CHEMISTRY

=========

1960

SovietRxiv

structural formulas of bicyclo-(2,2,1)-heptadiene-2,5 (I) and cycloheptatriene (II)

Figure 1: structural formulas of bicyclo-(2,2,1)-heptadiene-2,5 (I) and cycloheptatriene (II)

Abstract

Full Text

CHEMISTRY

M. A. PRYANISHNIKOVA, G. M. DUGACHEVA, A. F. PLATE, and A. G. ANIKIN

STUDY OF THE CRYSTALLIZATION TEMPERATURES OF BICYCLO-(2,2,1)-HEPTADIENE-2,5 AND CYCLOHEPTATRIENE AND THEIR MIXTURES

(Presented by Academician B. A. Kazanskii, January 14, 1960)

Recently (1) we described the synthesis and some physical properties of bicyclo-(2,2,1)-heptadiene-2,5 (I)—the starting material for the production of the insecticide aldrin—and of the product of its isomerization, cycloheptatriene (II)

It is known that the parameter most sensitive to the presence of foreign impurities in a substance and most suitable for determining the degree of purity of a preparation is the crystallization temperature. Therefore, in the present work the crystallization temperatures, cryoscopic constants, and degree of purity of hydrocarbons (I) and (II) were determined. The melting diagram of the bicycloheptadiene—cycloheptatriene system was also studied. The cryoscopic method that we used has been published previously (2).

The hydrocarbons were preliminarily purified by double distillation on a column with an efficiency of 50 theoretical plates and with a glass packing. For the investigation, several middle fractions obtained in the distillation were taken, lying on a plateau and having identical boiling temperatures, refractive index, and specific gravity. This made it possible to establish which fraction was the purest. The amount of impurities was determined from the lowering of the crystallization temperature. Each experiment required 1.5–2 ml of substance. The crystallization temperature was measured with an accuracy of up to ±0.05°C. The data obtained, as well as other constants of the substances investigated, are given in Table 1.

Fig. 1. Crystallization curve of cycloheptatriene

Figure 2: Fig. 1. Crystallization curve of cycloheptatriene

Fig. 2. Crystallization curve of bicycloheptadiene

Figure 3: Fig. 2. Crystallization curve of bicycloheptadiene

Table 1

Hydrocarbon	B.p., °C	n_D^{20}	d_4^{20}	Crystallization temp., °C, starting substance	Crystallization temp., °C, absolutely pure substance	Cryoscopic constant, mole fraction per °C	Purity of preparation, mol. %
Bicyclo-(2,2,1)-heptadiene-2,5	90.3	1.4702	0.9064	−19.1	−18.9	0.007	99.86
Cycloheptatriene	115.6	1.5244	0.8915	−75.1	−74.8	0.005	99.85

Figures 1 and 2 show the crystallization curves of the initial preparations. The data available in the literature on the crystallization temperature of bicycloheptadiene are approximate in character ($\sim -25°$) (3). Therefore we do not discuss them. The crystallization temperature of cycloheptatriene was determined by Kohler (4) and Finke (5). Kohler' s data ($-79.49°$) differ significantly from from ours. Such a, at first glance, large discrepancy in crystallization temperature with close boiling points and refractive indices (b.p. 115.50°, n_D^{20} 1.5243) is, in essence, quite natural, since cycloheptatriene has a small cryoscopic constant, 0.005 (the dimension of the cryoscopic constant is given in mole fractions per degree Celsius). This means that even a very small amount of impurity leads to a noticeable lowering of the crystallization temperature.*

According to our calculations, Köhler' s preparation contained about 2.3% impurity, which is quite probable, since the substance is very easily altered. It should be noted that, when determining the crystallization temperature of cycloheptatriene, the substance must be carefully protected from air, since even brief (1 hour) exposure of the preparation, open to the air, already leads to a lowering of the crystallization temperature. Later Finke (5) obtained a crystal-

Fig. 1. Crystallization curve of cycloheptatriene

Fig. 2. Crystallization curve of bicycloheptadiene

lization temperature of cycloheptatriene coinciding with ours (−75.24°). The cryoscopic constant he gives (0.003564) is also close to ours.

The cryoscopic constants of the substances, necessary for estimating purity, were determined by us by measuring the lowering of the crystallization temperature from a definite amount of artificially introduced impurity. Various amounts (from 0.5 to 2%) of toluene and *n*-heptane were added to (I) and (II). The results obtained coincided in all cases for one and the same substance. We then tried to contaminate (I) and (II) with each other. They may be obtained in one and the same synthesis. This makes mutual contamination probable in cases where the substances are insufficiently purified (with careful purification this probability decreases, since, as is evident from Table 1, their parameters are sufficiently different).

We carried out experiments in which various amounts of (I) were added to (II), and conversely, and observed proportionality between the change in temperature and the amount of artificial impurity. When bicycloheptadiene is contaminated with cycloheptatriene, the usual picture of a lowering of the crystallization temperature by impurities is observed. With slight contamination, the crystallization temperature decreases in proportion to the amount of added impurity, in accordance with the laws for ideal and dilute solutions (Table 2).

Table 2

Nos.	Composition of the investigated mixture, %	Composition of the investigated mixture, %	Crystallization temp., °C	Difference between the crystallization temperatures of the mixture and cycloheptatriene, °C
	bicycloheptadiene	cycloheptatriene		
1	–	100,00	–75,07	–
2	0,21	99,79	–75,23	–0,16
3	0,44	99,56	–75,40	–0,33
4	0,80	99,20	–75,13	–0,06
5	1,67	98,33	–74,81	+0,26
6	3,38	96,62	–73,69	+1,38
7	7,26	92,74	–72,52	+2,55
8	20,01	79,99	–69,00	+6,07
9	57,84	42,16	–60,00	+15,07
10	84,77	15,23	–43,50	+31,57

---

* This, in particular, explains the large slope of the plateaus of the crystallization curves of cycloheptatriene and bicycloheptadiene shown in Figs. 1 and 2.

Nos.	Composition of the investigated mixture, %	Composition of the investigated mixture, %	Crystallization temp., °C	Difference between the crystallization temperatures of the mixture and cycloheptatriene, °C
11	95,42	4,58	−26,60	+48,47
12	97,73	2,27	−22,14	+52,93
13	98,81	1,19	−21,00	+54,07
14	100,00	–	−19,09	–

The cryoscopic constant calculated on the basis of these data coincides with the value obtained for this substance when toluene and *n*-heptane were the artificial impurities.

Fig. 3. Melting diagram of the cycloheptatriene—bicycloheptadiene system: *I* —cycloheptatriene 100%, *II* —bicycloheptadiene 100%.

In the case of an admixture of bicycloheptadiene to cycloheptatriene, a slight decrease in the crystallization temperature was observed only upon the addition of 0,2; 0,4 and 0,8% bicycloheptadiene. At an impurity concentration even slightly greater than 1%, the crystallization temperature of the mixture was already higher than the crystallization temperature of the pure substance (see Table 2, No. 5, etc., and Fig. 3).

When the crystallization temperatures of two substances differ greatly from one another (in the case studied, the crystallization temperature of (II) is −75.1°; of (I), −19.1°), the formation of a eutectic with a temperature close to the crystallization temperature of one of the components (usually the more low-melting one) is probable at a low concentration of the second component. This may lead to incorrect conclusions regarding the crystallization temperature and the purity of the substance—causing a contaminated substance to be regarded as pure. However, such cases are rare among systems of organic substances. In the work of Rossini and others [6], a case is described of the formation of a eutectic mixture of *p*-xylene (crystallization temperature +13.26°) and ethylbenzene (crystallization temperature −94.98°) at a *p*-xylene concentration equal to 3.5%. A similar case also occurs for the cycloheptatriene-bicycloheptadiene mixture. Indeed, by continuing the study of the melting curve of system (I)—(II), we obtained the data of Table 2. From Fig. 3 it is seen that the eutectic point of such a system is located at a temperature of about −75.5° and corresponds to a mixture containing ∼ 0.5% bicycloheptadiene.

Institute of Organic Chemistry named after N. D. Zelinsky

Academy of Sciences of the USSR

Moscow State University
named after M. V. Lomonosov

Received
12 I 1960

CITED LITERATURE

1. A. F. Plate, M. A. Pryanishnikova, *Izv. AN SSSR, OKhN*, 1956, 741; N. A. Belikova, L. G. Vorontsova et al., *ZhPKh*, **33**, 454 (1960).
2. A. G. Anikin, G. M. Dugacheva, *DAN*, **119**, 939 (1958).
3. L. Schmerling, J. P. Luvisi, R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).
4. E. P. Kohler, M. Tishler et al., *J. Am. Chem. Soc.*, **61**, 1057 (1939).
5. H. L. Finke, D. W. Scott et al., *J. Am. Chem. Soc.*, **78**, 5469 (1956).
6. F. D. Rossini, B. J. Mair, A. J. Streiff, *Hydrocarbons of Petroleum*, L., 1957, p. 214.

Note: Figure translations are in progress. See original paper for figures.