naphthoquinone nucleus by treatment with an acid, a promoter and excess red lead. The 3-ethyl, 3-*n*-propyl and 3-isopropyl derivatives of 2-methylnaphthoquinone were synthesized with the use of propionic, *n*-butyric, and isobutyric acid, respectively, and the structures were established by the preparation of identical substances by the action of lead tetraacetate on 2-ethyl, 2-*n*-propyl, and 2-isopropyl-1,4-naphthoquinone. The 3-*n*-heptyl, 3-benzyl, and 3-β-phenylethyl derivatives of 2-methyl-1,4-naphthoquinone were synthesized by the new method.

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Methylation of Aromatic Nitro Compounds with Lead Tetraacetate

BY LOUIS F. FIESER, RICHARD C. CLAPP AND WILLIAM H. DAUDT

In an initial experiment, 2,4,6-trinitrotoluene was treated in acetic acid solution with lead tetraacetate in the expectation of introducing an acetoxyl group into the reactive methyl substituent. Much to our surprise, the only pure reaction product isolated proved to be trinitro-*m*-xylene. The reaction appears to constitute a second instance
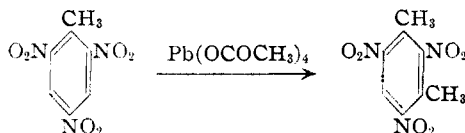
of the methylating action of lead tetraacetate, observed in this Laboratory as applied to various α-naphthoquinones.[1] In further analogy with the naphthoquinone methylation, it was found that carbon dioxide is evolved copiously in the reaction with trinitrotoluene and that a large excess of lead tetraacetate is consumed. Since an efficient method of methylating nitrohydrocarbons might have practical applications of value in the production of high explosives, an exploratory survey was made to test the applicability and efficiency of the novel reaction.

At the time the study was commenced, the parallel work in the quinone field was at a stage where it appeared that the methylating function of lead tetraacetate is evoked only in the presence of an active–hydrogen component such as malonic acid, which is itself attacked by the reagent. We thought at first that a part of the trinitrotoluene might be undergoing acetoxylation in the methyl group and thereby serving as the initiator of the methylation reaction. In the first applications of the reaction to *s*-trinitrobenzene and to *m*-dinitrobenzene, a suitable amount of malonic acid wa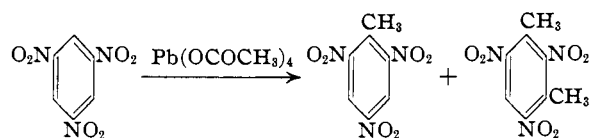s incorporated in the reaction mixture comprising the nitro compound, lead tetraacetate and acetic acid. Although the reactions proceeded under these conditions, it was subsequently discovered that the malonic acid serves only as a promoter of reactions which can be realized in the absence of this or similar component. The methylation reaction, which becomes quite evident from the gas evolution as well as by a marked darkening of the solution, often can be initiated by brief refluxing of the mixture, or by local heating of the flask with a free flame. Once the reaction has been set in progress, it will proceed briskly at a temperature previously found insufficient to cause it to start promptly. No significant differences, in this respect, were observed between trinitrobenzene and trinitrotoluene. In one experiment with the latter compound which was conducted throughout at the steam-bath temperature, the reaction started only after an induction period of about five hours but then proceeded easily to completion. Malonic acid, added as a promoter, promptly induces reaction at the temperature of the steam-bath, and methanol has the same influence. These reagents, however, seem to have no advantages over the method of initiating the reaction by heat, and they merely consume an additional mount of lead tetraacetate. In several parallel experiments the yields were essentially the same whether or not a promoter was used.

The conversion of trinitrotoluene to trinitro-*m*-xylene constitutes a particularly favorable case for study because the product is much less soluble and higher-melting than the starting material. The dimethyl compound also appears to be an end-product, for lead tetraacetate was found to be without action on trinitro-*m*-xylene in refluxing acetic acid. On treating trinitrotoluene with varying amounts of lead tetraacetate in the ab-

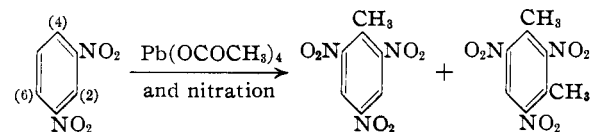(1) Fieser and Chang. THIS JOURNAL. 64. 2043 (1942).

sence of a promoter, no evident stopping point was found and as much as 4.7 equivalents of the reagent was consumed readily. The yield of trinitro-*m*-xylene (19%) was not as high, however, as when a more moderate amount of reagent was used. In three experiments employing 2.5–3 equivalents of lead tetraacetate, yields of 28–32% were obtained, and this appears to be approximately the optimum proportion of reagent for the yield dropped to 20% when but one equivalent was used. The methylation was accomplished also by adding red lead to a warm solution of trinitrotoluene in acetic acid, and by prolonged refluxing of the nitro compound with lead dioxide in acetic acid, but the resulting mixtures were not as easily processed and these methods have no advantages over the use of lead tetraacetate.

The action of lead tetraacetate on 1,3,5-trinitrobenzene was found to result in the formation of both trinitrotoluene and trinitro-*m*-xylene. Be-
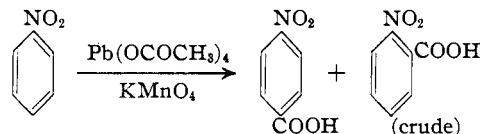

cause of the more complicated nature of the mixture and the less favorable solubility relationships, the yields are less easily determined; orienting experiments indicate merely that the reaction affords more of the monomethyl than of the dimethyl compound, and that the extent of total methylation is perhaps slightly less than found with trinitrotoluene.

In trials with *m*-dinitrobenzene, the reaction mixture was characterized after submitting it to nitration with mixed acid at 120°, for methylation products are thereby nitrated and converted to less soluble products, whereas any starting material is left unchanged. The crude products obtained by the action of lead tetraacetate on the dinitro compound, both with and without the use of a promoter, were nitrated and processed as follows. Crystallization from alcohol–acetone afforded trinitro-*m*-xylene, and addition of β-naphthylamine to the mother liquor gave an easily separated complex of this amine with trinitrotoluene, from which the nitro compound is recoverable by treatment with acid; unchanged *m*-dini-


trobenzene was recovered from the acidified mother liquor. The results show that 1,3-dinitrobenzene is converted in part by lead tetraacetate into its 4-methyl and 2,4- or 4,6-dimethyl derivatives. The extent of total methylation appears to be of the same order of magnitude as with the trinitro compounds.

The reaction was found applicable also to nitrobenzene, although this substance is attacked somewhat less readily than the polynitro compounds. In the first trials, carried out both with lead tetraacetate (3 equivalents) and with red lead and acetic acid, the reaction product was characterized subsequent to nitration, and trinitrotoluene was isolated from the final mixture in 4.9% yield through the β-naphthylamine complex. In another experiment, conducted on a large scale with equivalent amounts of nitrobenzene and lead tetraacetate, the bulk of the unchanged starting material was eliminated by fractionation and the slightly higher-boiling terminal fraction was characterized by oxidation with permanganate. *p*-Nitrobenzoic acid was isolated in a pure condition and a second acidic product was characterized as crude *o*-nitrobenzoic acid; the ortho isomer ap-

pears to predominate but the para compound is more easily separated from the mixture. The extent of the reaction, as indicated by the amounts of the two nitrobenzoic acids isolated, represented 4.3% methylation.

We next ventured to try the new reaction on benzene. When a solution of benzene (10 g.) in acetic acid (60 cc.) was refluxed with lead tetraacetate there was little change at first but, after an induction period of four to five hours, a rapid reaction set in and a total of 2.4 equivalents of reagent was consumed. The reaction mixture contained little if any benzene but consisted almost entirely of high-boiling material. The main constituent of the mixture, isolated by a simple and inefficient distillation technique in 18% yield, proved to be essentially pure benzyl acetate. The reaction evidently involves the separate steps of
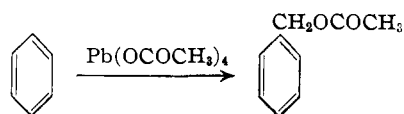
methylation and acetoxylation. The oxidative step has already been demonstrated, for Dimroth and Schweizer[2] found that toluene can be converted to benzyl acetate by the action of lead tetraacetate in refluxing acetic solution (four hours) under conditions very similar to those employed in the present work. Our yield of the product from benzene is even slightly better than theirs obtained starting with toluene (11.5%). The methylation step, therefore, must have proceeded with particular efficiency. Another point of interest is that Dimroth and Schweizer state that benzene is very stable to lead tetraacetate and cite in evidence an experiment in which a mixture of 15 cc. of benzene and 1 cc. of acetic acid was refluxed with the reagent for five and one-half hours with no more than 1% loss in the oxidation value. That they did not encounter the striking reaction observed in the present investigation, may have been because the refluxing was stopped somewhat short of the end of the induction period. Perhaps of greater importance is the difference in the relative amounts of benzene and acetic acid and the consequent difference in the reflux temperatures; the mixture containing an excess of acetic acid as the solvent would be more favorable for initiation of the reaction. It remains to be determined whether the nature of the solvent is of any consequence beyond controlling the boiling temperature. In past instances in which benzene has been employed as solvent for reactions conducted with lead tetraacetate, some attack of the solvent may well have occurred, only to remain undetected.

Chlorobenzene was found to react in a manner similar to benzene, giving a mixture probably consisting of isomeric chlorobenzyl acetates. After saponification, p-chlorobenzyl alcohol was isolated and identified, but no other component of the mixture was characterized. The behavior of naphthalene was different for, under the usual conditions of the methylation reaction, this hydrocarbon was converted in at least 26% yield into 1-acetoxynaphthalene. Thus naphthalene is sufficiently susceptible to oxidative attack to give this reaction precedence over methylation. Still more reactive hydrocarbons such as acenaphthene,[3] anthracene[4] and 3,4-benzpyrene[5] are known to undergo acetoxylation at temperatures well be-

low that at which the methylative action of lead tetraacetate becomes operative.

In completion of this survey of the applicability of the reaction to available starting materials, we tested the action of lead tetraacetate on various mono-, di-, tri- and tetra-nitronaphthalenes, but with invariably unpromising results. The reactions proceeded rather destructively, and a product of methylation was isolated in only one case and in small amounts.

Although any interpretations of the unusual reaction are at present necessarily tentative, it may be noted that the substances which thus far have been found capable of being methylated by lead tetraacetate all conform to the general definition of unsaturated cyclic compounds which are rather resistant to ordinary aromatic substitutions and which do not appear to be susceptible to the acetoxylating action of the reagent. This roughly defined category includes such otherwise widely divergent types as 2-methyl-1,4-naphthoquinone, nitro- and chloro-benzene, the polynitro benzenes and even benzene itself. Toluene and naphthalene fall outside the category, for they are subject to acetoxylation in the side-chain and in the nucleus, respectively. 2-Methyl-1,4-naphthoquinone is associated in behavior with the polynitro compounds in the respect that the yields are favorable and that the methyl group introduced resists subsequent attack. The quinone resembles trinitrobenzene in that the nuclear position undergoing methylation is flanked by unsaturated groups, and a certain similarity is indicated by the fact that a hydroxyl group situated at this position is in each case endowed with pronounced acidic characteristics. The fact that in the series of benzene derivatives the substituting methyl group enters positions ortho and para to the nitro group and the halogen atom, indicates that the reaction is in a class entirely distinct from the usual aromatic substitution.

The reaction has certain other characteristic peculiarities, including the marked induction period frequently noted, and the promoting effect of active-hydrogen compounds and of heat. The evolution of carbon dioxide must be an index of the breakdown of the lead tetraacetate molecule or of some product derived from it, possibly with the direct liberation of methyl radicals. Once this breakdown is initiated, it appears to proceed autocatalytically and to an extent which is excessive in comparison with the amount of methylated
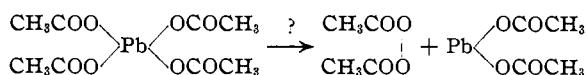
(2) Dimroth and Schweizer, Ber., 56, 1375 (1923).
(3) Fieser and Cason, THIS JOURNAL, 62, 432 (1940).
(4) K. H. Meyer, Ann., 379, 73 (1911).
(5) Fieser and Hershberg, THIS JOURNAL, 60, 1893, 2542 (1938).

material formed, for the yield is not improved beyond a certain point by increasing the amount of lead tetraacetate, and starting material almost always is recovered. Certain substances of adequate stability, when present at the time of the decomposition, seem capable of acting as acceptors of a certain amount of the actual or potential methyl radicals.

There may be a certain analogy between the catalyzed decomposition of this lead salt of acetic acid to carbon dioxide and possible hydrocarbon radicals and the electrolytic decomposition of sodium acetate in the Kolbe synthesis, and from a consideration of this possible analogy we were led to investigate two other lines of experimentation. One of these was suggested by Dr. A. E. Oxford and has been applied by him in an extension of the parallel work in progress in this Laboratory in the quinone field. Since, according to one of the current views concerning the mechanism of the Kolbe synthesis,[6] the reaction may proceed through the intermediary formation of the acyl peroxide, it might be supposed that lead tetraacetate undergoes decomposition to the same intermediate. In

$$CH_3COO \diagdown \quad \diagup OCOCH_3 \quad \overset{?}{\longrightarrow} \quad CH_3COO \quad \diagup OCOCH_3$$
$$ Pb \qquad\qquad \underset{CH_3COO}{|} + Pb \diagdown$$
$$CH_3COO \diagup \quad \diagdown OCOCH_3 \qquad\qquad\qquad\qquad \diagdown OCOCH_3$$

a trial made of the action of acetyl peroxide (3 equivalents) on trinitrotoluene in acetic acid solution, a reaction set in without delay at 85° and proceeded with steady gas evolution and darkening of the solution, in marked resemblance to the lead tetraacetate reaction. Processing of the reaction mixture afforded trinitro-*m*-xylene in 10.6% yield. The alkylation of quinones with acyl peroxides has been conducted with distinct success in several instances.

The second idea was that methylation might be realized by conducting the electrolytic decomposition of sodium acetate in the presence of a suitable acceptor. Initial trials were made with a solution of trinitrotoluene in acetic acid saturated with sodium acetate placed in a porcelain cell which constituted the anode chamber of the cell. On electrolysis over a period as long as twelve hours, some of the nitro compound was lost by diffusion, but there was little destruction of the material remaining in the anode chamber, and trinitro-*m*-xylene was isolated as a reaction product in yields up to 9%.

(6) Review papers: Fichter, *Trans. Electrochem. Soc.*, **75**, 309 (1939); Glasstone and Hickling, *ibid.*, **75**, 333 (1939).

These few exploratory experiments demonstrate that alkylations of a novel type may be accomplished by three different experimental methods which probably are interrelated and which may involve manifestations of the same general phenomenon. As for possible practical applications, the present survey indicates that methylation with either lead tetraacetate or acetyl peroxide is more likely to find uses in the synthesis of rare chemicals than in the quantity-production of polynitro alkylbenzenes. The electrolytic method of methylation has not been evaluated fully but does not appear promising for practical application.

Experimental Part[7]

Conversion of Trinitrotoluene into Trinitro-*m*-xylene

Identification of the Product.—In an initial experiment carried out by Dr. E. B. Hershberg, a mixture of 3 g. of 2,4,6-trinitrotoluene, 6.2 g. (1 equiv.) of lead tetraacetate and 20 cc. of glacial acetic acid was heated gently at first and then refluxed for one-half hour. The product precipitated with water (1.7 g.) on one crystallization from alcohol afforded 0.6 g. of material, m. p. 145–165°. After six further crystallizations from benzene–hexane, the purified substance melted at 182.7–183.2°, and a mixture with a sample of authentic trinitro-*m*-xylene (m. p. 180.5–182°) melted at 180.5–182°.

Anal. Calcd. for $C_8H_7O_6N_3$: C, 39.84; H, 2.93; N, 17.43. Found: C, 40.34; H, 3.06; N, 17.27.

With Red Lead and Acetic Acid.—Methylation also can be accomplished by the addition of red lead in portions to a stirred solution of trinitrotoluene in acetic acid at 95°, with subsequent gentle refluxing, and the formation of trinitro-*m*-xylene under these conditions was established. The reaction mixture is not as clean as when lead tetraacetate is used, and the processing is therefore less easily accomplished; the separation of lead dioxide from the acetic acid solution makes it difficult to follow the progress of the reaction. For these reasons, lead tetraacetate was employed in most of the exploratory experiments. Preliminary attempts to ethylate trinitrotoluene and trinitrobenzene with lead tetrapropionate or with propionic acid and red lead were unpromising.

With Lead Tetraacetate.—In trial runs made with 1.0, 2.5, and 4.7 equivalents of lead tetraacetate, which in each case was completely consumed, the yields of trinitro-*m*-xylene of comparable purity were 19.8, 28.2, and 18.8%, respectively. The product was more difficult to purify in the experiment utilizing the largest amount of reagent than in the other runs.

The most satisfactory of these experiments was carried out by adding 14.6 g. (0.033 mole) of lead tetraacetate to a solution of 3.0 g. (0.132 mole) of trinitrotoluene (m. p. 80.4–81.8°) in 40 cc. of acetic acid. The reaction was not initiated by heating the mixture on the steam-bath (90–95°), for no gas was evolved, and the originally undissolved lead tetraacetate remained colorless and showed no ten-

(7) Microanalyses by Lyon Southworth and B. Werble.

dency to go into solution. When the mixture was heated to the reflux temperature, however, a yellow coloration soon appeared at one spot in the lead tetraacetate crystals and soon spread over the entire mass, and there was a rapid evolution of gas containing carbon dioxide. After refluxing for about fifty minutes the evolution of gas had ceased and a test with moistened starch–iodide paper was negative. By this time the originally light yellow solution had acquired a rather deep red-orange color. The hot solution was diluted with water and cooled, when 1.4 g. of crude product separated; this melted at 135–165°. Two crystallizations from benzene–hexane (Norit) gave 0.90 g. (28.2%) of yellow needles of trinitro-*m*-xylene, m. p. 174–178°. A further crystallization from alcohol–acetone afforded 0.66 g. (20.7%) of long, light yellow needles, m. p. 178–180°, and the more fully purified material melted at 182.7–183.2° and did not depress the melting point of an authentic sample.

Effect of Promoters.—An experiment parallel to that just described was carried out with the same amounts of reagents (4.7 equiv. of lead tetraacetate) but with the addition of one equivalent of malonic acid. This functioned as a promoter, for the reaction started, as evidenced by the gas evolution, when the mixture was heated on the steam-bath. The reaction proceeded to completion at this temperature, and the test for lead tetraacetate was negative after one hour. The yield was practically the same as when no malonic acid was used. In other trials with varying proportions of lead tetraacetate, the yields tended to be slightly lower with malonic acid present than when no promoter was employed.

Methanol (1 cc. in 40 cc. of acetic acid, 3 equivalents of lead tetraacetate) also functioned as a promoter and induced a prompt reaction at the steam-bath temperature; the yield of trinitro-*m*-xylene, m. p. 177–179.5°, in this case was 28%. When an absolute methanol solution of trinitrotoluene and lead tetraacetate (3 equiv.) was refluxed, reaction set in immediately and was complete in about fifteen minutes. However, only starting material was recovered, indicating that the consumption of reagent was due to oxidation of the solvent.

Conversion at a Moderate Temperature.—A mixture of 1.0 g. of trinitrotoluene, 5.9 g. (3 equiv.) of lead tetraacetate, and 10 cc. of acetic acid was heated on the steam-bath without a promoter and without stirring. After an induction period of about five hours, gas evolution became discernible and the lead tetraacetate began to dissolve. After continued heating overnight on the steam-bath, the reaction was found to have gone to completion. The product which separated on adding water to the light red solution and cooling gave, on crystallization from acetone–alcohol (Norit), 0.37 g. of needles, m. p. 174–177°. Recrystallization afforded 0.34 g. (32%) of trinitro-*m*-xylene, m. p. 176–178.5°. The high yield and quality of the product may be due to the mild conditions of the reaction.

With Lead Dioxide and Acetic Acid.—A suspension of 10 g. (3.2 equiv.) of lead dioxide in a solution of 3 g. of trinitrotoluene in 50 cc. of acetic acid was heated under reflux, when a slow evolution of carbon dioxide was observed. After refluxing for twelve hours, all of the reagent had dissolved and the starch–iodide test was negative. The red-

dish solution was filtered from a small amount of black residue and diluted with water. The precipitated material on crystallization afforded 0.54 g. (17%) of trinitro-*m*-xylene, m. p. 175–178°, and from the mother liquor there was recovered 0.64 g. of trinitrotoluene, isolated through the β-naphthylamine complex.

In another trial acetic anhydride was added to a similar reaction mixture. This caused the lead dioxide to dissolve rapidly, and the reaction was completed in a much shorter time; the yield, however, was distinctly lower. The yield was also lower when the above experiment was repeated with the use of a larger excess of lead dioxide.

Stability of Trinitro-*m*-xylene to Lead Tetraacetate.—A solution of 0.5 g. of trinitro-*m*-xylene and 0.92 g. (1 equiv.) of lead tetraacetate in acetic acid was refluxed for four and one-half hours, but there was no pronounced gas evolution. lead tetraacetate was still present at the end of the period of refluxing, and unchanged starting material crystallized from solution on cooling. In another trial an acetic acid solution of equimolecular amounts of trinitro-*m*-xylene and malonic acid was heated on the steam-bath and treated with lead tetraacetate until a total of 4.7 equivalents of the reagent had been consumed. Practically all of the starting material was recovered unchanged.

Methylation with Acetyl Peroxide.—The reagent was prepared essentially according to Gambarjan[8] by adding ice with shaking to a cooled mixture of acetic anhydride. sodium peroxide and petroleum ether, and separating and evaporating the hydrocarbon layer. A solution of 4 g. of trinitrotoluene and 6.2 g. (3 equiv.) of acetyl peroxide in 50 cc. of acetic acid was warmed gradually in a water-bath to a temperature of 85°, when a steady gas evolution was noted. After heating for one hour at 85–95°, and for one hour longer at 95–100°, the evolution of gas had become feeble, and after one hour more at 95–100° it had ceased completely. The orange-red solution was diluted well with water, and the semisolid material which precipitated was collected, dried, and leached with about 100 cc. of warm alcohol. This dissolved the bulk of the material and left 0.32 g. of powdery, light brown solid, m. p. 170–177°. Crystallization of this material from acetone–alcohol gave 0.28 g. of characteristic needles of trinitro-*m*-xylene, m. p. 177–180°, and 0.17 g. of product of the same melting point was recovered from the alcoholic mother liquor; total yield 10.6%. Only a very small amount of trinitrotoluene could be recovered from the mother liquors.

Methylation by Electrolysis.—The electrolysis was conducted in a 400-cc. beaker in which was suspended a 4-inch porcelain cell about 1.5 inches in diameter to contain the anode liquid. The anode and cathode were made of bright platinum foil. A solution of 1 g. of trinitrotoluene in acetic acid saturated with sodium acetate was placed in the anode chamber and the cathode chamber was filled with a concentrated solution of sodium acetate in 50% aqueous acetic acid. The electrolysis was conducted for twelve hours with an average current of about 0.9 ampere and at a temperature maintained with minor exceptions at 35–45° by thorough external cooling with salt-ice. Additional 7–8 cc. portions of acetic acid containing sodium acetate were added after four and nine hours. The anodic solution acquired a light orange-yellow color soon after the reaction

(8) Gambarjan, *Ber.*, **42**, 4003 (1909).

was initiated. The cathodic solution, after remaining essentially colorless for several hours, gradually turned light orange-red, indicating loss of material from the anode compartment.

On pouring the anodic solution into water, there separated rather slowly a solid precipitate weighing 0.24 g. and melting from 80 to 130°. Crystallization from alcohol–acetone afforded 95 mg. (9%) of characteristic needles of trinitro-*m*-xylene, m. p. 155–170°, representing 40% of the material collected. In another experiment, in which electrolysis was continued for only five and one-half hours, the yield was lower but there was less diffusion and considerable starting material was present in undamaged condition. When a lead anode was used there was no gas evolution in the anode chamber and only starting material was recovered.

Other Trials.—Hydrogen peroxide (1.5 cc. of Superoxol, 3.8 equiv.) proved to be without effect on trinitrotoluene (1 g.) in acetic acid solution (10 cc.) at the temperature of the steam-bath. Gas was evolved only very slowly and after six hours the starch–iodide test had become faint. On cooling, 0.8 g. of trinitrotoluene (m. p. 80–82°) crystallized.

Mercuric acetate was tried in place of lead tetraacetate in refluxing acetic acid (twelve hours). but no methylation was observed.

Solutions of trinitrotoluene in acetic acid containing 3 equivalents of tetraethyllead or tetramethyllead were heated on the steam-bath, but although there was some gas evolution and a darkening of the solutions, nearly all of the original trinitrotoluene was recovered unchanged in each case.

Methylation of 1,3,5-Trinitrobenzene

With a Promoter.—A mixture of 2.5 g. of trinitrobenzene (m. p. 122–123°), 1.25 g. of malonic acid, 26 g. (5 equiv.) of lead tetraacetate, and 60 cc. of acetic acid was heated on the steam-bath until all of the solids had dissolved, including a lead salt which formed at first, and until the evolution of carbon dioxide had ceased and the starch–iodide test was negative. On pouring the red solution into water and allowing the mixture to stand for several hours in the cold, 1.85 g. of material separated, m. p. 50–60°. One crystallization from benzene–hexane and two from alcohol (Norit) afforded 0.13 g. of trinitrobenzene as plates, m. p. 120–122° (no depression). Processing of the mother liquor gave a small amount of trinitro-*m*-xylene (needles, m. p. 173–178°, after several crystallizations from alcohol–acetone) and, after several crystallizations, 0.15 g. of trinitrotoluene, m. p. 76.5–78.5°. The mono and dimethyl derivatives were identified by mixed melting point determinations. Additional small amounts of trinitrobenzene were recovered from the mother liquors as the phenanthrene complex (yellow needles, m. p. 155–158°).

Without a Promoter.—A mixture of 2.5 g. of trinitrobenzene, 21.6 g. (4.15 equiv.) of lead tetraacetate, and 60 cc. of acetic acid was heated on the steam-bath for four hours without visible sign of reaction; the colorless crystals of lead tetraacetate remained largely undissolved and no gas was evolved. When the mixture was refluxed, a yellow color soon appeared in one part of the crystal mass and soon spread, the solution turned yellow and then red, and carbon dioxide was evolved. The gas evolution ceased in about one-half hour and the test for tetravalent lead was

negative. Precipitation with water gave a total of 1.35 g. of material melting at about 80–130°. Systematic fractional crystallization afforded in all 0.11 g. of trinitro-*m*-xylene needles, m. p. 178–180°, and 0.26 g. of trinitrotoluene plates, m. p. 78–80°. No trinitrobenzene could be recovered, either as such or as the phenanthrene complex.

Methylation of *m*-Dinitrobenzene

In preliminary methylation experiments with twice recrystallized commercial *m*-dinitrobenzene, the reaction mixtures were found to contain small amounts of trinitro-*m*-xylene. Since this may well have arisen from a trace of trinitrobenzene present in the starting material as an impurity, the *m*-nitrobenzene employed in the final experiments was purified carefully by repeated crystallization, when it melted constantly at 89.8–90.5° and had the analysis: C, 42.90; H, 2.43 (calcd.: C, 42.86; H, 2.40). Since the preliminary trials had indicated that the separation of dinitrobenzene and dinitrotoluene presents considerable difficulty, the crude reaction mixtures (which with pure starting material afforded no trinitro-*m*-xylene) were, in subsequent experiments, submitted to nitration before being fractionated.

With a Promoter.—A stirred mixture of 3 g. of pure *m*-dinitrobenzene and 38 g. (4.8 equiv.) of lead tetraacetate in 40 cc. of acetic acid was maintained at 85–90° on the steam-cone and a portion of a solution of 1.9 g. (1 equiv.) of malonic acid in 40 cc. of acetic acid was added slowly by drops. When a little more than half of the solution had been added (in about thirty minutes), a marked deepening in the color of the liquid indicated that the reaction had started and no more malonic acid was added. After stirring at 95° for two and one-quarter hours the lead tetraacetate had all reacted and the solution was consequently poured into ice-water. The powdery precipitate was dissolved in ether and the cloudy aqueous solution was extracted three times with ether. The total ethereal solution was filtered from a trace of flocculent precipitate, washed well with water, dried over calcium chloride, and evaporated to a dark reddish brown, viscous oil. This was dissolved in 20 g. of concentrated sulfuric acid and treated dropwise at 75–95° with a mixture of 5 g. of fuming nitric acid and 30 g. of concentrated sulfuric acid. The temperature was raised to 110° in about twenty-five minutes and held at 110–120° for three and one-quarter hours. The crude, precipitated product (1.65 g.) was a brownish solid, m. p. 55–63°. The first crop from alcohol (0.18 g., m. p. 120–150°) afforded on further purification 80 mg. (1.9%) of crude trinitro-*m*-xylene, m. p. 168–175°. Treatment of the remaining mother liquor with 1.5 g. of β-naphthylamine afforded 0.78 g. of the trinitrotoluene–β-naphthylamine complex as red needles, m. p. 112–113°. Decomposition of the complex with dilute hydrochloric acid gave a total of 0.43 g. (10.6%) of trinitrotoluene, m. p. 77–79°. The mother liquor from the amine complex, after treatment with dilute hydrochloric acid, afforded 0.2 g. of *m*-dinitrobenzene, m. p. 90–92° (6.7% recovery).

Without a Promoter.—In this experiment a solution of 5 g. of analytically pure *m*-dinitrobenzene in 50 cc. of acetic acid was treated with 50 g. (3.9 equiv.) of lead tetraacetate in 5-g. portions, largely at the temperature of the steam-bath. It was discovered that the reaction can be initiated

either by refluxing the mixture for a short time at the outset or by application of localized heat. The reaction then proceeded at the temperature of the steam-bath (but not lower) at a moderate rate (about two bubbles of gas per second). The reaction product was collected and nitrated as described above, giving 2.35 g. of crude yellow solid, m. p. 75–85°. Systematic fractionation from alcohol–acetone afforded in all 0.7 g. of crude trinitro-*m*-xylene, m. p. 160–170°, which when recrystallized formed needles, m. p. 175–178° (no depression). The mother liquor material when processed as above gave 1.05 g. of red needles of trinitrotoluene–β-naphthylamine complex from which 0.53 g. of pure trinitrotoluene was obtained, m. p. 79–80° (no depression). The aqueous acid liquor was extracted with benzene and the solution was washed and concentrated and the residue taken up in alcohol, from which 150 mg. of *m*-dinitrobenzene (m. p. 89–91°) crystallized; a small amount of trinitrotoluene, m. p. 75–78°, was isolated from the mother liquor through the β-naphthylamine complex.

Methylation of Nitrobenzene

In one experiment a mixture of 5 g. of purified nitrobenzene (steam distilled and redistilled), 40 cc. of acetic acid, and 18 g. (1 equiv.) of lead tetraacetate was heated on the steam-cone and, when an attempt to initiate a reaction by local heating with a free flame failed, 0.1 g. of malonic acid was added. Heating on the steam-cone was continued for two hours, but gas was evolved only very slowly. When a second equivalent of reagent was added, however, a steady evolution of gas ensued and the color of the solution deepened to a red-orange. Four hours later, the addition of a third equivalent of lead tetraacetate further accelerated the reaction, and the reagent was all consumed in a total time of twelve hours. The crude product collected by dilution with water and extraction with ether was nitrated in the usual way, giving 2.67 g. of crude solid, m. p. 43–75°. This was treated in alcoholic solution with an equal weight of β-naphthylamine and yielded 0.79 g. of crude trinitrotoluene complex, m. p. 107–111°, which on cleavage with acid afforded 0.45 g. (4.9%) of trinitrotoluene, m. p. 79–81°. The mother liquor from the amine complex yielded, after acid treatment, a total of 1.88 g. (27.5%) of *m*-dinitrobenzene and a very small amount of high-melting material which probably is trinitro-*m*-xylene. The β-naphthylamine complex of trinitrotoluene was also isolated, after nitration, in a methylation experiment carried out with red lead, added in portions to a refluxing solution of nitrobenzene in acetic acid and acetic anhydride.

In another experiment designed to permit characterization of the methylated material as such, a total of 300 g. (0.68 mole) of lead tetraacetate was added in three portions, at intervals of about one hour, to a refluxing solution of 80 g. (0.65 mole) of purified nitrobenzene in 200 cc. of acetic acid. The reaction proceeded rapidly (gas evolution, darkening) at the reflux temperature, and each portion of reagent was consumed in about one hour. The very dark reddish brown solution was poured into water and the organic material extracted with ether and steam distilled (dark, tarry residue). The straw-colored distillate was washed in ether solution with water and with soda solution, and dried. The residual liquid (78 g.) was then fractionated in a 1-meter column packed with glass helices.

The first fraction consisted chiefly of 55.7 g. of nitrobenzene, b. p. 102.8–106.3° at 25 mm. Further distillation gave 2.8 g. of material boiling at 106.3–109.5° (25 mm.) before exhaustion of liquid in the boiling flask. This was combined with the hold-up liquid recovered by washing the column, and distillation from a modified Claisen flask yielded 10.7 g. of straw yellow liquid, b. p. 105–112° (17.5 mm.).

Attempted characterization of the liquid by reduction of the nitro group and preparation of acyl derivatives proved unpromising, for mixtures were obtained which could not be separated satisfactorily by fractional crystallization. Oxidation with permanganate provided a more effective means of identification and of obtaining a measure of the extent of methylation. Following a procedure[9] which has been shown to afford *o*-nitrobenzoic acid from *o*-nitrotoluene in 90% yield, a mixture of 2.5 g. of the liquid product and 100 cc. of water containing 5.4 g. of potassium permanganate was stirred on the steam-cone for seven and one-half hours. The aqueous liquor was made alkaline with soda, the manganese dioxide was removed by filtration, and some unoxidized liquid was extracted with ether. Since no precipitate appeared on acidification of the alkaline solution, the product was collected by five extractions with ether. Evaporation of the ether left a white solid which, on crystallization from alcohol, gave in the first crop 0.3 g. of long, flat needles, m. p. 230–236°. Recrystallization raised the melting point to 238–239.5°, and a mixed melting point determination with authentic *p*-nitrobenzoic acid showed no depression. Further crops yielded a total of 0.79 g. of crude needles, m. p. 133–138°. The melting point of this material could not be raised above 138.5–142°, but a mixture of this sample with *o*-nitrobenzoic acid (m. p. 144–145.5°) showed no depression, whereas a mixture with *m*-nitrobenzoic acid (m. p. 138.5–140.5°) melted from 106 to 119°.

The unoxidized material recovered from the ethereal extract of the neutral fraction was reduced with stannous chloride and the crude amine treated with benzoyl chloride. This afforded 0.79 g. of solid which was identified after purification as benzanilide. The amount of this derivative collected corresponds to the presence of 23.7% of nitrobenzene in the product submitted to oxidation. The amounts of the two nitrobenzoic acids isolated indicate the presence in the product of 9.8% of *p*-nitrotoluene and 26.0% of *o*-nitrotoluene. On the basis of the oxidation experiment, the total yield of identified nitrotoluenes produced in the reaction with lead tetraacetate is 3.85 g., representing 4.3% methylation (compare 4.9%, found after nitration).

In view of the low yields in these experiments, it seemed desirable to examine the purified nitrobenzene employed as starting material for the possible presence of nitrotoluenes. For this purpose, 490 cc. of the nitrobenzene used was fractionated through the 1-m. column, when 465 cc. of material distilled at 97.9–98.1° at 20 mm. The tail fraction was recovered from the pot residue and the column by ether extraction. One 5-g. portion of the residual material was nitrated and gave 5.0 g. of crude *m*-dinitrobenzene, m. p. 75–83°; this when recrystallized afforded 2.72 g. of the dinitro compound, m. p. 89.5–90°, and on processing of the

(9) Ullmann and Uzbachian, *Ber.*, **36**, 1799 (1903).

mother liquor with β-naphthylamine no indication was obtained of the presence of trinitrotoluene. Another portion (5 cc.) of the tail fraction was oxidized with permanganate exactly as described above and the alkaline filtrate was acidified and extracted thoroughly with ether; there was no significant residue on evaporation of solution.

Other Actions of Lead Tetraacetate

Conversion of Benzene to Benzyl Acetate.—A mixture of 10 g. of thiophene-free benzene in 60 cc. of acetic acid with 57 g. (1 equiv.) of lead tetraacetate was refluxed for two and one-half hours with but little sign of reaction (light yellow solution), although toward the end of this period a slight evolution of carbon dioxide was noted. An additional 80-g. lot of lead tetraacetate (total = 2.42 equiv.) was added, together with 20 cc. more acetic acid. After a total time of about four hours of refluxing, the gas evolution became somewhat stronger and the color began to deepen. At about five hours, the solution was yellow-orange and the reaction began to proceed very rapidly. Within another half hour the solution had turned dark red-brown and all of the lead tetraacetate was found to have been consumed.

The mixture was drowned and extracted with ether, and the product collected, after washing with water and soda, was distilled at atmospheric pressure from a Claisen flask. Only 1.5 g. of distillate was obtained up to 190°, and the main fraction was taken at 190–250° and consisted of 7.0 g. of a slightly yellow liquid with a pleasant odor; a gummy residue of about 2 g. remained undistilled. The main fraction was redistilled and a cut taken of 3.45 g. (18%) of colorless liquid boiling at 95–110° (20 mm.); most of this distilled at 105–107°. Hydrolysis of this fraction with 10% sodium hydroxide gave a liquid which was identified as benzyl alcohol by the preparation of the α-naphthyl-urethan; this derivative melted at 131.4–132.0° and did not depress the melting point of an authentic sample. The alkaline solution from the hydrolysis was steam distilled for several hours and then acidified carefully with phosphoric acid and distilled. The Duclaux numbers found by the usual procedure[10] for three fractions were 7.04, 7.40, and 8.05, which demonstrates the presence of acetic acid. The reaction product is thereby identified completely as benzyl acetate.

A check run, in which all of the lead tetraacetate was added at the start, proceeded similarly and afforded benzyl acetate, b. p. 93–104° at 16 mm., in 16.2% yield (the bulk of the product distilled at 102–103°). The undistilled residues from the two runs were combined and hydrolyzed, but the only product recognized was a small additional amount of benzyl alcohol. It was noticed that the acidified aqueous solution obtained after hydrolysis of the main fraction has a phenolic odor, but no test for phenol could be obtained.

Action of Lead Tetraacetate on Chlorobenzene.—A mixture of 10 g. of chlorobenzene, 80 g. (2 equiv.) of lead tetraacetate, and 80 cc. of acetic acid was refluxed until the reagent was consumed; as with benzene, there was an induction period of three to four hours before the reaction became rapid. Distillation of the collected product gave 2.9 g. of material boiling at 115–140° at 12.5 mm., and re-

distillation of this fraction afforded 2.12 g. (12.9%) of clear, pleasant smelling liquid, b. p. 115–130° at 12.5 mm. (chiefly at 120–123°). Hydrolysis with dilute alcoholic alkali yielded 1.25 g. of material, b. p. 112–117° (11 mm.), which partially crystallized. Crystallization of the distillate from ligroin (70–90°) gave 0.45 g. (3.5%) of irregular plates, m. p. 60–63°, and the recrystallized sample formed flat needles, m. p. 69.4–70.4°. The melting point is close to that of p-chlorobenzyl alcohol (m. p. 71–72.5°[11]), but not far from that of the ortho isomer (m. p. 64–65°[11]), and consequently a sample of the alcohol melting at 60–63° was oxidized to the acid with refluxing permanganate solution. This afforded an acid which on recrystallization formed small plates melting at 238–240° and gave no depression when mixed with authentic p-chlorobenzoic acid. Since the yield of crystallized para acid was low (10–15%), it is quite possible that more soluble isomers may have been present. Oxidation of the crude product of hydrolysis gave evident mixtures of acids from which, however, only p-chlorobenzoic acid was isolated.

Acetoxylation of Naphthalene.—A mixture of 20 g. of naphthalene, 50 g. of lead tetraacetate and 100 cc. of acetic acid was heated with a flame adjusted so as to maintain a steady and moderate gas evolution. When the reagent had been consumed, another 50-g. portion was added (total, 2.9 equiv.) and heating was continued until it had all reacted (very dark solution). After collection of the product by drowning and extraction with ether, distillation at 10 mm. gave 7.8 g. of low-boiling material (to 140°). from which there was obtained 4.1 g. of naphthalene by crystallization. The next fraction taken (140–180° at 10 mm.) was redistilled and a middle fraction, b. p. 150–175° at 10 mm. (insoluble in alkali), was saponified with 10% sodium hydroxide and alcohol. Two distillations of the dark product of hydrolysis gave 4.0 g. of phenolic product, b. p. 140–150° (10 mm.). Crystallization from ether–hexane yielded 2.9 g. (26%) of crude α-naphthol, m. p. 91–94°, and two further crystallizations gave plates, m. p. 94–96°, which gave no depression when mixed with authentic α-naphthol.

Preliminary Trials with Nitronaphthalenes.—Trial experiments carried out essentially as described above with α-nitronaphthalene, 1,5- and 1,8-dinitronaphthalene, 1,3,8- and 1,4,5-trinitronaphthalene, and 1,3,6,8-tetranitronaphthalene gave unpromising results; oxides of nitrogen were evolved in some cases, the reaction mixtures were very dark, and brief processing afforded a pure transformation in only one instance. The reaction mixture from 1,8-dinitronaphthalene and lead tetraacetate yielded a very small amount of crystalline material melting at 207–210°. The substance corresponds in melting point and composition to 1,8-dinitro-2-methylnaphthalene.

Anal. Calcd. for $C_{11}H_8O_4N_2$: C, 56.90; H, 3.47. Found: C, 56.74; H, 3.22.

Summary

Aromatic nitro compounds can be methylated in low or moderate yield by the action of lead tetraacetate in acetic acid solution. The reaction is akin to the recently observed alkylation of

(10) Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 120.

(11) Carothers and Adams, THIS JOURNAL, **46**, 1675 (1924).

methylnaphthoquinone by the same reagent and is similarly initiated by the use of active-hydrogen promoters or by heating. By this method trinitrotoluene has been converted in yields as high as 32% into trinitro-m-xylene, which appears to be an end product. Trinitrobenzene affords trinitrotoluene and trinitro-m-xylene as reaction products, and the same two substances were obtained from m-dinitrobenzene by treatment with lead tetraacetate, followed by nitration. Nitrobenzene is converted in low yield into o- and p-nitrotoluene, identified as the corresponding nitrobenzoic acids.

Under similar conditions, benzene is converted by lead tetraacetate in acetic acid into benzyl acetate in yields up to 18%. Chlorobenzene behaves similarly and yields a mixture which has been characterized as containing p-chlorobenzyl acetate. Naphthalene is converted into the 1-acetoxy derivative in 26% yield. The reaction does not appear promising as applied to nitro and polynitronaphthalenes.

Analogies to the electrolytic decomposition of metal salts of carboxylic acids in the Kolbe synthesis have led to the discovery of related methods of alkylation consisting in the treatment of the nitro compound in acetic acid solution with acetyl peroxide and the electrolysis of a solution of the nitro compound in acetic acid containing sodium acetate. Trinitrotoluene was converted by both methods into trinitro-m-xylene in low yields.

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Alkylation of Para Quinones with Acyl Peroxides

BY LOUIS F. FIESER AND ALBERT E. OXFORD[1]

In continuation of previous work in this Laboratory on the alkylating action of esters of tetravalent lead,[2,3] a few exploratory experiments were made to see if the reaction of lead tetraacetate with 2-methyl-1,4-naphthoquinone in acetic acid solution to give 2,3-dimethyl-1,4-naphthoquinone can be promoted by the addition of substances other than active-hydrogen reagents and methanol.[2] It was found that a number of solvents, including some which do not themselves appear to be attacked, not only promote the methylation reaction but also, in the absence of a quinone or other methyl acceptor, exert a presumably catalytic effect and promote the decomposition of lead tetraacetate to carbon dioxide and an inflammable gas.

In experiments conducted with 0.005 mole of methylnaphthoquinone in 14 cc. of acetic acid at 90–100° with excess solid lead tetraacetate present throughout, no reaction occurred in the absence of a promoter, as previously observed,[2] but a usually vigorous gas evolution ensued, with darkening of the solution and ultimate production of the 2,3-dimethyl compound, on the addition of

1–3 g. of any one of the following substances: methanol,[2] water, isopropyl alcohol, t-butyl alcohol (thirty-minute lag, then gentle effervescence), isopropyl ether, benzene, toluene, cyclohexane (benzene-free), n-octane (synthetic). Under the same conditions but in the absence of methylnaphthoquinone, all of these substances except t-butyl alcohol brought about a steady if somewhat less vigorous decomposition of lead tetraacetate in the acetic acid solution. The gas evolution was particularly rapid and vigorous in the presence of added benzene, while with toluene as the promoter there was a prolonged induction period followed by a very slow gas evolution. Cyclohexane is a slightly less effective promoter for the decomposition than benzene, and n-octane produces, after a brief lag, a still more moderate gas evolution. The cyclohexane employed as a promoter was found to be largely recoverable unchanged after a reaction period of eight hours, in which time a considerable amount of lead tetraacetate had suffered decomposition before the reaction had come to a standstill. Although the action of the hydrocarbon somewhat resembles that of a true catalyst, it is noteworthy that the reaction slows down after a time and that a given quantity of cyclohexane brings about the decomposition of only a limited amount of lead tetraacetate. The

(1) International Fellow of the Rockefeller Foundation on leave of absence from the London School of Hygiene and Tropical Medicine.

(2) Fieser and Chang. THIS JOURNAL. 64, 2043 (1942).

(3) Fieser. Clapp and Daudt, ibid., 64, 2052 (1942)