

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY OF THE UNIVERSITY OF ROME]

Substitution in Polymethylbenzenes. II. The Course of the Nitration of Durene in Sulfuric Acid-Chloroform Mixtures¹

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In contrast to all previous reports, 3-nitrodurene has been found among the products of the nitration of durene in sulfuric acid-chloroform mixtures. Competitive nitrations of durene and 3-nitrodurene indicate that the latter compound, despite its lower reactivity, may disappear from the heterogeneous medium at a rate even higher than durene itself, provided that transport processes are important in controlling their relative reaction rate. A previous interpretation of the nitration of durene by Willstätter and Kubli has appeared to be erroneous.

As part of a general investigation on substitution reactions in polymethylbenzenes, a detailed study of the nitration of durene in sulfuric acid-chloroform mixtures was desirable, because the course of this reaction did not seem to be quite clear from the data available in the literature. Under all conditions studied so far, the nuclear nitration of durene has always led to 3,6-dinitrodurene, while no 3-nitrodurene was ever detected as a result of direct mononitration of the hydrocarbon. In the nitration by nitric acid in sulfuric acid-chloroform mixtures, which is the best, clean-cut reaction for the nuclear nitration of the hydrocarbon,² either 3,6-dinitrodurene or unchanged durene only could be found.^{3,2b} The only reported interpretation of the reaction, which had tentatively been given many years ago by Willstätter and Kubli,³ resulted not to be in accordance with the present views on aromatic electrophilic substitutions. These authors assumed that the hydrocarbon was likely to be dinitrated by way of an intermediate, labile addition compound with nitric acid, and seemed to exclude the formation of any 3-nitrodurene in the course of the reaction. They also attributed the deep brown color observed while the reaction was in progress to the intermediate compound proposed by them. In more recent times, the nitration of durene has often been referred to as anomalous.⁴

In the present work we have proved that 3-nitrodurene does form during the reaction and that 3,6-dinitrodurene results from durene by two successive substitutions at positions 3 and 6 of the aromatic ring. We have established the following facts: (1) in nitration runs involving the use of a stoichiometric amount of nitric acid corresponding to the mononitration of the hydrocarbon, 3-nitrodurene can be isolated together with larger amounts of 3,6-dinitrodurene and of unchanged durene by chromatographic product analysis; (2) like durene, 3-nitrodurene is rapidly nitrated to 3,6-dinitrodurene; (3) in competitive reactions with 3-nitrodurene, durene is present in the system up to the end-point of the total nitration of the mixture.

As shown by chromatographic product analysis, both the nitration of durene and of 3-nitrodurene

proceed to completion with the respective stoichiometric amounts of nitric acid to give 3,6-dinitrodurene. The two nitrations differ markedly in the depth of the color arising since the first addition of nitric acid, in a manner which is in accordance with a higher reactivity of the hydrocarbon with respect to the nitrohydrocarbon and with the general observations reported by Benford and Ingold⁵ on the color accompanying nitration. In the case of durene the color developed in the sulfuric acid layer is dark brown and fades sharply as soon as the last trace of the hydrocarbon is used up, whereas in the case of 3-nitrodurene the color is light orange and undergoes no detectable change at the end of the reaction. Such a difference in color behavior enabled us to follow competitive nitrations by determining the amount of nitric acid necessary to reach color change, namely, to use up all durene contained in the initial mixture with 3-nitrodurene. The observed color change was found to correspond to the total conversion to 3,6-dinitrodurene of mixtures containing up to two moles of 3-nitrodurene per mole of durene. A plot of the amount of nitric acid employed *vs.* the number of moles of 3-nitrodurene present in the nitration of a fixed amount of durene resulted as a straight line (Fig. 1). The details are recorded in the Experimental part (see Table I).

Such results are in agreement with the fact that, although the dinitration of durene occurs by two ordinary successive substitutions: durene \rightarrow 3-nitrodurene \rightarrow 3,6-dinitrodurene, the intermediate mononitro compound can never be obtained in relatively large amounts at all stages of the heterogeneous reaction in sulfuric acid-chloroform mixtures. They also indicate that, even in the presence of a substantial initial excess of 3-nitrodurene, at the end-point of the reaction of durene (color change) there is no detectable amount of 3-nitrodurene left over, and that the disappearance of 3-nitrodurene from the system can be distinctly more rapid than that of durene. Although 3-nitrodurene is subject to steric hindrance of resonance due to the presence of two *o*-methyl groups preventing coplanarity of the nitro group with the aromatic ring,⁶ the deactivating effect of the nitro group in electrophilic substitutions can be lessened but not totally suppressed by the structural fea-

(1) Part I of this series: G. Illuminati, *THIS JOURNAL*, **74**, 4951 (1952).

(2) (a) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 254; (b) L. I. Smith and F. J. Dobrovolsky, *THIS JOURNAL*, **48**, 1420 (1926).

(3) R. Willstätter and H. Kubli, *Ber.*, **42**, 4151 (1909).

(4) See, for example, W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd Ed., Longmans, Green and Co., London, 1948, p. 56.

(5) G. A. Benford and C. K. Ingold, *J. Chem. Soc.*, 929 (1938).

(6) R. H. Birtles and G. C. Hampson, *ibid.*, 10 (1937); H. Kofod, L. E. Sutton, W. A. De Jong, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 521 (1952); M. Fields, C. Valle and M. Kane, *THIS JOURNAL*, **71**, 421 (1949).

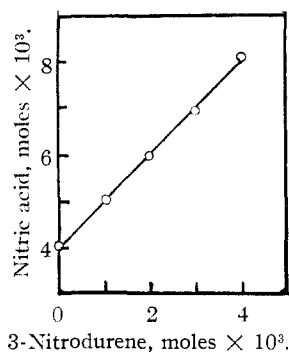


Fig. 1.—Linear dependence of the nitric acid necessary to use up 0.002 mole of durene on the 3-nitrodurene initially present.

tures of the molecule. However, as these reactions occur in a heterogeneous system, their relative rate may be critically affected by transport processes⁷ and 3-nitrodurene can be supposed to react even more rapidly than durene.

Because of the difficulties encountered in performing nitrations with these compounds in homogeneous solution, work is still in progress in this Laboratory for the determination of the relative reactivity of durene and 3-nitrodurene in electrophilic substitutions with special regard to nitration.

Experimental

Materials.—3-Nitrodurene was prepared according to the procedure described in Part I.¹ In the course of the chromatographic experiments described below we observed that the light yellow color often accompanying the compound can be removed by adsorption on aluminum oxide and successive elution with petroleum ether. Such a treatment yielded nearly colorless crystals but did not affect their melting point. Both colorless and light-colored 3-nitrodurene, m.p. 113–114°, were used in the present study with no detectable difference in the results.

Nitric acid was obtained by distillation at 20–30 mm. from a mixture of fuming nitric acid and sulfuric acid in an all-glass apparatus. Savory and Moore (London) aluminum oxide was directly used as such for the adsorption experiments.

Nitration Experiments.—The reactions were carried out in a straight-wall beaker of 105-mm. height and 25-mm. width. Mechanical stirring was provided by means of a twisted glass rod with its lower part bent upward by a length approximately equal to the height of the chloroform layer to be used. A solution of a weighed amount of durene or a mixture of durene and 3-nitrodurene (0.003–0.006 mole) in dry chloroform (3–6 ml.) was directly made up in the beaker, which was then immersed in an ice-water bath. At the equilibrium temperature and under fairly rapid stirring, 98% sulfuric acid (2.3–4.5 ml.) was added. Then nitric acid was slowly added from a calibrated 1-ml. pipet and the stirring was continued for an over-all time of five minutes. In the competitive nitrations, involving either durene or a mixture of durene and 3-nitrodurene, nitric acid was added until color change of the sulfuric acid layer from dark brown to light tan or orange was attained (see Table I), whereas in the experiments devised for the isolation of 3-nitrodurene from the product of the nitration of durene alone, nitric acid was added in such an amount as to correspond to a molar ratio 1:1 with respect to the hydrocarbon.

The reaction mixtures were decomposed by pouring them into a separatory funnel containing enough of a chilled solution of potassium hydroxide as to neutralize the acid approximately. With the aid of a second separatory funnel the chloroform layer was then washed once with a diluted solution of potassium carbonate and once with distilled water. In order to avoid losses of material during these operations,

(7) For a classification of heterogeneous reactions see, for example, L. L. Bircumshaw and A. C. Riddiford, *Quart. Revs.*, **6**, 157 (1952).

TABLE I
COMPETITIVE NITRATIONS OF DURENE AND 3-NITRODURENE

Expt.	Durene, g.	3-Nitrodurene, g.	Nitric acid, ml. up to color change	3,6-Dinitrodurene ^a Yield, %	M.p., °C. ^a
1	0.5373	0	0.34	95.48	205–207
2	.2686	.1794	.21	97.0	208–210
3	.2689	.3584	.25	97.16	208–210
4	.2689	.5377	.29	97.41	209–210.5
5	.2684	.7171	.34	95.08	205–208

^a A pure sample of 3,6-dinitrodurene melted at 210–211°. All melting points are uncorrected.

all apparatus was carefully rinsed with small amounts of chloroform and water. Then the chloroform layer was placed in a 100-ml. erlenmeyer flask, dried over the minimum amount of calcium chloride for two days and finally filtered through a small sintered glass funnel into a weighed 100-ml. erlenmeyer flask. This flask was covered with a little cotton and the solution was allowed to evaporate to dryness over periods of several hours to some days. Such a mild evaporation was in some cases favored by application of dry heat at temperatures not higher than 50° and was intended to reduce losses of any unchanged durene due to the volatility of the hydrocarbon.

The weight of the product was determined by difference. The yields and the melting points of the product, namely, dinitrodurene, obtained from the competitive reactions are reported in Table I. The results from the chromatographic product analysis are reported below.

Nitration of 3-Nitrodurene.—To a solution of 0.720 g. of 3-nitrodurene (0.004 mole) in 5 ml. of chloroform, 3.02 ml. of 98% sulfuric acid was added and the mixture was nitrated with 0.20 ml. of nitric acid (0.004 mole + 20% excess), under the conditions just described. Upon the slow addition of nitric acid, no color change was noticed at the end of the reaction, even after a substantial excess of the acid (20%) had been added. After evaporation of the chloroform solution of the product, a residue of 0.87 g. of dinitrodurene, m.p. 204–207°, was obtained (93%). Recrystallization from ethanol yielded 0.68 g. of crystals, m.p. 209–211°. As in the nitration of durene, better yields and higher melting points of the crude product were observed when no excess of nitric acid was used.

Chromatographic Product Analysis. (a) **Isolation of 3-Nitrodurene from the Nitration of Durene.**—The reaction product obtained as a residue from the complete evaporation of the solvent, was thoroughly mixed with 30–40 ml. of petroleum ether (b.p. 40–47°). The resulting solution was filtered through a sintered glass funnel from most of the dinitrodurene, which remained undissolved, and was then applied on alumina (30 g.) for adsorption. In a typical experiment related to the nitration of 0.8055 g. of durene (0.006 mole) with 0.25 ml. of nitric acid (0.006 mole), 1.0424 g. of reaction product was obtained and 0.4882 g. was therefrom taken up in 40 ml. of petroleum ether. On application of the solution to the alumina column, the elution was carried out as shown in Table II. The eluted material in each fraction was recovered by careful evaporation and weighed by difference. The residue from fraction 4 was found to be pure 3-nitrodurene and its mixed melting point with an authentic specimen of the compound was not depressed. 3-Nitrodurene was also a major constituent of fraction 5, which was, however, contaminated by 3,6-dinitrodurene. The amount of the whole material recovered on elution was 0.4769 g., so that the loss with respect to the weight of the adsorbate was 0.0113 g. Such a small loss is about 1.1% with respect to the total weight of the reaction product and may be accounted for by the presence of a reddish pigment which remained adsorbed on the alumina after fraction 6 was collected.

(b) **Composition of the Product from Competitive Nitrations.**—Some of the products described in Table I and obtained from competitive nitrations, namely, from reactions involving the use of a stoichiometric amount of nitric acid with respect to the complete dinitration of the starting material, were treated with petroleum ether for the adsorption experiment according to the general procedure described in (a). On elution, no material was found either in the pe-

TABLE II
 ISOLATION OF 3-NITRODURENE BY PRODUCT ANALYSIS

Fraction	Eluant	Volume, ml.	Weight, g.	M.p., °C.	Product
1	Petroleum ether	40	0.1005	79.5-80.5	Durene
2	Petroleum ether	10	.0785	78.5-80	Durene
3	Pet. ether-ethanol, 95:5	25	.1232	77-79	Durene (impure)
4	Pet. ether-ethanol, 95:5	25	.0637	113-114	3-Nitrodurene
5	Pet. ether-ethanol, 95:5	15	.0596	99-105	3-Nitrodurene (impure)
6	Chloroform	25	.0514	203-207	3,6-Dinitrodurene

roleum ether fraction or in the petroleum ether-ethanol fraction, whereas 3,6-dinitrodurene was contained in the chloroform fraction. Also in this case, a very small amount of a reddish pigment remained adsorbed on the alumina.

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Esters of γ -(Tetrahydro-2-furyl)-alkanols

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The preparation and properties of esters derived from 3-(tetrahydro-2-furyl)-1-propanol, 4-(tetrahydro-2-furyl)-2-butanol and 1,5-bis-(tetrahydro-2-furyl)-3-pentanol with fat acids from C₂ to C₁₈ and with aliphatic dicarboxylic acids from C₆ to C₁₀ are described.

Further studies relative to a program of developing new chemicals from furfural have led to the preparation of a series of esters derived from 3-(tetrahydro-2-furyl)-1-propanol, 4-(tetrahydro-2-furyl)-2-butanol and 1,5-bis-(tetrahydro-2-furyl)-3-pentanol with the fat acids from C₂ to C₁₈, and with adipic, azelaic and sebacic acids. The properties of these esters are described in this paper.

The γ -(tetrahydro-2-furyl)-alkanols employed in this investigation were obtained as by-products in the synthesis of a number of polyhydroxyalkanes previously reported.² Few derivatives of these ether-alcohols have been described, although the parent compounds have been known for some time.^{3,4,5} A number of esters of 1,5-bis-(tetrahydro-2-furyl)-3-pentanol, including the azelate, have been previously reported.⁶ Little information about the properties of these esters, most of which were derived from alkoxy acids, was given other than that they were effective plasticizers for vinyl, acrylic and cellulose type polymers. No esters of 4-(tetrahydro-2-furyl)-2-butanol have been reported, and only the acetate of 3-(tetrahydro-2-furyl)-1-propanol has been prepared.⁷

The esters of the present series were prepared by

heating the reactants and a catalytic amount of *p*-toluenesulfonic acid dissolved in benzene to reflux, and removing the water of reaction. Purification of the esters was accomplished by distillation. The more volatile esters were fractionated by distillation through conventional columns, whereas the higher boiling esters were distilled from falling-film and alembic flask type molecular stills previously described.⁸ Most of the once-distilled esters contained impurities in amounts varying from 1 to 5%, and were reprocessed until analytically pure samples having constant physical properties were obtained. In a few cases it was necessary to remove free acid, which co-distilled with the ester, by passing the ester dissolved in *n*-heptane through a column of adsorptive alumina. The methods of purification and the order in which they were applied are given in Table I.

No attempts were made to obtain maximum yields of purified products. The yields recorded in Table I are based on those fractions of the once-distilled esters having a degree of purity in excess of 95%, as determined by the saponification equivalent and the free acid content.

All of the esters except the stearates were clear liquids. A few of the higher members of the series were slightly straw-colored. The stearates were white solids. A number of the more volatile esters possessed pleasant fruity odors characteristic of low molecular weight esters in general.

Experimental

Preparation of Esters, General Procedure.—To 200 ml. of benzene containing 2 g. of *p*-toluenesulfonic acid were

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

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