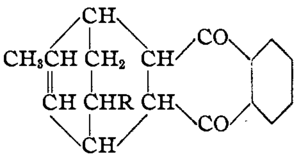
NOTES

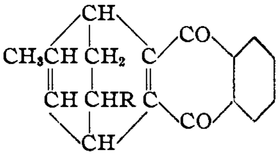
The Thermal Decomposition of Some Bicyclic Compounds

By Edwin R. Littmann

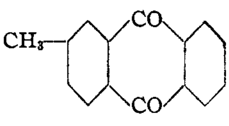
The addition product between naphthoquinone and α-phellandrene was shown by Diels, Alder and Stein[1] to possess structure I. Oxidation with air gave II by loss of two hydrogens. Thermal decomposition of II yielded 2-methylanthraquinone, III, and isopropylethylene. Several other diene–quinone addition products, when oxidized, decomposed similarly.



I (R = isopropyl)



II

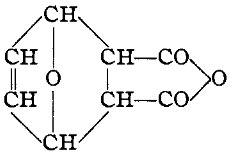


III

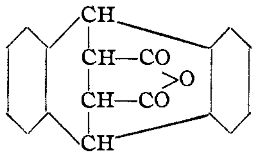
The present paper deals with the pyrolysis of diene–maleic anhydride addition products. One such compound studied by Diels and Alder,[2] namely, that from furan and maleic anhydride (IV), was shown to break on heating into its original components. For purposes of comparison, it should be noted that IV is related to I, not II.

Anthracene–maleic anhydride, V, was found in the present work to resemble IV because it decomposed also into its components. The study of α-phellandrene–maleic anhydride, VI, and α-terpinene–maleic anhydride, VII, was illuminating for the course of the pyrolysis was not reversal as in IV or olefin production as in II. Instead both compounds yielded *p*-cymene and succinic anhydride.

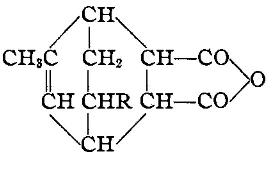
Superficially, it might appear that these several cases have displayed three distinct modes of breakdown but, as a matter of fact, they all have one fundamental characteristic. They all demonstrate that the C–C bonds which undergo pyrolytic rupture are the ones once removed from unsaturation rather than the ones adjacent to unsaturation. Thus, the $C\overset{\alpha}{-}C$ bond in $C{=}C\overset{\alpha}{-}C\overset{\beta}{-}C$ is a position of strength whereas the $C\overset{\beta}{-}C$ bond is one of weakness, an observation in agreement with previous results reported by Hurd.[3] On this basis, it may be predicted that a structure such as VIII, which is related to VI in the same way that II is to I, should pyrolyze into an olefin, $RCH{=}CH_2$, and 4-methylphthalic anhydride.



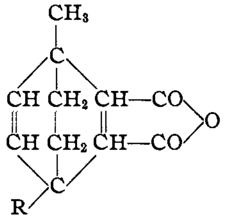
IV



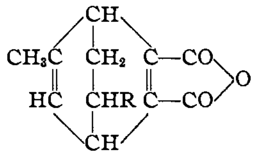
V



VI, R = isopropyl



VII



VIII

Experimental

α-Phellandrene–Maleic Anhydride.—This material was prepared according to the procedure described by Diels and Alder.[4] The product was decomposed by distilling through a 50-cm. column at atmospheric pressure, a free flame in constant motion being used as a source of heat. Heating was so controlled that a 5–8 g. sample was decomposed in twenty to thirty minutes. With the exception of a small amount (estimated 10%) of charred residue no products other than those indicated in the following experiments were isolated. The distillate, containing any succinic anhydride deposited in the cooler part of the apparatus, was steam distilled. The distillate from this distillation was separated from the water, dried over sodium and distilled from sodium: b. p. 173–175° (corr.); n^{20}_{D} 1.4813; d^{20}_{4} 0.861. On oxidation with chromic acid the oil gave only terephthalic acid which was identified by the following data. Subs., 0.0516 g.; NaOH (0.0509), 11.53 cc.; n. e. 87.0; calcd. for $C_2H_6O_4$; n. e. 88.0; m. p. methyl ester 141.7° (corr.). A mixed melting point with methyl terephthalate showed no depression.

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[1] Diels, Alder and Stein, *Ber.*, **62**, 2337 (1929).

[2] Diels and Alder, *ibid.*, **62**, 554 (1929).

[3] Hurd, *Ind. Eng. Chem.*, **26**, 53 (1934); Hurd and Bollman, This Journal, **55**, 699 (1933); **56**, 447 (1934).

[4] Diels and Alder, *Ann.*, **460**, 98 (1927).

The aqueous residue from the steam distillation was evaporated to dryness, after filtration, the product dried overnight at 100° and then sublimed, m. p. 184.5° (corr.). A mixed melting point with pure succinic acid showed no depression.

Anthracene–Maleic Anhydride.—This product was prepared according to the method of Diels, Alder and Beckmann.[5] The decomposition was carried out as described above except that no appreciable distillation took place. The sublimate which adhered to the upper portion of the decomposition apparatus was resublimed, m. p. 58–59°. Microscopic examination confirmed the existence of maleic anhydride.

The residue from the decomposition was digested with an excess of 10% sodium hydroxide solution and the insoluble portion washed twice by decantation. This material, after drying, was sublimed, m. p. 215.1° (corr.). A mixed melting point with anthracene showed no depression.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.40; H, 5.60. Found: C, 94.20, 94.33; H, 5.27, 5.55.

α-Terpinene.—This terpene was synthesized from linaloöl by the method of Bertram and Walbaum.[6]

α-Terpinene–Maleic Anhydride.[7]—To 0.3 mole of terpene there was added 0.2 mole of maleic anhydride. The mixture was refluxed for three hours and then distilled with steam to remove the unused terpinene and extract some of the unused maleic anhydride. The residual oil was taken up in ether, dried and distilled twice under reduced pressure; yield, 16 g. of product which boiled at 152–154° at 1 mm.; $n^{67}{}_D$ 1.4913; $d^{67}{}_4$ 1.100; M_R calcd. for $C_{14}H_{18}O_3{}^{(=)}$, 61.47; found, 61.64. *Anal.* Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.75. Found: C, 71.37; H, 7.56. The decomposition was carried out as described for the phellandrene–maleic anhydride. The products were also isolated by the same procedure. The oil was found to have the following characteristics: b. p. 173–175° (corr.); $n^{20}{}_D$ 1.4820; $d^{20}{}_4$ 0.852; M_R calcd. for $C_{10}H_{14}{}^{(=)}$, 44.8; found, 44.8. On oxidation with chromic acid the only acid obtained was terephthalic, which was identified through its methyl ester in the usual way. The acidic portion of the decomposition products was proved to be succinic anhydride by the same procedure previously described. The analytical data were: subs., 0.0703 g. NaOH (0.518 *N*), 23.25 cc.; n. e., calcd. for $C_4H_6O_2$, 59.0; found, 58.5; m. p. 184° (corr.). A mixed melting point with succinic acid of known purity showed no depression.

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

(6) Bertram and Walbaum, *J. prakt. Chem.*, **45**, 601 (1892).

(7) Koch, Dissertation, Christian Albrecht University, Kiel, 1932.

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RECEIVED JUNE 16, 1934

New Method of Preparation of Methylmaltoside Heptaacetate with Orthoester Structure

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In our attempts to prepare the "γ"-methylmaltoside heptaacetate of Freudenberg,[1] we have found that his method of preparation of the necessary chloroacetylmaltose[1,2] with ortho ester structure is very laborious, and frequently gives negative results. We have succeeded in discovering a new method by which it is possible to obtain the former compound in one step, and in fairly good yield. Our procedure consists in the treatment of β-maltose octaacetate in chloroform solution with aluminum chloride at room temperature. Freudenberg's chloroacetylmaltose so formed is not isolated in crystalline form. Its methyl alcoholic solution, in presence of pyridine, gives rise to the "γ"-methylmaltoside heptaacetate which crystallizes from the solution in a very pure state.

The formation of Freudenberg's chloroacetylmaltose under the above experimental conditions is remarkable. Kunz and Hudson[3] have shown that both octaacetyl lactose and cellobiose suffer double epimerization in the presence of aluminum chloride in boiling chloroform solution, the two sugars being converted into two new disaccharides, namely, neolactose and celtrobiose. We have attempted to apply our method to both lactose and cellobiose octaacetates, but, in contrast to the maltose acetate, no appreciable reaction could be detected; the starting materials were recovered virtually unchanged. Haworth and co-workers[4] have found that maltose, cellobiose and lactose differ only in that maltose is a 4-α-glucosidoglucose, while cellobiose and lactose are, respectively, 4-β-glucosido-glucose, and 4-β-galactosido-glucose. Such a conclusion, while in best accord with many properties of these sugars and their derivatives, fails to explain the sharp distinction observed between the behavior of these sugar acetates toward aluminum chloride at low temperature. At the present time the reason for this difference remains obscure.

Experimental

Preparation of "γ"-Methylmaltoside Heptaacetate.—Thirteen grams of β-octaacetylmaltose was dissolved in ice-cold absolute chloroform; to the solution 6 g. of aluminum chloride (Merck) was added, and the mixture was kept at room temperature for an hour, with occasional shaking. The resulting almost colorless, thick mass was poured into a separatory funnel containing cracked ice. After addition of more chloroform, the colorless chloro-

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(1) Freudenberg, v. Hochstetter and Engels, *Ber.*, **58**, 666 (1925); Freudenberg and Scholz, *ibid.*, **63**, 1969 (1930).

(2) Freudenberg and Ivers, *ibid.*, **55**, 929 (1922).

(3) Kunz and Hudson, THIS JOURNAL, **48**, 1978, 2435 (1926); Hudson, *ibid.*, **48**, 2002 (1926).

(4) Haworth and Peat, *J. Chem. Soc.*, 3094 (1926); Haworth and Long, *ibid.*, 544 (1927); Haworth, Long and Plant, *ibid.*, 2809 (1927).