are readily distinguishable by characteristic infrared bands for each ring structure.

4. The properties of hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane are given.

5. New crystalline isomers of methyl phenyl and ethyl phenyl cyclotetrasiloxane systems are presented.

6. Optical as well as geometrical stereoisomeric cyclosiloxane compounds are postulated.

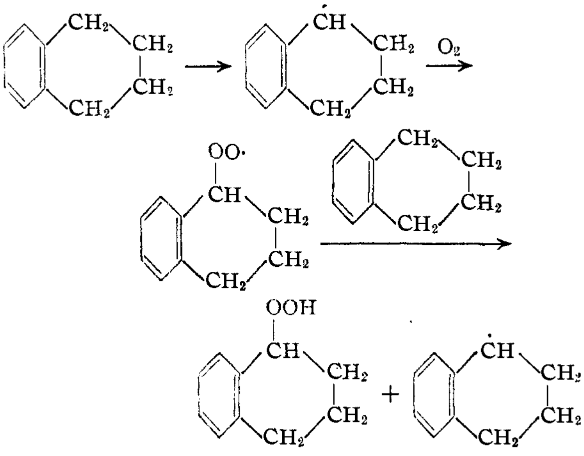
MIDLAND, MICHIGAN RECEIVED JUNE 7, 1948

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

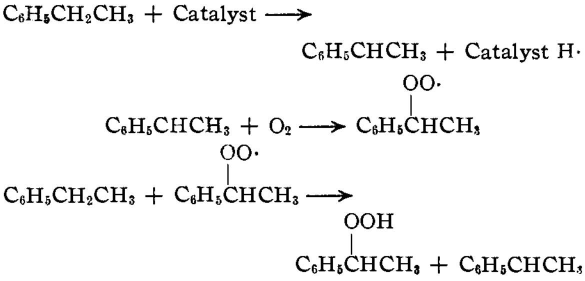
The Liquid Phase Oxidation of Ethylbenzene

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS,[1] WILLIAM B. COOK,[2] WARREN I. LYNESS[3] AND JAMES K. STEVENSON[4]

The catalytic liquid phase oxidation of tetralin to α-tetralone has been shown to proceed through tetralin hydroperoxide by a free radical mechanism.[5] The formation of the hydroperoxide is a simple chain reaction.[6] The exact process by which the peroxide decomposes is not known, although a mechanism involving the formation of hydroxyl free radicals has been suggested.[5]



The catalytic, liquid phase oxidation of ethylbenzene by air to give acetophenone probably proceeds by a similar mechanism.

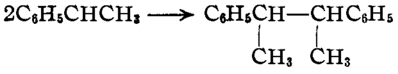


$$C_6H_5CH_2CH_3 + \text{Catalyst} \longrightarrow C_6H_5CHCH_3 + \text{Catalyst H}\cdot$$

$$C_6H_5CHCH_3 + O_2 \longrightarrow C_6H_5\overset{OO\cdot}{C}HCH_3$$

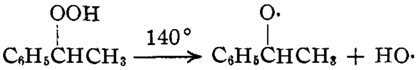
$$C_6H_5CH_2CH_3 + C_6H_5\overset{OO\cdot}{C}HCH_3 \longrightarrow C_6H_5\overset{OOH}{C}HCH_3 + C_6H_5CHCH_3$$

That the first step is the loss of a hydrogen atom to give an α-phenylethyl free radical is shown by the fact that Sully[7] isolated its dimer, 2,3-diphenylbutane, from the higher boiling by-products of the oxidation. We also have isolated and identified 2,3-diphenylbutane.



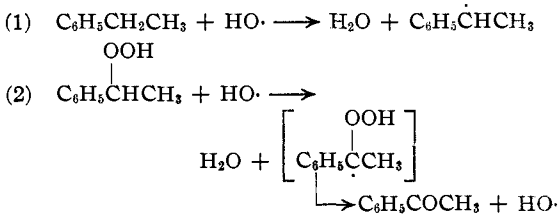
$$2C_6H_5\dot{C}HCH_3 \longrightarrow C_6H_5\underset{CH_3}{CH}-\underset{CH_3}{CH}C_6H_5$$

The decomposition of α-phenylethyl hydroperoxide may occur by a number of mechanisms of which two seem the most probable. At 140° it could decompose thermally into two free radicals. Dialkyl peroxides



$$C_6H_5\overset{OOH}{C}HCH_3 \xrightarrow{140°} C_6H_5\overset{O\cdot}{C}HCH_3 + HO\cdot$$

are known to decompose at 130–160°.[8] The hydroxyl free radicals thus generated could either attack an ethylbenzene molecule or assist in the decomposition of the hydroperoxide.

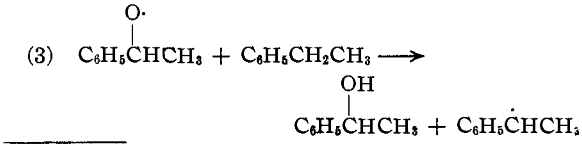


$$(1)\quad C_6H_5CH_2CH_3 + HO\cdot \longrightarrow H_2O + C_6H_5\dot{C}HCH_3$$

$$(2)\quad C_6H_5\overset{OOH}{C}HCH_3 + HO\cdot \longrightarrow H_2O + \left[C_6H_5\overset{OOH}{\underset{\cdot}{C}}CH_3\right] \rightarrow C_6H_5COCH_3 + HO\cdot$$

This last reaction is the same as that suggested by Robertson and Waters[5] in the case of tetralin hydroperoxide, except that they generated their initial hydroxyl free radicals by reaction between the catalyst and the hydroperoxide. This type of hydroxyl free radical generation also could occur in the case of α-phenylethyl hydroperoxide.

The α-phenylethoxy free radicals, from the thermal decomposition of the hydroperoxide, would undergo the same reactions as the hydroxyl free radicals.



$$(3)\quad C_6H_5\overset{O\cdot}{C}HCH_3 + C_6H_5CH_2CH_3 \longrightarrow C_6H_5\overset{OH}{C}HCH_3 + C_6H_5\dot{C}HCH_3$$

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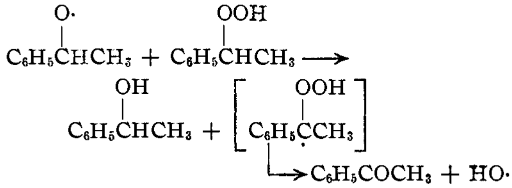
(5) Robertson and Waters, *Trans. Faraday Soc.*, **42**, 201 (1946).

(6) George and Robertson, *ibid.*, **42**, 217 (1946).

(7) Sully, *ibid.*, **42**, 260 (1946).

(8) Raley, Rust and Vaughan, THIS JOURNAL, **70**, 88 (1948).

(4) 

$$C_6H_5\overset{O\cdot}{C}HCH_3 + C_6H_5\overset{OOH}{C}HCH_3 \longrightarrow C_6H_5\overset{OH}{C}HCH_3 + \left[C_6H_5\underset{\cdot}{\overset{OOH}{C}}CH_3\right] \longrightarrow C_6H_5COCH_3 + HO\cdot$$

Both of these reactions lead to the formation of methylphenylcarbinol. Such a thermal decomposition of α-phenylethyl hydroperoxide would account for the fact that in our work and in that of others[7,9] the acetophenone produced always contains 20–25% of methylphenylcarbinol.

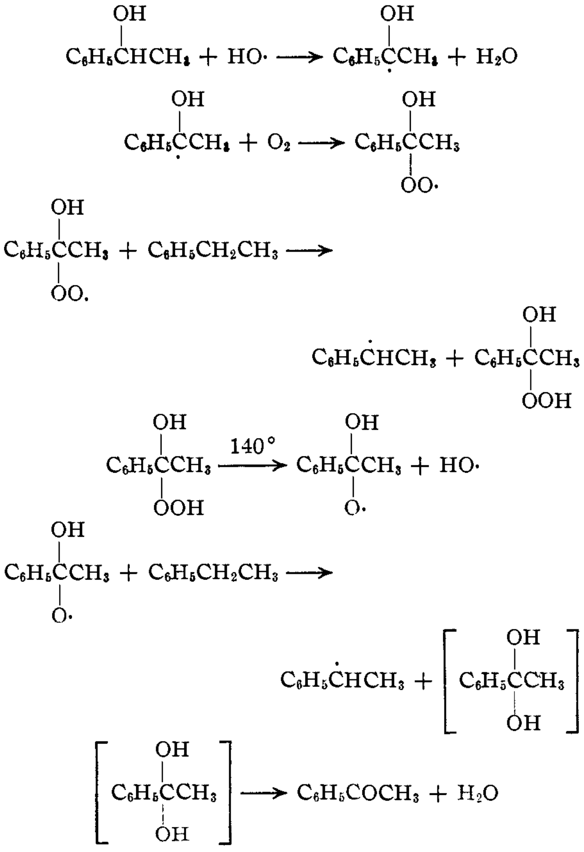
Water is known to inhibit this type of oxidation.[10] We have found that while water prevents such oxidations from starting, its addition after hydroperoxide formation is well established does not decrease the conversion but does increase the amount of carbinol in the product. In two runs of three and one-half hours duration the conversion was 21.7–22.6% to a mixture of 74% of acetophenone and 26% of methylphenylcarbinol. When the water was not allowed to distill from the reaction mixture after the first one-half hour, the conversion in two similar runs was 22.7–23.0% to a product in which the methylphenylcarbinol content had increased to 30–44%.

The initial inhibition by water probably is due to combination of the polar water molecules with the catalyst, which so deactivates the latter as to prevent its taking part in the chain initiating formation of α-phenylethyl free radicals. After hydroperoxide formation is well established, deactivation of the catalyst would have no further effect on the continuance of the reaction. The increase in the amount of carbinol with added water is probably due to deactivation (or removal from the site of reaction) of the hydroxyl free radicals, by solution in the water, perhaps through hydrogen bonding or some similar phenomenon. As shown in equations (1) and (2), propagation of the chain by hydroxyl free radicals leads only to acetophenone, whereas propagation by α-phenylethoxy free radicals (equations 3 and 4) leads to both acetophenone and methylphenylcarbinol. Therefore, deactivation of the hydroxyl free radicals would lead to increased carbinol in the product.

The fact that no decrease in the conversion was observed suggests that the hydroxyl free radicals normally play no part in the autoxidation chain, since their removal must be a chain ending reaction. By this scheme the oxidation of ethylbenzene would proceed entirely according to equation (3) rather than according to equation (1).

The addition of 2% of methylphenylcarbinol to an ethylbenzene oxidation mixture markedly lowered the conversion (from 30.1–33.4% to 20.2–21.8%). The addition of 5% stopped it almost completely (0.3–1.0% conversion). The mechanism of this methylphenylcarbinol inhibition at the start of the reaction is probably similar to that for water; that is, deactivation of the catalyst by combination at its surface.

On the other hand, when methylphenylcarbinol is added after hydroperoxide formation is well established, no decrease in the conversion is observed and no additional carbinol is found in the product. Thus the addition of 2 or 5% of methylphenylcarbinol one-half to one and one-half hours after the oxidation mixture reached reaction temperature led to practically identical conversions to products containing the same amount of methylphenylcarbinol as in oxidations where the carbinol was omitted. This result is not surprising considering the fact that methylphenylcarbinol is formed during the entire course of the reaction (equations 3 and 4). It means that the carbinol is oxidized continuously to acetophenone during the course of the ethylbenzene oxidation, perhaps by the mechanism shown below.



$$C_6H_5\overset{OH}{C}HCH_3 + HO\cdot \longrightarrow C_6H_5\underset{\cdot}{\overset{OH}{C}}CH_3 + H_2O$$

$$C_6H_5\underset{\cdot}{\overset{OH}{C}}CH_3 + O_2 \longrightarrow C_6H_5\underset{OO\cdot}{\overset{OH}{C}}CH_3$$

$$C_6H_5\underset{OO.}{\overset{OH}{C}}CH_3 + C_6H_5CH_2CH_3 \longrightarrow C_6H_5\dot{C}HCH_3 + C_6H_5\underset{OOH}{\overset{OH}{C}}CH_3$$

$$C_6H_5\underset{OOH}{\overset{OH}{C}}CH_3 \xrightarrow{140^\circ} C_6H_5\underset{O\cdot}{\overset{OH}{C}}CH_3 + HO\cdot$$

$$C_6H_5\underset{O\cdot}{\overset{OH}{C}}CH_3 + C_6H_5CH_2CH_3 \longrightarrow C_6H_5\dot{C}HCH_3 + \left[C_6H_5\underset{OH}{\overset{OH}{C}}CH_3\right]$$

$$\left[C_6H_5\underset{OH}{\overset{OH}{C}}CH_3\right] \longrightarrow C_6H_5COCH_3 + H_2O$$

The suggestion, made previously, that hydroxyl free radicals are removed by the addition of water to the reaction mixture is in accord with the above mechanism, since under such conditions more carbinol is found in the product.

In conclusion then a course for the catalytic liquid phase oxidation of ethylbenzene to acetophenone has been suggested based on the mech-

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[9] Binapfl and Krey, U. S. Patent, 1,813,606; *Chem. Zentr.*, **102**, II, 2058 (1931).

[10] Stephens, THIS JOURNAL, **48**, 1834, 2920 (1926); **50**, 2523 (1928).

anism proposed by Robertson and Waters[5] for the oxidation of tetralin. The proposed scheme explains the presence of methylphenylcarbinol in the acetophenone produced, the initial inhibition of the oxidation by water or carbinol, and the fact that the carbinol is oxidized to acetophenone if it is introduced after the ethylbenzene oxidation has been started.

The authors are grateful for a discussion with Prof. Charles C. Price of the University of Notre Dame and Prof. Paul D. Bartlett of Harvard University in which they made a number of very helpful suggestions with regard to the details of the mechanism.

Experimental

General Procedure.—All of the oxidations were conducted in a stainless steel autoclave of 6 in. internal diameter and 11 in. internal depth. It was fitted with a thermocouple well and reflux condenser equipped with a Dean and Stark type trap. A turbo mixer of 2-in. diameter was fixed 2 in. from the bottom of the pot and operated at 750 r. p. m. Air from the inlet tube was blown directly into the mixer during the run. The autoclave was equipped with a filling flange at the top for loading and a valve at the bottom through which the charge could be blown into a metal receiver. Heating was effected by means of resistance wire wound around the bomb and the head was heated with steam coils. The temperatures were automatically controlled and recorded.

The charge consisted of 18 g. of chromium oxide (J. T. Baker Analyzed), 20 g. of product fraction (about 80% acetophenone and 20% methylphenylcarbinol) and 1800 g. of ethylbenzene (Monsanto or Dow, $n^{25}D$ 1.4930). The oxidations were conducted at 100 lb./sq. in. pressure with an air flow of 15 cu. ft./hour. The time of the run was measured from the time the pot reached the reaction temperature of 140°. Water was periodically withdrawn from the trap during the course of the oxidation. At the close of the run, the heat and air were turned off and the mixture was allowed to cool somewhat. After the pressure had been allowed to fall to about 15 lb./sq. in., the charge was blown into the receiver. This receiver was equipped with a condensing system adequate to avoid losses.

The oxidation mixture was filtered free of catalyst and then analyzed by working up the entire mixture or an aliquot thereof. The material for analysis was washed with 10% aqueous sodium hydroxide to remove benzoic acid and then with water. The combined washes were concentrated by removing excess water (and traces of ethylbenzene and acetophenone) by distillation. The organic layer of the distillate was added to the acid-free reaction mixture, which was then dried over anhydrous potassium carbonate, filtered and fractionated through a 19-mm. i.d. Vigreux column 125 cm. long equipped with a Penn State head.

No attempt was made to separate acetophenone (b. p. 202.3°) from methylphenylcarbinol (b. p. 205°). After the ethylbenzene had distilled, the intermediate cut between ethylbenzene and the acetophenone–methylphenylcarbinol mixture was collected until the refractive index reached a maximum value. The percentages of ethylbenzene and the acetophenone–methylphenylcarbinol mixture in this cut were calculated from the refractive index of the cut. The assumption was made that the ketone–carbinol ratio was the same in this intermediate as in the main product fraction. The remainder of the acetophenone–methylphenylcarbinol mixture was distilled and the sum of this weight and the amount in the intermediate fraction was used for the conversion calculation. The amount of carbinol in this product mixture was calculated from the refractive index curve shown.

The acid was determined directly by precipitation with hydrochloric acid from the concentrated alkaline washes. It was collected on a filter, washed with water and dried to constant weight in a 45° oven. The tar was calculated as mole per cent. on the basis of a molecular weight of 120. It constituted everything boiling higher than the acetophenone–methylphenylcarbinol mixture.

Rate of Conversion.—In Table I are summarized a number of runs which show the effect of time on the conversion. By per cent. carbinol is meant the per cent. of methylphenylcarbinol in the acetophenone–methylphenylcarbinol product mixture.

TABLE I

RATE OF CONVERSION

Run	Time, hr.	Conversion, %	Carbinol, %	Acid, %	Tar, %	Material balance, %
1	1.5	13.1	44	0.5	0.9	96.8
2	1.5	13.2	52	0.6	1.2	95.1
3	2.5	26.2	38	1.5	1.9	95.6
4	2.5	24.1	32	1.2	1.5	96.3
5	3.5	22.6	26	1.1	1.6	95.3
6	3.5	21.7	26	1.1	2.1	82.0
7	4.5	27.4	26	2.4	2.1	95.0
8	4.5	26.2	24	1.7	1.7	93.5
9	5.0	24.6	22	1.1	1.7	93.2
10	5.0	28.0	22	1.9	1.8	90.5
11	5.5	30.0	22	1.7	1.3	94.4
12	5.5	29.5	24	2.0	1.6	92.3
13	5.5	30.1	22	1.9	1.7	92.1
14	6.5	31.8	26	1.9	1.6	92.5
15	6.5	30.4	28	2.0	1.1	92.7
16	6.5	33.4	22	2.5	1.8	92.7
17	6.5	30.9	30	2.3	1.6	94.5
18	6.5	30.1	22	2.3	2.3	91.6
19	8.5	32.8	24	2.4	2.0	92.2
20	8.5	33.6	22	3.0	2.9	93.6
21	8.5	32.3	26	2.7	1.9	95.0

In Table II is shown the amount of water collected in the trap during the course of three runs of eight and one-half hours duration.

TABLE II

RATE OF WATER EVOLUTION

Run	H_2O collected (cc.)					
	1.5 hr.	3.5 hr.	5.5 hr.	6.5 hr.	7.0 hr.	8.5 hr.
19	12	55	..	93	...	106
20	16	58	..	99	...	113
21	14	59	86	..	100	110

Effect of Added Water.—In Table III are shown along with runs 5 and 6, two comparable runs in which the steam in the coils on the head of the bomb was turned off after one-half hour. This was equivalent to adding water to the reaction since only 18 and 35 cc., respectively, were collected in the trap.

TABLE III

EFFECT OF ADDED WATER

Run	Water collected in trap, cc.	Conversion, %	Carbinol, %	Acid, %	Tar, %	Material balance, %
5	52	22.6	26	1.1	1.6	95.3
6	62	21.7	26	1.1	2.1	82.0
22	18	23.0	44	0.9	1.4	95.3
23	35	22.7	30	1.2	1.8	97.1

Effect of Added Methylphenylcarbinol.—In Table IV along with run 14 (a representative six and one-half hour run) are shown runs in which methylphenylcarbinol and a mixture of methylphenylcarbinol and product fractions (about 80% acetophenone) were added with the charge. All of these runs were for six and one-half hours.

TABLE IV

EFFECT OF ADDED METHYLPHENYLCARBINOL

Run	Carbinol added, %	Extra product added, %	Conversion, %	Carbinol, %	Acid, %	Tar, %	Material balance, %
14	0	0	31.8	26	1.9	1.6	92.5
24	2	0	21.8	32	1.7	1.6	87.8
25	2	0	32.4	20	2.4	2.0	95.4
26	2	10	20.2	22	1.8	2.1	96.1
27	2	10	20.7	22	2.0	2.1	93.8
28	5	0	0.3	77	...	0.2	94.1
29	5	10	1.0	61	...	0.8	91.6

In Table V is summarized a series of six and one-half hour runs (except 35 and 36 which were for five and one-half hours) in which a mixture of equal parts of acetophenone and methylphenylcarbinol was added through the air inlet after the oxidation had started. The amount of carbinol, as shown in the table, was calculated from refractive index data.

TABLE V

METHYLPHENYLCARBINOL ADDED AFTER OXIDATION STARTED

Run	50/50 acetophenone–carbinol mixture added, g.	Time addition, hr. after start	Conversion, %	Carbinol in product, %
30	None	...	33.7	26
31	72	1.5	33.0	26
32	72	1.5	33.0	24
33	180	1.5	33.2	24
34	180	1.5	33.2	24
35	72	0.5	30.0	24
36	72	0.5	31.0	24

In two additional experiments the autoclave was fitted with a sampler, which made possible the withdrawal of a small portion of the reaction mixture. During the time of the initial heating of each run to the reaction temperature, the reaction mixture was sampled at intervals. It was possible to note quite accurately the point at which oxidation commenced as evidenced by an increase in the refractive index. For the first experiment the 90 g. of methylphenylcarbinol was not charged until a definite increase in the refractive index of the reaction mixture from n^{25}_D 1.4932 to n^{25}_D 1.4959 had occurred. The conversion obtained in this experiment was 44.3% of product which contained 18% of carbinol. In the second experiment the carbinol was charged before any increase in the refractive index of the reaction mixture had taken place. In this case only a 1.6% conversion to product which contained 77% of carbinol was obtained.

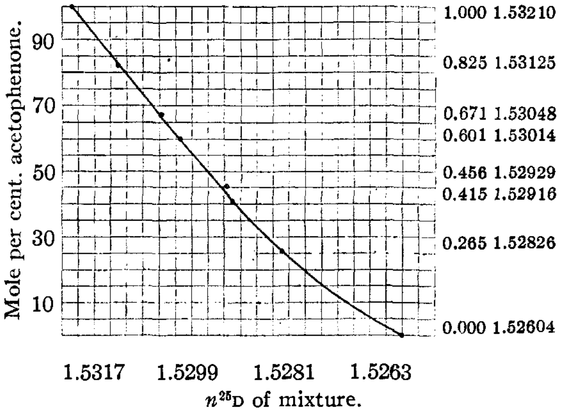

Fig. 1.—Refractive index of acetophenone–methylphenylcarbinol mixtures.

Estimation of Acetophenone–Methylphenylcarbinol Mixtures.—Acetophenone was purified as follows. A sample, f. p. > 19.0° obtained by fractional distillation, was placed in a large brown bottle. The latter was immersed in a bath held at about 18°. When the temperature of the acetophenone equalled the bath temperature, seed crystals were introduced. The acetophenone was allowed to freeze until only a small core remained liquid. This core was poured off, the bulk of the acetophenone remelted, and the process repeated. When no further rise occurred in the freezing point of the decanted cores, the acetophenone was adjudged pure, f. p. 19.66° ± 0.02°,[11] n^{25}_D 1.53210.

Methylphenylcarbinol, prepared by the hydrogenation of acetophenone in the presence of a copper chromite catalyst, was purified similarly. Two crystalline forms of this compound were discovered and the lower-melting was used for purification, since it formed a better core. The pure material had f. p. 15.48° or 21.47°, n^{25}_D 1.52604. These freezing points were measured on a thermometer calibrated by the Bureau of Standards and the refractive indices on a precision refractometer.

The attached curve was obtained by determining the refractive indices of acetophenone–methylphenylcarbinol mixtures. The composition of product fractions was read directly from this curve.

Composition of Tar.—The combined tars from a number of experiments were fractionally distilled. After the first quarter, consisting principally of acetophenone, a variety of solid and liquid fractions was obtained. One of these solid fractions, b. p. 120–158° (3 mm.) was crystallized three times from ethanol, m. p. 125–126° (uncor.) alone and when mixed with an authentic sample of 2,3-diphenylbutane. When the filtrates were diluted with water, benzoic acid was obtained m. p. 121–122° (uncor.) alone and when mixed with an authentic sample.

Summary

The free radical mechanism for the air oxidation of tetralin, proposed by Robertson and Waters, had been used to explain certain features of the air oxidation of ethylbenzene.

DAYTON, OHIO RECEIVED JANUARY 26, 1948

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[11] Timmermans and Hennaut-Roland, *J. Chim. Phys.*, **32**, 501, 589 (1935), give f. p. 19.6°.