found to be 181 and the molecular weight as determined by the melting point depression of naphthalene as 373. Evidently there were two carboxyl groups in the molecule. The compound was analyzed for carbon and hydrogen. *Anal.* C, 73.1, 73.3; H, 4.4, 4.4. From the carbon and hydrogen analysis and the molecular weight determination the molecular formula of the yellow compound was calculated to be most probably $C_{23}H_{16}O_5$.

With Nitrogen Bases.—Portions of the bromo acid were treated in turn with anhydrous pyridine, aniline, dimethylaniline and diethylamine. In all cases an evolution of carbon dioxide resulted, and considerable heat was evolved. All three amines gave tarry and gummy masses from which the reaction products could not be isolated. With aqueous ammonium hydroxide a dark brown solution was obtained which yielded a little benzoylcarbinol by

extraction with ether. Upon acidification a tar precipitated which was almost insoluble in most organic solvents.

Summary

1. The dehalogenation of β-bromophenylpyruvic acid has been studied under a variety of conditions. Evidence has been obtained for the intermediate formation of phenylketene under certain of the above conditions.

2. The possibilities and some of the difficulties of utilizing the dehalogenation of α-keto-β-bromo acids as a new method of synthesis of ketene derivatives have been pointed out.


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reactions between Organomercury Compounds and Nitrosyl Compounds[1,2]

BY LEE IRVIN SMITH AND F. LOWELL TAYLOR

The reactions between nitrosyl compounds and organomercury compounds were discovered by Baeyer,[3] who first prepared nitrosobenzene by the action of nitrosyl bromide upon diphenylmercury.[4]

Bamberger[5] studied the reactions between nitrogen oxides and bis-arylmercury compounds. Apparently, he concluded that the action of nitrogen sesquioxide upon organomercury compounds was entirely different from that of nitrogen dioxide. He represented the reaction between nitrogen dioxide and diphenylmercury by equation (1).

$$(C_6H_5)_2Hg + N_2O_4 \longrightarrow C_6H_5HgNO_3 + C_6H_5NO \quad (1)$$
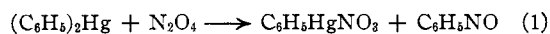
Despite the fact that he also obtained a small quantity of nitrosobenzene by the action of nitrogen sesquioxide, Bamberger represented the reaction between the sesquioxide and diphenylmercury by equation (2).

$$(C_6H_5)_2Hg + 2N_2O_3 \longrightarrow$$
$$C_6H_5HgNO_3 + C_6H_5N_2NO_3 \quad (2)$$

He ascribed the formation of the nitrosobenzene to

the action of nitrogen dioxide formed by dissociation of the sesquioxide. Moreover, nitric oxide did not act upon diphenylmercury, but did act upon nitrosobenzene, o-nitrosotoluene, and p-bromonitrosobenzene. The corresponding diazonium nitrates were formed (equation 3).

$$C_6H_5NO + 2(NO) \longrightarrow C_6H_5N_2NO_3 \quad (3)$$
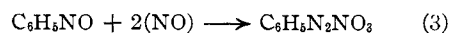
In the present work it was found that nitrogen sesquioxide, nitrogen dioxide, and nitrosyl chloride formed nitroso compounds by their action upon organomercury derivatives of polymethylbenzenes. The nitroso group replaced the mercury, which was removed as an inorganic salt. Equations (4) and (5) express the reactions in general forms, where NOX denotes the nitrosyl compounds.[6]

$$R_2Hg + NOX \longrightarrow RHgX + RNO \quad (4)$$
$$RHgX + NOX \longrightarrow HgX_2 + RNO \quad (5)$$
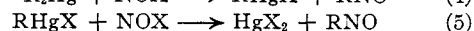
A diazonium nitrate was formed only when a mixture of nitrogen sesquioxide and excess nitric oxide was allowed to act upon a mercury compound. It seemed, then, that the primary reaction (5) between nitrogen sesquioxide and the arylmercury compound was accompanied by a

(1) Polymethylbenzenes. XIV. Paper XIII, THIS JOURNAL, **57**, 2370 (1935).

(2) Abstracted from the thesis of F. L. Taylor, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, March, 1935.

(3) Baeyer, *Ber.*, **7**, 1638 (1874).

(4) Gilman and Wright [THIS JOURNAL, **55**, 3302 (1933); **56**, 1415 (1934)] treated 2-chloromercurifuran with nitrosyl chloride, but did not isolate a product from the reaction.

(5) E. Bamberger, *Ber.*, **30**, 506 (1897); **32**, 3546 (1899); Kunz, *ibid.*, **31**, 1528 (1898).

(6) If conclusions as to the structures of nitrogen oxides are valid when based upon their reaction products, nitrogen sesquioxide is nitrosyl nitrite and the dioxide is nitrosyl nitrate. See, Wieland, *Ann.*, **328**, 154; **329**, 225 (1903); **340**, 63 (1905); **424**, 71 (1921); *Ber.*, **53**, 210, 1343 (1920); **54**, 1776 (1921); Battegay *et al.*, *Bull soc. chim.*, **41**, 1336 (1927); **43**, 109 (1928); Reihlen and Hake, *Ann.*, **452**, 47 (1927); Schaarschmidt *et al.*, *Ber.*, **57**, 32, 2065 (1924).

secondary reaction (3) between nitric oxide and the nitroso compound.[7]

The yields which were obtained in preparation of the mercury compounds described in the previous paper and in preparation of the nitroso compounds were sufficient to make the reactions satisfactory for synthesis of the compounds in quantity. The most convenient procedure made use of the reaction between organomercury compounds and nitrosyl chloride. Nitrosyl chloride was prepared in the reaction mixture from ethyl nitrite.[8] Nitrosopolymethylbenzenes are valuable intermediates for preparation of the amino methylbenzenes because the mono-nitro compounds cannot be prepared by direct nitration of the hydrocarbons.[9] The nitroso compounds were characterized by conversion to the known amines and acetamines. Nitrosomesitylene[10] and 5-

dilute or warm. The new nitroso compounds are listed in the table with their melting points and analytical data.

The action of nitric acid upon arylmercury compounds usually causes replacement of the mercury by a nitro group, although the replacement is probably not direct.[4,12] Under certain conditions, nitration of the aryl group in arylmercury compounds may occur without destruction of the carbon–mercury bond.[13]

Nitric acid of specific gravity 1.26 formed nitrodurene and nitroisodurene by action upon the corresponding acetoxymercurimethylbenzenes. Probably the nitroso compounds were formed as intermediates. Nitrodurene and nitroisodurene were prepared also by oxidation of the nitroso compounds with nitric acid (sp. gr. 1.26). The substances are listed in the table.

Table I
Nitroso- and Nitro-polymethylbenzenes

| Substance | Yield, % | M. p., °C. | Formula | Analyses, % | | | |
| | | | | Carbon | | Hydrogen | |
				Calcd.	Found	Calcd.	Found
Nitrosopentamethylbenzene	80	160[a]	$C_{11}H_{15}NO$	74.52	74.2	8.54	8.42
Nitrosodurene	81	160[a]	$C_{10}H_{13}NO$	73.57	73.3	8.03	8.16
Nitrosoisodurene	61	134	$C_{10}H_{13}NO$	73.57	71.5[b]	8.03	7.9[b]
Nitrosoprehnitene	70	72	$C_{10}H_{13}NO$	73.57	73.3[b]	8.03	8.0[b]
Nitrodurene	40	112–113	$C_{10}H_{13}NO_2$	67.00	67.1	7.32	7.49
Nitroisodurene	39		$C_{10}H_{13}NO_2$	67.00	66.7	7.32	7.41

[a] Decomposition, rapid heating; slow heating, m. p. 152–155°. [b] Average of several concordant analyses.

nitrosopseudocumene[11] were known previously. Both forms of 5-nitrosopseudocumene, the green, labile form, m. p. 45–46°, and the white form, m. p. 65°, were isolated. Nitrosoprehnitene, which has a structure very similar to that of nitrosopseudocumene, was isolated only in a green, stable form, m. p. 72°. The other nitroso compounds resembled nitrosomesitylene in that their melting points were high and their solutions were colorless, or yellow, in the cold but green when

(7) Since nitrosopolymethylbenzenes were formed by the action of either nitrogen sesquioxide or dioxide, it was concluded that the nitrosobenzene found by Bamberger was probably the primary product, and that the diazonium nitrate was formed from nitrosobenzene by the action of nitric oxide (equation 3) which resulted from dissociation of the sesquioxide. If the reaction between nitric oxide and nitrosobenzene were much faster than the reaction between nitrogen sesquioxide and diphenylmercury (equation 4), then most of the nitroso compound would be converted to the diazonium nitrate which Bamberger found. Apparently, the reactivity of mercury derivatives of benzene hydrocarbons toward nitrogen sesquioxide increases with the number of methyl groups attached to the ring; the reverse is true of the nitroso derivatives.

(8) O. Wallach, *Ann.*, **253**, 251 Anm. (1889).

(9) Willstätter and Kubli, *Ber.*, **42**, 4151 (1909); Töhl, *ibid.*, **21**, 904 (1888); see also the previous papers in this series.

(10) (a) V. Pechmann and Nold, *ibid.*, **31**, 561 (1898); (b) Bamberger and Rising, *ibid.*, **33**, 274, 3632 (1900).

(11) Bamberger, *ibid.*, **43**, 1842 (1910).

Experimental Part

A. Preparation of Nitrosopolymethylbenzenes

1. General Method.—The acetoxymercuri polymethylbenzene (20 g.) was dissolved in chloroform (100 cc.); the solution was cooled in an ice-bath and stirred mechanically. Ethyl nitrite (5 cc.; 1 + mole)[14] was added; this was followed by addition, in one portion, of a mixture of hydrochloric acid (15 cc. concd.; 3 moles) and acetic acid (20 cc.). The fresh precipitates of arylmercuric halides reacted quickly with nitrosyl chloride. The reaction mixtures were stirred for fifteen minutes to one hour. The procedures for isolation of the products are described separately.

2. Nitrosopentamethylbenzene.—The reaction mixture was washed with water (mercury salt recovered) and filtered. The precipitate was crude nitroso compound (4.5 g.). The green filtrate, evaporated to 40 cc. and cooled, deposited an additional 4 g. of nitroso compound. The substance was crystallized from chloroform; needles, m. p. 160°; yield, 80%. The melting (decomposition) point depended upon the rate of heating.

(12) Hanke, This Journal, **45**, 1321 (1923); Dreher and Otto, *Ber.*, **2**, 542 (1869); *Ann.*, **154**, 93 (1870); Henry and Sharp, *J. Chem. Soc.*, 2432 (1926).

(13) Challenger and Rothstein, *ibid.*, 1258 (1934); see also Whitmore and Culhane, This Journal, **51**, 602 (1929).

(14) Prepared by the method of Wallach, ref. 8.

Reduction of the nitroso compound by stannous chloride in alcohol and hydrochloric acid gave 6-aminopentamethylbenzene, m. p. 151°; reported m. p. 151-152°[15] and 151°.[16] The amine was acetylated by acetic anhydride. The melting point of acetaminopentamethylbenzene was 211°; reported, m. p., 213°[15] and 212-213°.[16]

3. **Nitrosodurene.**—The chloroform solution was extracted with water, warmed to dissolve all the product, extracted three more times, treated with 10 cc. of methanol, filtered, concentrated to 50 cc. by distillation, and cooled. The pure white, crystalline product changed to a powder when it was dried in air; m. p. 160° (decomposition, rapid heating); yield, 73%.

The melting point of crude aminodurene obtained by reduction of nitrosodurene was 74-75°. The reported melting points are 75°;[16] after sublimation, 72-73°.[17] The amine was crystallized from 60% methanol; the product, m. p. 71°, was analyzed.

Anal. Calcd. for $C_{10}H_{16}N$: C, 75.40; H, 10.13. Found: C, 75.23, 76.20; H, 9.48, 9.24.

The melting point of acetaminodurene was 207-208°; reported m. p. 207°.[16]

4. **Nitrosoisodurene.**—After the chloroform solution was washed, it was concentrated to 40 cc., treated with 40 cc. of methanol, distilled until a precipitate formed, cooled and filtered. The melting point of the product was 132°; yield, 61%.

For analysis, 1 g. of nitrosoisodurene was crystallized from 15 cc. of methanol and 5 cc. of benzene. The crystalline product, m. p. 137°, was dried in vacuum for five hours at 55°. It changed to a powder, m. p. 134°. Analyses gave values for carbon which were 2% low. However, when reduced, a liquid amine was formed; reported melting point of aminoisodurene, 14°[18a] and 23-24°.[18b] The melting point of acetaminoisodurene was 215°; reported m. p. 215°,[18b] 210-211°,[19a] 216°,[19b] and 214-215°.[15]

When 1 g. of nitrosoisodurene, m. p. 132°, was crystallized from methanol (10 cc.) and chloroform (3 cc.) the melting point of the product (dried over sulfuric acid) was 138°.

Anal. Found: C, 67.42, 67.35; H, 7.51, 7.54. Calcd. for $C_{10}H_{13}N + CH_3OH$: C, 67.64; H, 8.78.

The compound was not characterized; it was probably an addition product. In solution it behaved as nitrosoisodurene.

5. **Nitrosoprehnitene.**—The chloroform solution was washed, excess methanol was added, and the solution evaporated nearly to dryness to remove all of the chloroform. The methanol solution was cooled and filtered; the melting point of the product was 72°, yield 35%. Crude material (35%) was obtained from the filtrate. Nitrosoprehnitene (0.7 g.) was crystallized from 3 cc. of methanol and dried over sulfuric acid, m. p. 72°; when

dried in vacuum for six hours at 55°, the melting point was 72°. The green solid did not change color during several months.

Reduction formed aminoprehnitene, m. p. 64-65°; reported m. p. 64-66°,[18b] and 70°.[20] The melting point of acetaminoprehnitene was 170-171°; reported m. p. 169.5°[18b] and 172°.[20]

6. **Nitrosomesitylene.**—The solvent was washed, excess methanol added, and the solution evaporated until the chloroform was removed. The final mixture (75 cc.) was cooled and filtered. The melting point of nitrosomesitylene was 121-122°; yield, 90%; reported m. p. 122°[10b] and 129°.[10a]

7. **Nitrosopseudocumene.**—The crude substance was obtained by evaporation of the solvent; yield, 68%. The melting point of the green form was 44°; of the white form, 64-65°; recorded m. p., green, 45-46°; white, 65°.[11]

B. Reactions between Nitrogen Oxides and Mercury Compounds

1. **Preparation of the Nitrogen Oxides.**—The red oxides of nitrogen were prepared by the reaction between nitric acid and copper, in an all-glass apparatus which was connected directly to a reaction flask through the hollow mechanical stirrer.

(a) **Nitrogen Sesquioxide.**—The red oxides were treated with dry nitric oxide until the condensate was converted to blue sesquioxide; the oxide was dried by phosphorus pentoxide.

(b) **Nitrogen Dioxide.**—Dry oxygen was used to oxidize the red oxides to the light yellow dioxide; the dioxide was dried by phosphorus pentoxide.

(c) **Nitric oxide** was prepared from sodium nitrite by the method of Noyes,[21] and dried by passing it through a train of concentrated sulfuric acid and phosphorus pentoxide.

2. **Nitrogen Sesquioxide and Acetoxymercuriisodurene.**—Acetoxymercuriisodurene (15 g.) was dissolved in 125 cc. of absolute chloroform and the solution was kept at −10°. Nitrogen sesquioxide was distilled into the solution. A voluminous white precipitate (I) formed and then dissolved and left a brown precipitate (II). The precipitate was removed by filtration (filtrate III), washed with absolute chloroform, and dried at 60°; weight 7 g. The material was almost completely soluble in water. The solution contained mercuric and nitrite ions. Values for mercury content of the solid varied from 59 to 70%; calcd. for mercuric nitrite, 68.5% mercury. The substance was evidently impure mercuric nitrite.

The filtrate (III) was treated as described in part A 4. The product was nitrosoisodurene, m. p. 125°; weight, 4 g. (64%).

The white precipitate (I) was removed (in a separate experiment), washed with absolute chloroform, and dried in a desiccator. Values for mercury content were 54 and 58%; calculated for $C_{10}H_{13}HgNO_2$, 52.8%. The substance was probably nitritomercuriisodurene contaminated with mercuric nitrite.

3. **Nitrogen Dioxide and Acetoxymercuriisodurene.**—The experiment was performed as described in part 2;

(15) A. W. Hofmann, *Ber.*, **18**, 1822 (1885); Smith and Paden, This Journal, **56**, 2171 (1934).

(16) Willstätter and Kubli, *Ber.*, **42**, 4162 (1909).

(17) Smith and Tenenbaum, private communication.

(18) (a) A. W. Hofman, *Ber.*, **17**, 1913 (1884); (b) Limpach, *ibid.*, **21**, 644 (1888).

(19) (a) Noelting and Baumann, *ibid.*, **18**, 1149 (1885); (b) Liebermann and Kardos, *ibid.*, **47**, 1575 (1914).

(20) Töhl, *ibid.*, **21**, 905 (1888).

(21) W. A. Noyes, This Journal, **47**, 2170 (1925).

dioxide was used instead of sesquioxide. Crude nitroso-isodurene was obtained, m. p. 123°; yield, 4.5 g. (72%).

C. Preparation of Nitrodurene and Nitroisodurene

Oxidation of Nitrosodurene.—A mixture of 2 g. of nitrosodurene and 40 cc. of nitric acid (sp. gr. 1.26) was heated to 70° and shaken for ten minutes. The material was dissolved and nitrogen oxides were evolved. The solution was cooled immediately, poured into 100 cc. of ice and water, and filtered. The product was crystallized from 14 cc. of alcohol; pale yellow prisms, m. p. 112–113°; yield, 0.87 g. (40%). Reduction of nitrodurene formed aminodurene, m. p. 71°.

Acetoxymercuridurene and Nitric Acid.—The mercury compound (11.8 g.) was heated and shaken with 120 cc. of nitric acid (sp. gr. 1.26); the substance was changed to material which floated (probably nitrosodurene). Nitrogen oxides were evolved. At 70°, the material was dissolved within five minutes; the solution was kept warm two minutes longer, then it was poured into ice and water, and filtered. The precipitate was triturated and washed with water, and dried for one day over sulfuric acid. The crude nitrodurene weighed 4.8 g. (89%); m. p. 100–105°.

Oxidation of Nitrosoisodurene.—The substance was oxidized with nitric acid at 70–80°; the oxidation was stopped by dilution with ice and water as soon as the material had dissolved. The diluted mixture was extracted with ether; the ether was washed and evaporated. The residual oil was steam distilled; the yellow oil was removed from the distillate by extraction with ether; the residue from evaporation of the ether was crystallized from methanol at the temperature of liquid air. The product was dried for three days in a desiccator. The melting point of nitroisodurene was 38–39°.

Nitrosoisodurene was oxidized also by nitrogen dioxide. The solvent, absolute chloroform, was heated nearly to the boiling point by the heat of reaction. After action had subsided the chloroform was washed with water and evaporated. The residual oil was steam distilled; the distillate was extracted with ether, the ether was evaporated and the residue crystallized from low boiling petroleum ether. The melting point of nitroisodurene was 39°.

Acetoxymercuriisodurene and Nitric Acid.—The procedure was the same as for the reaction between nitric acid and acetoxymercuridurene. From 4 g. of the mercury compound, there was obtained 1.5 g. (82%) of crude (liquid) nitroisodurene. Further oxidation of nitroisodurene occurred when the reactions were continued too long, or were allowed to proceed at higher temperatures. Reduction of nitroisodurene formed a liquid amine. The melting point of acetaminoisodurene was 215°.

Summary

1. A method was developed for synthesis of nitroso compounds by the action of nitrosyl chloride upon organomercury derivatives of polymethylbenzenes. Four new nitroso and two new nitro compounds were prepared.

2. The action of nitrogen sesquioxide upon arylmercury compounds, like that of the dioxide, formed nitroso compounds as the primary products.

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. X. The Addition of Hydrogen Bromide to Methylacetylene (Allylene)

BY M. S. KHARASCH, J. G. MCNAB[1] AND M. C. MCNAB

Introduction

In previous communications from this Laboratory Kharasch and his collaborators[2] have demonstrated the importance of peroxides in directing the addition of hydrogen bromide to olefinic hydrocarbons, in which the double bond is at the end of the chain. It seemed desirable to extend the investigation to the acetylene series, and so the addition of hydrogen bromide to methylacetylene was studied in some detail.

The experiments of Réboul[3] have previously

(1) The authors wish to express here their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

(2) Kharasch and co-workers, THIS JOURNAL, **55**, 2468, 2521, 2531 (1933); **56**, 1642 (1934).

(3) Réboul, *Ann. chim.*, [5] **14**, 365 (1878).

shown that hydrogen bromide in aqueous solution adds to methylacetylene to yield 2,2-dibromopropane.

Addition of Hydrogen Bromide to Methylacetylene.—We found it expedient, after a few preliminary experiments, to limit our investigation to a study of the final product formed by the addition of two moles of hydrogen bromide to methylacetylene. These experiments were carried out in the presence of peroxides and also *in vacuo* under peroxide-free conditions.

The structure of the molecule first formed, under peroxide-free conditions, by the addition of one mole of hydrogen bromide to methylacetylene, can be inferred readily from a consideration of the products isolated in this investigation, together