

of the grouping  $-\text{C}(\text{OH})=\text{C}(\text{OH})-$ . As a matter of fact, benzoin is nearly quantitatively converted into benzil by the same procedure as above.

### Experimental Part

#### Dehydrogenation of Isolated Diene Addition Products.—

(a) Seven grams of 1,2,3,6-tetrahydro-3,6-diphenylphthalic anhydride<sup>6</sup> was dissolved in nitrobenzene (35 cc.) and slowly heated to 200° during two hours, then kept boiling for one hour, whereby drops of water distilled into the condenser. After two days crystals with m. p. 220° were deposited. These did not depress the m. p. of 3,6-diphenylphthalic anhydride (m. p. 221–222°). The yield was low (45%) apparently because of partial dissociation of the adduct at the high temperature of the reaction.

(b) 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride (4 g.) was warmed in nitrobenzene (25 cc.) for twelve hours at 170–175°. After removal of the solvent, the residue was distilled at 220–240° (1.5 mm.). The distillate crystallized on trituration with acetone and was recrystallized from acetic anhydride; m. p. 305°. It does not depress the m. p. of the authentic octahydrophenanthrene derivative I.<sup>2</sup>

**Dehydrogenation with Other Nitro Compounds.**—1,4-Diphenylbutadiene (10.3 g.), maleic anhydride (5 g.) and *p*-bromonitrobenzene (6.6 g.) were refluxed for four hours in xylene (50 cc.). After cooling the whole mass became solid; recrystallization from xylene gave m. p. 214°; mixed m. p. with the tetrahydro product,<sup>5</sup> 212°.

Likewise with *p*-chloronitrobenzene or *m*-dinitrobenzene no dehydrogenation occurred. The same results were obtained in an analogous experiment with dicyclohexenyl.

**Diene Reactions of Dicyclohexenyl with Various Phloidiene Components.**—(a) Dicyclohexenyl (3.2 g.) and maleic anhydride (2 g.) were boiled in nitrobenzene (10 cc.) for five hours and the reaction mixture worked up as described above. The product had a m. p. 305°.

(b) 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-methylphenanthrene-10-carboxylic acid (II, R = CH<sub>3</sub>).—Cro-

tonic acid (4 g.) and dicyclohexenyl (8 g.) in nitrobenzene (25 cc.) were heated for six hours and the mixture worked up as in the foregoing example, to give a product of b. p. 180–200° (3.5 mm.). The sirup crystallized on trituration with acetone and ligroin; long rods from butyl acetate, from xylene beautiful rhombohedra, m. p. 164°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>: C, 77.4; H, 9.7. Found: C, 76.8; H, 10.0.

(c) 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-phenylphenanthrene-10-carboxylic Acid (II, R = C<sub>6</sub>H<sub>5</sub>).—Cinnamic acid (7 g.) and dicyclohexenyl (8 g.) were heated for five hours in nitrobenzene solution (35 cc.). On cooling a mixture of unreacted cinnamic acid and the condensation product settled down. The latter was recrystallized from a mixture of xylene and petroleum ether (130°), m. p. 224°. It gave no depression with an authentic sample.<sup>2</sup>

*Anal.* Calcd. for C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>: C, 81.3; H, 8.4. Found: C, 81.2; H, 8.8.

**Miscellaneous Reactions.**—Anthracene endosuccinic anhydride<sup>6</sup> (4 g., m. p. 264°) was heated in nitrobenzene (25 cc.) for twelve hours. Part of the substance crystallized directly, part only after removal of the solvent. After one crystallization from ethyl benzoate, the substances were identified as starting material.

Three grams of *meso*-diphenylsuccinic acid (m. p. 245–246°) was heated in nitrobenzene (25 cc.) for twelve hours, whereupon the solution became dark. The solvent was driven off by steam and the residue filtered while hot in order to remove a black tar on the bottom. From the filtrate white crystals were obtained on cooling. Recrystallization from dilute alcohol gave m. p. 242° and mixed m. p. with the starting material, 245–246°; yield 1.5 g. The black tar was pulverized in a mortar with the aid of ethanol and then recrystallized in rods from glacial acetic acid or xylene; m. p. 157°; yield, 1.2 g.

For identification of this diphenylmaleic anhydride, it was converted into the anil<sup>7</sup> by heating in aniline for five minutes to 150° and pouring into hydrochloric acid. The yellow precipitate was recrystallized from xylene and high-boiling petroleum ether, m. p. 172°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>15</sub>O<sub>2</sub>N: N, 4.3. Found: N, 4.5.

Benzoin (6 g.) was heated in nitrobenzene (25 cc.) for three hours and the black solution distilled with steam. After the solvent, long yellow needles appeared in the distillate, which were identified as benzil by mixed m. p.

(6) Diels and Alder, *Ann.*, **486**, 191 (1931).

(7) Anschütz and Bendix, *ibid.*, **289**, 65 (1890).

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### Statistics of Intramolecular Aldol Condensations in Unsaturated Ketone Polymers

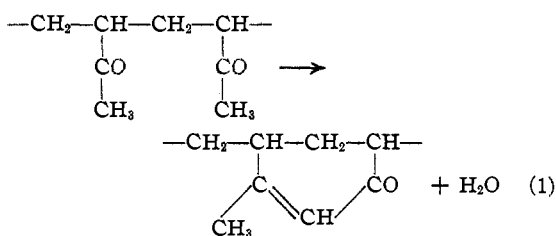
BY PAUL J. FLORY

When pairs of neighboring substituents of a long chain polymer molecule condense intramolecularly with one another, some of the substituents fail to react because they become isolated

(5) Diels and Alder, *Ber.*, **62**, 2081 (1929).

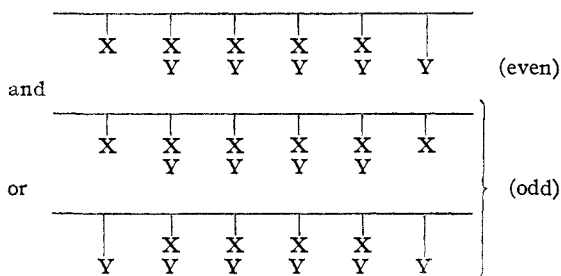
between neighbors which have reacted. The fraction of the substituents which become isolated in this way at "completion" of the reaction can be calculated by statistical methods introduced by the writer<sup>1</sup> and extended by Marvel and Levesque<sup>2</sup> and by Wall.<sup>3</sup> This fraction is  $1/e^2$ , or 13.5%,<sup>1</sup> when the substituents occur at regular intervals along the chain, and each of them bears a single functional group X.

In presenting the statistical treatment for this case,<sup>1</sup> the writer erroneously included as an example the intramolecular aldol condensation (1) of the polymer of methyl vinyl ketone.<sup>4</sup> Here



each substituent bears *two* functional groups, a carbonyl and a methyl, instead of one as the situation previously analyzed would require. The treatment presented below shows that the correct result for this special case is  $1/2e$  or 18.4% of the substituents being isolated. This revision does not depreciate the previous treatment of the more important simpler case of a single substituent, nor does it invalidate the applications of these calculations to experimental data.<sup>5,6</sup>

For the statistical analysis of the special case exemplified by (1) in which each substituent bears two functional groups, X and Y, a procedure very similar to that set forth previously<sup>1</sup> will be followed. The two types of sequences of unreacted substituents represented below must be considered.



(1) P. J. Flory, *THIS JOURNAL*, **61**, 1518 (1939).

(2) C. S. Marvel and C. L. Levesque, *ibid.*, **61**, 1682 (1939).

(3) F. T. Wall, *ibid.*, **62**, 803 (1940); **63**, 821 (1941).

(4) C. S. Marvel and C. L. Levesque, *ibid.*, **60**, 230 (1938).

(5) C. S. Marvel and C. L. Levesque, *ibid.*, **61**, 3234 (1939).

(6) C. S. Marvel, J. H. Sample and M. F. Roy, *ibid.*, **61**, 3241 (1939).

A sequence composed of  $2n$  functional groups of both kinds will be referred to as an " $n$ -sequence." An X may condense with a Y functional group of either of its immediate neighbors, and it will be assumed that the probability that each of the 2 ( $n - 1$ ) adjacent XY pairs in an  $n$ -sequence has an equal chance to be the first to condense. Condensation of a pair in an *even*,  $n$ -sequence produces two new sequences which may be either *even*,  $i$  and *even*,  $n - i - 1$ , where  $i$  is any integer from zero to  $n - 1$ , or they may be *odd*,  $i$  and *odd*,  $n - i - 1$ , where  $i = 1$  to  $n - 2$ . Similarly, an *odd*,  $n$ -sequence will give rise to an *even*,  $i$  and an *odd*,  $n - i - 1$ -sequence, where  $i = 0$  to  $n - 2$ ; each of these combinations can be formed in two different ways.

If  $S_n^*$  represents the expected number of isolated X's or Y's which will remain unreacted after random condensation of pairs in an *even*,  $n$ -sequence is completed, and  $S_n^o$  is the corresponding expectancy for an *odd*,  $n$ -sequence, it follows from the above considerations that

$$S_n^* = \left[ \sum_{i=0}^{n-1} (S_i^* + S_{n-i-1}^*) + \sum_{i=1}^{n-2} (S_i^o + S_{n-i-1}^o) \right] / 2(n-1)$$

or

$$S_n^* = \left[ \sum_{i=1}^{n-2} (S_i^* + S_i^o) + S_{n-1}^* \right] / (n-1) \quad (2)$$

where  $S_0^o$  is neglected since it is equal to zero. Similarly

$$S_n^o = \left[ \sum_{i=1}^{n-2} (S_i^* + S_i) + S_{n-1}^o \right] / (n-1) \quad (3)$$

For the mean expected number  $S_n$  of isolated substituents in an  $n$ -sequence

$$\begin{aligned}
 S_n &= (S_n^* + S_n^o) / 2 \\
 &= \left[ 2 \sum_{i=0}^{n-2} S_i + S_{n-1} \right] / (n-1) \quad (4)
 \end{aligned}$$

To solve the primary recurrence relationship (4),  $(n - 2)S_{n-1}$  is subtracted from  $(n - 1)S_n$ . Letting  $S_n - S_{n-1} = \Delta_n$ , there is obtained

$$(n-1)\Delta_n = S_{n-2}$$

Subtraction of  $(n - 2)\Delta_{n-1} = S_{n-3}$  from the above equation yields the second difference equation

$$\Delta_n - \Delta_{n-1} = -(\Delta_{n-1} - \Delta_{n-2}) / (n-1) \quad (5)$$

or

$$\Delta_n - \Delta_{n-1} = (\Delta_1 - \Delta_0)(-1)^{n-1} / (n-1)! \quad (6)$$

By trial it is found that  $S_0 = 0$ ,  $S_1 = 1/2$  and  $S_2 = 1/2$ . Thus,  $\Delta_1 = 1/2$  and  $\Delta_2 = 0$ . Substituting these in (5), we find  $\Delta_1 - \Delta_0 = 1/2$ . According to (6), therefore

$$\Delta_n = (1/2) \sum_{i=1}^n (-1)^{i-1} / (i-1)! \quad (7)$$

and

$$S_n = 1/2 \sum_{i=1}^n (n-i+1)(-1)^{i-1} / (i-1)! \quad (8)$$

When  $n$  is large,  $\Delta_n$  represents the average number of isolated functional groups of either variety, X or Y, per substituent.<sup>1</sup> The series in (7) converges rapidly as  $n$  increases giving in the limit  $\Delta_\infty = 1/2e$ . That is, a fraction equal to  $1/2e$ , or 18.4%, of the functional groups is isolated at completion of the condensation.

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### Some Heat Capacity Data for Gaseous 2,2,4-Trimethylpentane

BY MILO KIPERASH AND GEORGE S. PARKS

Recently Pitzer<sup>1</sup> has reported a single experimental value for the heat capacity at 423°K. and 1 atm. (constant pressure) of gaseous 2,2,4-trimethylpentane. On the basis of statistical calculations and with the guidance of this value he also has suggested the general equation

$$C_p = -227.3 + 110 \log T \quad (1)$$

for the heat capacity of this hydrocarbon as a function of the absolute temperature.

Two years ago, in connection with some other work on organic compounds in the gaseous state, we likewise made five determinations of the molal heat capacity at 1 atm. pressure of gaseous 2,2,4-trimethylpentane. A "constant flow" method, briefly described elsewhere by Parks and Shomate,<sup>2</sup> was employed, and the uncertainty in the resulting data is probably within 1.5%. Our results lie between 442 and 458°K. and are given in the second column of Table I. For comparison the value of Pitzer is included parenthetically. Column 3 contains the corresponding values calculated by Pitzer's equation, from which our data differ on the average by 1.4%. In view of the facts this is a reasonable check.

In Column 4 appear  $C_p^0$  values for the gas at zero pressure. These have been derived from the previous experimental results by use of Berthelot's equation of state ( $C_p^0 = C_p - 81RPT_c^3 / 32P_cT^3$ ) and with the assumption of 25 atm. and

(1) Pitzer, *THIS JOURNAL*, **62**, 1224 (1940).

(2) Parks and Shomate, *J. Chem. Phys.*, **8**, 429 (1940).

TABLE I  
SOME HEAT CAPACITY DATA FOR GASEOUS 2,2,4-TRIMETHYLPENTANE

Units are cal. per degree per mole.

| T, °K. | $C_p$ (1 atm.) |             | $C_p^0$ |             |
|--------|----------------|-------------|---------|-------------|
|        | Expt.          | Calc. eq. 1 | Expt.   | Calc. eq. 2 |
| 423    | (61.6 ± 0.6)   | 61.6        | (61.1)  | 60.3        |
| 442    | 63.8 ± 1.0     | 63.7        | 63.4    | 62.2        |
| 442    | 64.6 ± 1.0     | 63.7        | 64.2    | 62.2        |
| 448    | 65.6 ± 1.0     | 64.3        | 65.2    | 62.9        |
| 449    | 65.3 ± 1.0     | 64.4        | 64.9    | 63.0        |
| 458    | 66.7 ± 1.0     | 65.4        | 66.3    | 63.9        |

550° for  $P_c$  and  $T_c$ , respectively. The calculated values for  $C_p^0$  in the last column have been obtained from Pitzer's general empirical equation for gaseous paraffins

$$C_p^0 = 5.65n - 0.62 + t(0.0111n + 0.0158) \quad (2)$$

where  $n$  is the number of carbon atoms and  $t$  is the centigrade temperature.<sup>3</sup> While he suggests that this latter equation is probably applicable to branched paraffins as well as to the normal compounds, it apparently runs a little low in the case of this highly branched compound. In passing, we should note here that heat capacity values calculated for 2,2,4-trimethylpentane by the semi-theoretical methods of Bennewitz and Rossner<sup>4</sup> are of the order of 10 per cent. low, or more, as Pitzer likewise found in the case of their experimental determination on *n*-heptane.

(3) Pitzer, *THIS JOURNAL*, **63**, 2413 (1941).

(4) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

DEPARTMENT OF CHEMISTRY  
STANFORD UNIVERSITY RECEIVED OCTOBER 14, 1941  
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### The Identification of Alcohols in Aqueous Solution

BY WILLIAM N. LIPSCOMB AND ROBERT H. BAKER<sup>1</sup>

The identification of an alcohol when it appears in aqueous solution as from the saponification of an ester usually involves its isolation by repeated distillation, salting out, and drying. Henstock<sup>2</sup> was able to avoid this time-consuming procedure by the use of the Schotten-Baumann reaction of *p*-nitrobenzoyl chloride at -15°.

We have found that the more satisfactory 3,5-dinitrobenzoates may be formed by slight modification of the Henstock procedure. The process involves adding alkali and sodium acetate to the aqueous solution of the alcohol and shaking it at

(1) Present address, Northwestern University, Evanston, Illinois.

(2) Henstock, *J. Chem. Soc.*, 216 (1933).