three-necked flask equipped with a stirrer and a condenser connected to a trap containing an aqueous solution of barium hydroxide, a mixture of 100 g. of 80% sulfuric acid and 21 g. of bis-(2-pyridyl)-acetonitrile was heated at 125–130° with stirring for about two hours. At the end of this time no more carbon dioxide was evolved. The dark mixture was poured on ice, basified with gaseous ammonia, the oil extracted with ether, the ether layer dried, concentrated and the residue distilled.

2-(Cyclohexylmethyl)-pyridine.—To a solution of potassium amide prepared from 20 g. (0.51 mole) of potassium and 1,500 ml. of liquid ammonia, there was added slowly 46.5 g. (0.5 mole) of α-picoline. After ten minutes, 83.1 g. (0.51 mole) of cyclohexyl bromide was added as rapidly as possible, and stirring was continued until all of the ammonia had evaporated. The reaction mixture was decomposed with water, the oil extracted with ether, the ether extracts washed with water, dried over sodium sulfate, concentrated and the residue fractionated.

1-(2-Thienyl)-2-(2-pyridyl)-ethane was prepared according to the preceding experiment by condensing the potassium salt of α-picoline with 2-thenyl chloride in liquid ammonia; yield 56%, b.p. 106–110° (0.5 mm.).

Anal. Calcd. for $C_{11}H_{11}NS$: N, 7.40. Found: N, 7.31.

In a subsequent large-scale experiment a 35% yield of the desired product was obtained. Fractionation of the higher residue yielded 24% of di-(2-thenyl)-α-picoline as a viscous oil, b.p. 176–180° (1 mm.).

Anal. Calcd. for $C_{16}H_{15}NS_2$: N, 4.90. Found: N, 4.81.

1-(5-Chloro-2-thienyl)-2-(2-pyridyl)-ethane was prepared from the potassium salt of α-picoline and 5-chloro-2-thenyl chloride; yield 31%, b.p. 126–128° (0.5 mm.).

Anal. Calcd. for $C_{11}H_{10}NSCl$: Cl, 15.85. Found: Cl, 15.35.

1-(5-Bromo-2-thienyl)-2-(2-pyridyl)-ethane.—To a stirred, cooled solution (10°) of 9.4 g. of 1-(2-thienyl)-2-(2-pyridyl)-ethane in 25 ml. of glacial acetic acid, there was added slowly 3 ml. of bromine in 40 cc. of glacial acetic acid. The solution was made alkaline with gaseous ammonia, ether extracted, the ether layer dried, concentrated and the residue distilled; yield 60%, b.p. 129–133° (0.5 mm.).

Anal. Calcd. for $C_{11}H_{10}NSBr$: Br, 29.79. Found: Br, 29.58.

BLOOMFIELD, N. J.

RECEIVED FEBRUARY 27, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

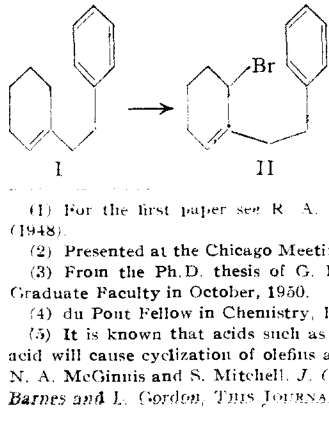
Reactions of N-Bromosuccinimide. II[1,2]

BY RODERICK A. BARNES AND GEOFFREY R. BUCKWALTER[3,4]

The reaction of N-bromosuccinimide with four hydrocarbons has been studied in order to gain some information concerning possible side reactions which may limit the use of this substance as a dehydrogenating agent. 1-(β-Phenylethyl)-1-cyclohexene was dehydrogenated to stilbene; no cyclization products were detected. Ionene was converted in a stepwise process to a bromide which rearranged with migration of a methyl group to produce 1,2,6-trimethylnaphthalene. Limonene could be converted to p-cymene and with more reagent the latter substance reacted to yield a bromide and a dimeric hydrocarbon.

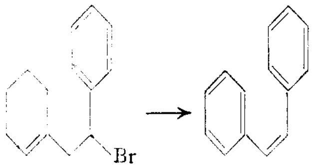
Previous work[1] on the reaction of N-bromosuccinimide with hydrocarbons has illustrated the usefulness of this reagent in effecting the low temperature dehydrogenation of some hydroaromatic compounds. The main purpose of the present work was to investigate the reactions of some substances which might be expected to dehydrogenate with rearrangement or which are known to rearrange when the usual high temperature methods are employed.

In the reaction of 1-(β-phenylethyl)-1-cyclohexene (I) with N-bromosuccinimide some phenanthrene might be expected either by hydrogen bromide catalyzed cyclization[5] of the olefin (I) or by intramolecular reaction of bromide II or the free radical intermediate in formation of II.



I II

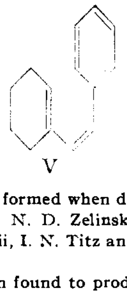
or



III IV

The isolation of stilbene (IV) as the major reaction product and the absence of any detectable amount of phenanthrene showed that in this case cyclization is not a factor which need be considered in interpreting the results of a dehydrogenation by N-bromosuccinimide.[6]

It is to be noted that the reaction with this cyclohexene derivative does not take the same course as with unsubstituted cyclohexene.[7] The explanation for the difference probably lies in the fact that bromide III is produced most rapidly from I and then with loss of hydrogen bromide 1-styryl-1-cyclohexene (V) is formed as the next intermediate.



V

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[1] For the first paper see R. A. Barnes, THIS JOURNAL, **70**, 145 (1948).

[2] Presented at the Chicago Meeting of the A. C. S., Sept. 6, 1950.

[3] From the Ph.D. thesis of G. R. Buckwalter presented to the Graduate Faculty in October, 1950.

[4] du Pont Fellow in Chemistry, 1949–1950.

[5] It is known that acids such as aluminum chloride and sulfuric acid will cause cyclization of olefins analogous to I; see J. W. Cook, N. A. McGinnis and S. Mitchell, *J. Chem. Soc.*, 286 (1944), and R. A. Barnes and L. Gordon, THIS JOURNAL, **71**, 2644 (1949).

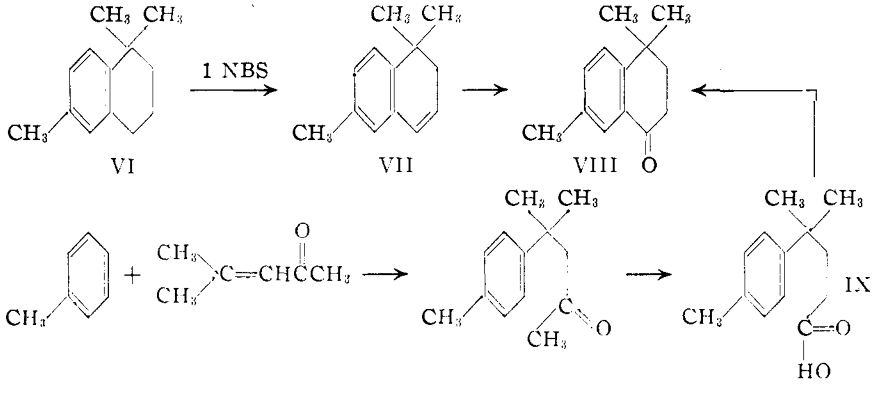
[6] Phenanthrene can be formed when dibenzyl is heated with platinum on charcoal at 300°: N. D. Zelinskii and I. N. Titz, *Ber.*, **62**, 2869 (1929); N. D. Zelinskii, I. N. Titz and M. V. Gaverdovskii, *ibid.*, **59**, 2596 (1926).

[7] Cyclohexene has been found to produce a mixture of m- and p-dibromobenzenes when treated with excess N-bromosuccinimide; ref. 1.

This substance (V) by virtue of its conjugation with the benzenoid ring would be expected to undergo bromination and also to lose hydrogen bromide more readily than cyclohexene.[8]

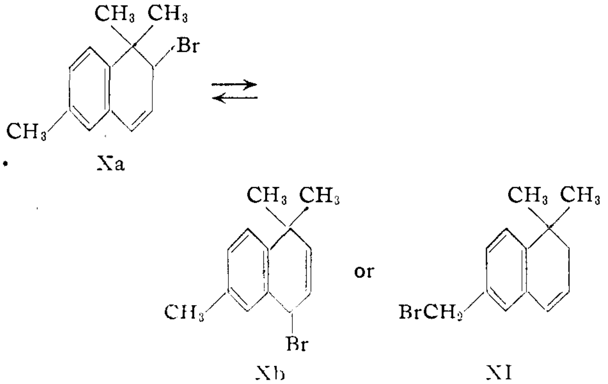
Ionene (VI) has been found to undergo dehydrogenation with elimination of a methyl group using various high temperature methods.[9] The course of the reaction of ionene with N-bromosuccinimide has been rather carefully investigated. With one mole of the reagent an olefin (VII) is produced in 80–85% yield.

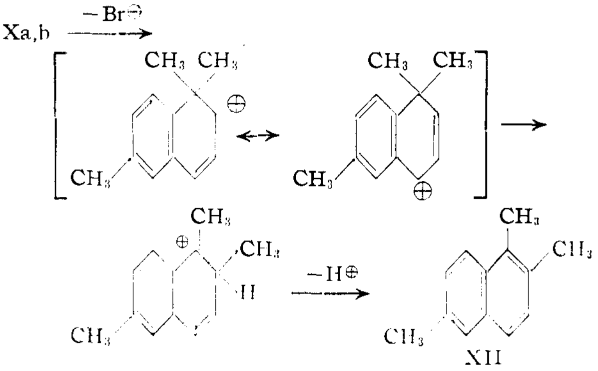
The structure of olefin VII has been proved by conversion to 4,4,7-trimethyl-1,4-dihydro-1(2H)-naphthalenone (VIII) which was synthesized by an independent route.



A sample of the tetralone VIII prepared by cyclization of IX was reduced and dehydrated to yield VII. However, since the olefin is a liquid and no satisfactory solid derivatives were found, comparison of the products of the two series at the tetralone stage using the semicarbazone and 2,4-dinitrophenylhydrazone derivatives was the more positive confirmation of the assigned structures.

The first mole of N-bromosuccinimide reacted at the methylene group adjacent to the benzenoid ring rather than at the methyl group. The further reaction of olefin VII could proceed to give two possibilities.





Although the bromide could not be obtained analytically pure (the best sample analyzed for a mixture of 86% bromide and 14% of hydrocarbon impurity) its structure has been established as Xa,b. Either silver ion or heat converted the bromide to 1,2,6-trimethylnaphthalene (XII).

Careful processing of the reaction mixture avoiding heat resulted in the isolation of 13% of XII indicating that rearrangement of the bromide[10] had taken place even during the reaction with N-bromosuccinimide at 76°.

When the alcoholic product from hydrolysis of the bromide was oxidized only neutral products[11] were isolated; an acid would be expected if the bromide had structure XI.

Limonene reacted with N-bromosuccinimide to produce a mixture of *p*-cymene and some unstable brominated products which were converted mainly to *p*-cymene by reaction with a methanol solution of potassium hydroxide. This procedure gave a better yield (80%) of *p*-cymene from limonene than by most other methods of dehydrogenation.[12]

p-Cymene reacted exothermically with N-bromosuccinimide to produce a mixture of three products, two of which have been identified.

The combined yield of XIII and hydrocarbon XV account for 47% of the *p*-cymene. The considerable amount of polymer produced in this reaction probably arises from the free-radical catalyzed polymerization of olefin XIV. It has been demonstrated[13] that when sulfuric acid is the only catalyst olefin XIV is converted in very good yield to hydrocarbon XV.

From these results it is apparent that N-bromosuccinimide is selective in its action and under suit-

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[8] Conjugation results in the stabilization of the free radical and ionic intermediates in the bromination and dehydrobromination steps. Thus, in the bromination of 1-styryl-1-cyclohexene there are six important resonance structures for the intermediate free radical but in the bromination of cyclohexene there are only two.

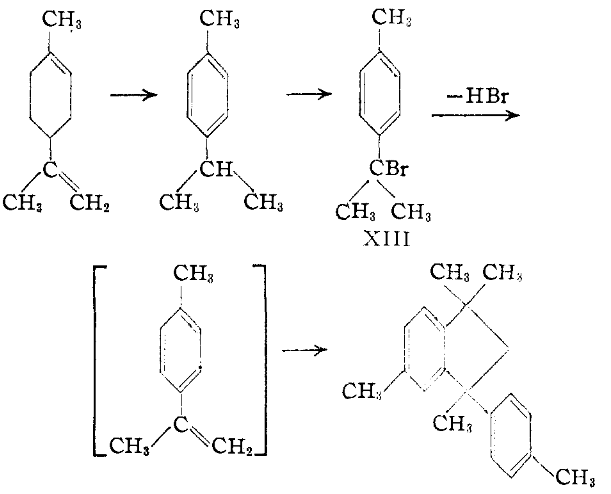
[9] J. J. Ritter and E. D. Sharpe, THIS JOURNAL, **59**, 2351 (1937); R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940); L. Ruzicka and E. A. Rudolph, *Helv. Chim. Acta*, **10**, 920 (1910).

[10] A study of the rearrangement of other bromides similar to Xa,b is in progress.

[11] One of the two possible naphthalenones has been separated as its 2,4-dinitrophenylhydrazone. Details of the separation and structure proof for this ketone will be reported later.

[12] V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **67**, 693 (1945); V. N. Ipatieff and H. Pines, U. S. Patent 2,431,756, Dec. 2, 1947; R. P. Linstead, K. O. A. Michaelis and S. L. S. Thomas, *J. Chem. Soc.*, 1139 (1940).

[13] V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2127 (1948).



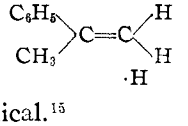
XIII

XIV XV

able conditions[14] will attack almost exclusively at the most reactive center in a molecule. We believe that this results from the difference in stability of the free radical intermediate resulting by removal of a hydrogen atom from the molecule being attacked. From the observations made in this work it is possible to arrange these proposed intermediates in order of decreasing stability.

$$\text{Aryl-}\underset{\cdot}{\text{C}}\text{R}_2 > \text{Aryl-}\underset{\cdot}{\text{C}}\text{HR} \sim \text{Aryl-CH=CH-}\underset{\cdot}{\text{C}}\text{HR} > \text{Aryl }\underset{\cdot}{\text{C}}\text{H}_2 > \text{RCH=CH}\underset{\cdot}{\text{C}}\text{HR}$$

This observed order is in harmony with the general concept of resonance stabilization of free radicals. The considerable difference in stability of radicals such as $C_6H_5CH_2\cdot$ and $C_6H_5(CH_3)_2C\cdot$ suggests that hyperconjugated structures such as XVI make an important contribution to the structure of the latter type of radical.[15]



XVI

Experimental[16]

Reaction of 1-(β-Phenylethyl)-1-cyclohexene (I) with N-Bromosuccinimide.—A mixture of 1-(β-phenylethyl)-1-cyclohexene (4.7 g.), N-bromosuccinimide (13.4 g.), benzoyl peroxide (1.2 g.) and carbon tetrachloride (50 ml.) was refluxed for four hours. The succinimide was filtered, the solution washed with water and concentrated using the water-pump. The residue was partly soluble in ligroin and from the ligroin solution 2.2 g. (48%) of stilbene was isolated. This sample and a mixture with authentic stilbene both melted at 123–124°. By fractional crystallization of the ligroin insoluble material from ethyl acetate–ethanol there were obtained small amounts of stilbene dibromide (m.p. 237–238°) and a substance which melted at 182–183°.

Anal. Calcd. for $C_{14}H_8Br_4$: C, 33.88; H, 1.63; Br, 64.48. Found: C, 33.78; H, 2.18; Br, 64.06.

Reaction of Ionene with N-Bromosuccinimide.—A mixture of ionene (43.5 g.), N-bromosuccinimide (44.5 g.), benzoyl peroxide (2.4 g.) and carbon tetrachloride (500 ml.) was refluxed for four hours. The reaction mixture was processed as for the previous preparation and by fractional distillation the main product, 1,1,6-trimethyl-1,2-dihydronaphthalene (35.2 g., 82%) was separated from a smaller amount (6.5 g.) of a higher boiling substance. The main product was redistilled through a Widmer column and boiled at 74–75° (1 mm.), n^{25}D 1.5454, $d^{25}{}_4$ 0.9454, absorption maxima at 262.5 mμ (log ε 2.57) and 268 mμ (log ε 2.56).[17]

Anal. Calcd. for $C_{13}H_{16}$: C, 90.61; H, 9.37. Found: C, 90.62; H, 9.43.

This olefin could be converted in very low yield to a nitrosochloride, m.p. 134–136°, which was unstable and could not be recrystallized to analytical purity.

4-Methyl-4-*p*-tolyl-2-pentanone.[18]—A mixture of dry toluene (310 g.) and aluminum chloride (134 g.) was cooled to 15–20° and mesityl oxide (75 g.) was added dropwise (one hour). The reaction was maintained at this temperature for three hours and then poured on ice (200 g.) and water (200 ml.). The organic layer was separated, washed several times with water, dried and fractionated. There was obtained 94.4 g. (65%) of the ketone which boiled at 125–127° (11 mm.), n^{25}D 1.5059, $d^{25}{}_4$ 0.9565. A semicarbazone of this ketone melted at 191–192°.

Anal. Calcd. for $C_{24}H_{21}ON_3$: C, 67.98; H, 8.56; N, 16.99. Found: C, 67.87; H, 8.52; N, 16.95.

4-Methyl-4-*p*-tolylthiopentanomorpholide.—4-Methyl-4-*p*-tolyl-2-pentanone (38.1 g.), morpholine (69.7 g.) and sulfur (9.6 g.) were refluxed for eight hours. The hot reaction mixture was poured into ethyl alcohol (100 ml.) and allowed to stand until crystallization was complete. The crystals were filtered off and by concentrating the filtrate more crude thiomorpholide was obtained. The combined product weighed 46.4 g. (80%) and melted at 75–76°.

Anal. Calcd. for $C_{17}H_{25}ONS$: C, 70.05; H, 8.65; N, 4.81. Found: C, 70.06; H, 8.61; N, 4.80.

4-Methyl-4-*p*-tolylpentanoic Acid.—A mixture of 4-methyl-4-*p*-tolylthiopentanomorpholide (34 g.), glycerol (200 ml.) and potassium hydroxide (13 g.) was heated at 190–200° for six days. During the first two days it was necessary to remove the reflux condenser occasionally and distil out the morpholine being liberated. The cold reaction mixture was poured into water and acidified (congo red) with hydrochloric acid. The organic products were extracted with ether and the acid separated by washing the ether extract with sodium bicarbonate solution. The sodium bicarbonate extract was processed to yield 8.6 g. (37%) of the desired acid which boiled at 140–142° (1 mm.), n^{25}D 1.5172, $d^{25}{}_4$ 1.0375.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.67; H, 8.79. Found: C, 75.63; H, 8.84.

Evaporation of the original ether extract left a residue of 16.5 g. (48%) of recovered thiomorpholide. A variety of other procedures using both acid and basic solutions for hydrolysis gave even lower yields of the desired acid.

4,4,7-Trimethyl-1,4-dihydro-1(2H)naphthalenone (VIII). A.—4-Methyl-4-*p*-tolylpentanoic acid (10.3 g.) was cyclized according to the procedure of Johnson and Glenn.[19] There was obtained 4.9 g. (52%) of ketone VIII which boiled at 103–104° (1 mm.), n^{25}D 1.5470, $d^{25}{}_4$ 1.0295.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.81; H, 8.45.

The 2,4-dinitrophenylhydrazone melted at 253–254°.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47. Found: C, 61.89; H, 5.45.

The semicarbazone melted at 214–215°.

Anal. Calcd. for $C_{14}H_{19}ON_3$: C, 68.53; H, 7.81. Found: C, 68.34; H, 7.94.

B.—Dry hydrogen chloride was bubbled through 1,1,6-trimethyl-1,2-dihydronaphthalene (17.2 g.) at 5–10° until

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[14] When chloroform was used in place of carbon tetrachloride as a solvent for the reaction of N-bromosuccinimide with ionene and 1-(β-phenylethyl)-1-cyclohexene lower yields of the major product and a greater diversity of polybrominated substances were observed.

[15] It is to be noted that in structure XVI two hydrogen atoms of the methyl group must be in the plane of the double bond (the hydrogen with the unpaired electron is not in this plane), hence for each methyl group there is only a single hyperconjugated structure.

[16] All melting points were corrected. Analyses were by W. Manser (Zurich Switzerland).

[17] While this work was in progress P. Karrer and P. Ochsner, *Helv. Chim. Acta*, **31**, 2093 (1949), reported that 1,1,6-trimethyl-1,2-dihydronaphthalene was produced in low yield when either α- or β-ionone was brominated with N-bromosuccinimide and the product heated with diethylaniline.

[18] V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2123 (1948), have also prepared this ketone in 40% yield using carbon disulfide as a solvent for the reaction.

[19] W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949).

3.7 g. was absorbed. The crude chloride was added dropwise to a mechanically stirred mixture of chromic anhydride (16 g.), glacial acetic acid (15 ml.) and water (15 ml.). The temperature was maintained at 35–40° during the addition (30 minutes) and for an additional 15 minutes. After adding to water (150 ml.) the organic product was removed by ether extraction and acidic products washed from the ether with sodium bicarbonate solution. The neutral fraction remaining after evaporation of the ether was purified by converting to the semicarbazone. The recrystallized semicarbazone (19 g.) was steam distilled in the presence of phthalic anhydride (12 g.) to regenerate the ketone. This product proved to be identical with the ketone obtained in part A since the semicarbazone and 2,4-dinitrophenylhydrazones of the two substances had the same melting points separately or when mixed together.

Reaction of N-Bromosuccinimide with 1,1,6-Trimethyl-1,2-dihydronaphthalene. A.—A mixture of 1,1,6-trimethyl-1,2-dihydronaphthalene (VII) (71.4 g.), N-bromosuccinimide (74 g.), benzoyl peroxide (2.4 g.) and carbon tetrachloride (500 ml.) was refluxed for four hours. The succinimide was filtered, the carbon tetrachloride was distilled and the residue fractionated. Both fraction I (27.2 g.), b.p. 109–112° (3 mm.), and fraction II (37.3 g.), b.p. 118–120° (3 mm.), proved to be mixtures containing a hydrocarbon and bromide. Redistillation of fraction II produced a sample which analyzed for bromide Xa,b (86%) and hydrocarbon XII (14%).

Anal. Calcd. for $C_{13}H_{15}Br$: C, 62.2; H, 6.0; Br, 31.8. Found: C, 66.2; H, 6.67; Br, 27.3. Calcd. for $C_{13}H_{14}$: C, 91.8; H, 8.28.

Further fractionation did not improve the purity of the bromide, indicating that thermal decomposition to the hydrocarbon was taking place. After several distillations fraction I, which was mostly hydrocarbon XII, had increased considerably at the expense of fraction II.

Hydrocarbon XII was obtained in pure form by washing the bromide–hydrocarbon mixture with sodium bicarbonate solution (which hydrolyzed most of the bromide) and distilling several times. A final distillation over sodium produced 1,2,6-trimethylnaphthalene (XII) which boiled at 100–105° (3 mm.), m.p. 8–11°, n^{25}_D 1.5988.[20]

This hydrocarbon formed as orange picrate which melted at 122–123°.[20] The melting point of a mixture of the picrate and picric acid was 109–116°. 1,2,6-Trimethylnaphthalene also formed complexes with trinitrobenzene (m.p. 147–148°) and with 3,5-dinitrobenzoic acid (m.p. 72–73°). Neither of these addition compounds could be recrystallized to analytical purity.

Anal. Calcd. for $C_{13}H_{14}\cdot C_6H_3N_3O_6$: C, 59.5; H, 4.47. Found: C, 58.5; H, 4.43. Calcd. for $C_{13}H_{14}\cdot C_7H_4N_2O_6$: C, 62.8; H, 4.74. Found: C, 63.9; H, 5.55.

B.—The reaction was carried out as before using 9.2 g. of VII. The cool reaction mixture was shaken well with sodium bicarbonate solution and the solvent removed at room temperature. The residue was treated with pyridine (15 ml.) and phthalic anhydride (8.1 g.) at room temperature for 15 hours. An ether solution of this reaction mixture was washed free of phthalic acid ester and pyridine with sodium bicarbonate solution and dilute hydrochloric acid. Evaporation of the ether left 1.2 g. (13%) of 1,2,6-trimethylnaphthalene which formed a trinitrobenzene adduct and a picrate identical with those obtained in part A.

Oxidation of Bromide Xa,b. A.—A solution of crude bromide (3.7 g.) (fraction II from previous experiment) in acetic acid (10 ml.) was stirred at 95° as a suspension of silver chromate (4.9 g.) in acetic acid (5 ml.) was added. After two hours the reaction mixture was cooled, filtered, diluted with water and extracted with ether. The ether extract was washed with sodium bicarbonate solution, dried and concentrated. The residual liquid was treated with 2,4-dinitrophenylhydrazine to yield about 0.2 g. of a hydrazone which melted at 254–255°. A mixture of this substance and the derivative of authentic 4,4,7-trimethyl-1,4-dihydro-1(2H)naphthalenone (VIII) also melted at 254°. Thus bromide Xa,b was rearranged by silver ions to 1,2,6-trimethylnaphthalene before oxidation could take place, while a more stable bromide (1-bromo-4,4,7-trimethyl-1,2,3,4-tetrahydronaphthalene formed by addition of HBr to olefin VII) present to the extent of about 5% was oxidized to VIII.

B.—The crude bromide was washed with sodium bicarbonate solution and the resulting alcohol distilled (considerable dehydration to trimethylnaphthalene occurred). A sample of the impure alcohol (9.4 g., b.p. 112° (1 mm.), n^{25}_D 1.5959) was dissolved in glacial acetic acid (20 ml.) and oxidized at 90° with chromic anhydride (5 g.) dissolved in a minimum of water. Fractionation at 0.5 mm. produced 1,2,6-trimethylnaphthalene (5.8 g., b.p. 90–92°), a mixture of ketones (1.7 g., b.p. 95–100°)[11] and a small amount of a white solid which melted at 162–163°, and was insoluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.16; H, 6.97. Found: C, 77.27; H, 7.13.

Reaction of Limonene with N-Bromosuccinimide.—A mixture of *d*-limonene (68 g.), N-bromosuccinimide (89 g.), benzoyl peroxide (2.4 g.) and carbon tetrachloride (500 ml.) was refluxed for four hours. The reaction mixture was processed and fractionated to yield three fractions. The first fraction (39.8 g.) which boiled at 26–27° (1 mm.), n^{25}_D 1.4902, d^{25}_4 0.8620 was *p*-cymene. The second fraction (19.3 g., n^{25}_D 1.5122) was an unstable bromide, b.p. 78–79° (2 mm.), which always evolved some hydrogen bromide on distillation. The best sample of this substance analyzed for a mixture of monobromide (91%) and *p*-cymene (9%). Fraction three (14 g.) was extremely unstable and continuously evolved hydrogen bromide, b.p. 78–80° (1 mm.), n^{25}_D 1.5450. Both of these fractions could be converted almost completely to *p*-cymene by reaction with a solution of potassium hydroxide in methanol. The total yield of *p*-cymene was 53 g. (80%).

Reaction of *p*-Cymene with N-Bromosuccinimide.—When *p*-cymene (67 g.) was treated with N-bromosuccinimide (89 g.), benzoyl peroxide (2.4 g.) and carbon tetrachloride (500 ml.) in the usual manner three products were isolated. A crystalline solid 5.2 g. (8%) separated when the crude oily product was cooled at 0° for 24 hours. This substance melted at 137–138° after recrystallization from ligroin.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.8; H, 9.2. Found: C, 90.8; H, 8.74.

The liquid products were separated by fractionation into 8-bromo-*p*-cymene (26 g., 24%) and 1,3,3,6-tetramethyl-1-*p*-tolylindane (15 g., 23%) and a yellow glassy polymer. Pure 8-bromo-*p*-cymene boiled at 87° (1 mm.), n^{25}_D 1.5642, d^{25}_4 1.2701.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.35; H, 6.15. Found: C, 56.24; H, 5.95.

This bromide was converted in good yield to the dimeric hydrocarbon XV by heating on the steam-bath for several hours. 1,3,3,6-Tetramethyl-1-*p*-tolylindane (XV) was obtained as a colorless liquid which boiled at 138–140° (1 mm.), n^{25}_D 1.5594. After this substance was seeded with an authentic sample[21] it crystallized and melted at 37–38°. The nitration product of the two samples melted at 251–252° separately or when mixed together.

NEW BRUNSWICK, N. J. RECEIVED DECEMBER 13, 1950

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[20] V. Veselý and F. Štursa, *Collection Czechoslov. Chem. Communications*, **4**, 21 (1932), report the m.p. as 14°; L. Ruzicka and L. Ehmann, *Helv. Chim. Acta*, **15**, 140 (1932), report the melting point of the picrate as 122–123°.

[21] Kindly furnished by Dr. V. N. Ipatieff and Dr. H. Pines, see reference 13.