pressure. The structure of the reductive cyclization product was established by comparison with a sample prepared by an unequivocal method. 1-*n*-Propylpyrrolizidine was also prepared for comparison with the isomeric base.

The reductive cyclization of oximino diesters over copper chromite catalyst at high temperature and high hydrogen pressure has been shown to be a method generally applicable to the synthesis of 1-azabicyclo compounds possessing five-, six- or seven-membered rings (I).[2] Similar conditions applied to γ-nitropimelic esters provide the most convenient route to pyrrolizidine (I, $x = y = 1$) and substituted pyrrolizidines.[3] Thus far, γ-nitropimelic esters, as obtained by the addition of nitroparaffins to acrylic or substituted acrylic esters, constitute the only group of nitro diesters available and successfully applied in the reductive cyclization process. It should be possible to obtain 1-azabicyclo[5.3.0]decane (I, $x = 1$, $y = 3$) and substituted bases possessing this ring system if the requisite precursor γ(ε')-nitro diesters could be made available by 1,6-addition of a γ-nitro monoester to an α,β;γ,δ-unsaturated ester.


I

The model γ(ε')-nitro diester (II) selected for study would, it was hoped, be available by 1,6-addition of methyl γ-nitrobutyrate to methyl sorbate. The reductive cyclization product from II would then be 6-methyl-1-azabicyclo[5.3.0]decane (III). By contrast, if the Michael addition of methyl γ-nitrobutyrate to methyl sorbate occurred in the 1,4-manner, the intermediate γ(γ')-nitro diester (IV) would give 1-*n*-propylpyrrolizidine (V) on reductive cyclization. The addition of methyl γ-nitrobutyrate[3] to methyl sorbate was carried out in the presence of diisopropylamine[4] to give, in 32% yield, a nitro diester with the molecular formula, $C_{12}H_{19}NO_6$, requisite for II, IIa or IV. Evidence available from infrared and molar refractivity data favored an unconjugated structure for this diester and therefore, presumably, formula II. Hydrogenation of $C_{12}H_{19}NO_6$ in dioxane at 260° and 300 atmospheres in the presence of copper chromite catalyst produced a tertiary amine, $C_{10}H_{19}N$, in 60% yield. The base was characterized by the formation of picrate (m.p. 188.5–189.5°) and picrolonate (m.p. 200–202°) derivatives.

Since a general method exists for the facile preparation of 1-alkylpyrrolizidines,[4] the possibility that the $C_{10}H_{19}N$ reductive-cyclization product might be 1-*n*-propylpyrrolizidine was explored by utilizing this method for the unequivocal synthesis of V. The addition of nitromethane to ethyl 2-hexenoate in the presence of benzyltrimethylammonium butoxide at 80° gave ethyl β-*n*-propyl-γ-nitrobutyrate in 71% yield, and this product, on condensation with ethyl acrylate in the presence of the same catalyst, gave diethyl β-*n*-propyl-γ-nitropimelate (VI) in 53% yield. Reductive cyclization of the nitro diester VI over copper chromite catalyst produced 1-*n*-propylpyrrolizidine (V) in 79% yield. The picrate (m.p. 143–145°) and picrolonate (m.p. 164–166°) formed by V differed from the corresponding derivatives of the $C_{10}H_{19}N$ base obtained by the methyl sorbate route. The physical properties (infrared absorption spectra, refractive indices) of the bases were also substantially different. Such evidence can be considered as eliminating 1-*n*-propylpyrrolizidine (which will exist in two racemic forms) as the structure of the methyl sorbate final product only if it is argued that equivalent racemates should

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[1] This work was supported in part by a grant from E. I. du Pont de Nemours and Company, Inc.

[2] N. J. Leonard and W. E. Goode, THIS JOURNAL, **72**, 5404 (1950).

[3] For leading reference, see N. J. Leonard and D. L. Felley, *ibid.*, **72**, 2537 (1950).

[4] N. J. Leonard and D. L. Felley, *ibid.*, **71**, 1758 (1949).