

## Syntheses and Catalytic Dehydrogenation of Benzsuberans

S. C. Sen Gupta and Parimal Krishna Sen

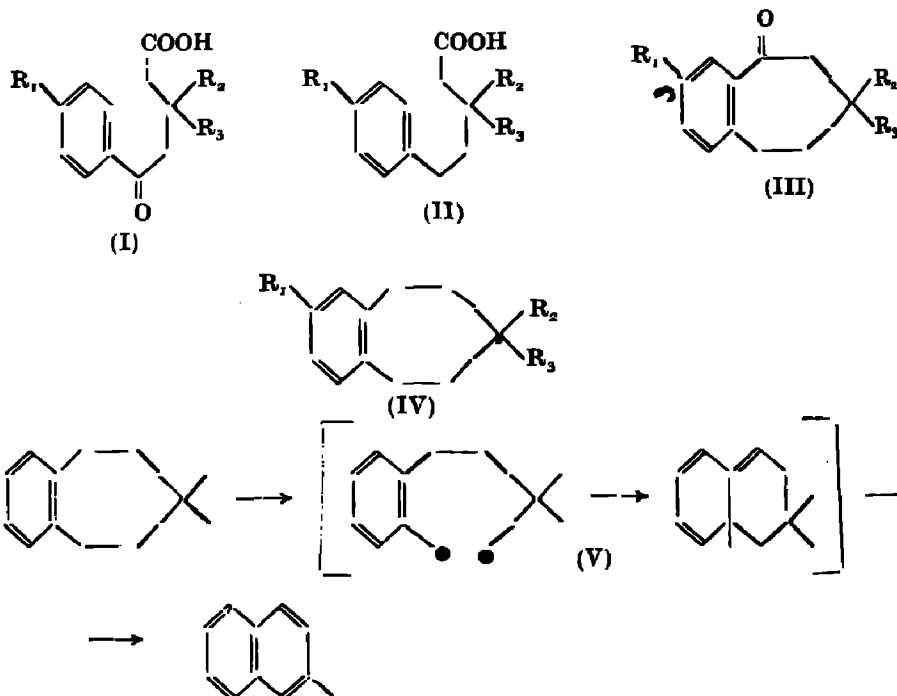
Syntheses of 2'-methyl-6,7-benzsuberan, 3-methyl-6,7-benzsuberan, 3,3-dimethyl-6,7-benzsuberan and 3-ethyl-3-methyl-6,7-benzsuberan have been described. Catalytic dehydrogenation of these benzsuberans has been carried out by heating with Pd-C catalyst at 380° in a sealed tube. In every case, 2-methylnaphthalene has been obtained as the chief dehydrogenation product.

It was observed by Ruzicka and Seidel<sup>1</sup> that cycloheptane was converted into toluene when heated with selenium at 440°. They further noted that no dehydrogenation and ring contraction of cycloheptane took place below 400°. With a view to studying thoroughly the catalytic dehydrogenation of seven-carbon ring systems, several alkylated benzsuberans have been successfully synthesised and subjected to catalytic dehydrogenation. It has been found that these benzsuberans are not affected by heating with Pd-C catalyst at 350° in a metal bath, but dehydrogenation accompanied by ring contraction occurs when these are heated with Pd-C in a sealed tube at 380°. 2'-Methyl-6,7-benzsuberan (IV:  $R_1=Me$ ;  $R_2=R_3=H$ ) on heating with Pd-C in a sealed tube at 380° gives 2-methylnaphthalene as the main dehydrogenation product. Under a similar condition catalytic dehydrogenation of 3-methyl-6,7-benzsuberan (IV:  $R_1=R_2=H$ ;  $R_3=Me$ ), 3,3-dimethyl-6,7-benzsuberan (IV:  $R_2=R_3=Me$ ;  $R_1=H$ ) and 3-ethyl-3-methyl-6,7-benzsuberan (IV:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ) gave in every case 2-methylnaphthalene as the main dehydrogenation product. In the last two cases, along with 2-methylnaphthalene, traces of dinaphthyl derivatives were isolated as dehydrogenation products. During dehydrogenation ring contraction and loss of carbon were found in all these cases to take place. The *gem*-dialkylated benzsuberans further lose one of the alkyl groups linked to the quaternary carbon atom.

It is difficult to offer a satisfactory explanation of the mechanism of dehydrogenation of these benzsuberans. It seems that the seven-carbon ring opens, as shown in (V), with the formation of a biradical which by ring closure and loss of one angular methyl group and one alkyl group from the *gem*-dialkyl group during aromatisation affords ultimately 2-methylnaphthalene. The isolation of traces of a binaphthyl derivative as a dehydrogenation product in two cases indicates the formation of an intermediate naphthyl radical.

The four alkylated benzsuberans, required for catalytic dehydrogenation studies, have been synthesised by starting from an aromatic hydrocarbon and glutaric anhydride or its alkyl derivatives. 2'-Methyl-6,7-benzsuberan (IV:  $R_1=Me$ ;  $R_2=R_3=H$ ) has been synthesised starting from toluene and glutaric anhydride. These two condensed in presence of anhydrous aluminium chloride, affording  $\gamma$ -(*p*-toluyl)butyric acid (I:  $R_1=Me$ ;

$R_2=R_3=H$ ). That the Friedel-Crafts reaction takes place in *para* position. The methyl group has been proved by oxidation of this keto-acid with alkaline permanganate to terephthalic acid. This keto-acid on reduction by the Clemmensen method gave  $\delta$ -(*p*-tolyl)-valeric acid (II:  $R_1=Me$ ;  $R_2=R_3=H$ ); this on being heated with polyphosphoric acid mixture furnished a good yield of the cyclic ketone (III:  $R_1=Me$ ;  $R_2=R_3=H$ ). It was noted that this valeric acid derivative could not be cyclised with concentrated or 85% sulphuric acid. On the Clemmensen reduction, the cyclic ketone provided a good yield of 2'-methyl-6,7-benzsuberan (IV:  $R_1=Me$ ;  $R_2=R_3=H$ ).



In a similar manner, 3-methyl-6,7-benzsuberan (IV:  $R_1=R_2=H$ ;  $R_3=Me$ ) has been synthesised starting from benzene and  $\beta$ -methylglutaric anhydride. Using  $\beta\beta$ -dimethylglutaric anhydride and  $\beta$ -ethyl- $\beta$ -methylglutaric anhydride in place of  $\beta$ -methylglutaric anhydride in the above synthesis, 3,3-dimethyl-6,7-benzsuberan (IV:  $R_1=H$ ;  $R_2=R_3=Me$ ) and 3-ethyl-3-methylbenzsuberan (IV:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ) have been synthesised.

## EXPERIMENTAL

### 2'-Methyl-6,7-benzsuberan

$\gamma$ -(*p*-Tolyl)butyric Acid (I:  $R_1=Me$ ;  $R_2=R_3=H$ ).—A solution of glutaric anhydride (17 g.) in dry toluene was added with stirring to an ice-cold suspension of powdered anhydrous aluminium chloride (50 g.) in dry toluene (70 ml). The mixture was kept at

room temperature for 12 hours and then warmed at 60-65° for half an hour. The product was decomposed with ice and HCl and excess of toluene removed by steam distillation. The solid product was extracted with hot sodium carbonate solution and charcoalised; the keto-acid was precipitated with HCl and crystallised from ethanol. After recrystallisation from hexane it melted at 154-55°; yield 20 g. (Found: C, 69.7; H, 6.7.  $C_{12}H_{14}O_3$  requires C, 69.7; H, 6.79%).

The semicarbazone was crystallised from ethanol, m.p. 225° (decomp.). (Found: C, 59.0; H, 6.35; N, 15.7.  $C_{13}H_{17}O_3N_3$  requires C, 59.31; H, 6.46; N, 15.96%).

*Oxidation of the Keto-acid* (I:  $R_1=Me$ ;  $R_2=R_3=H$ ).—The keto-acid was oxidised by heating with excess alkaline potassium permanganate solution. The oxidation product was isolated according to usual methods and crystallised from HCl (conc.). The product was characterised as terephthalic acid by preparing its methyl ester, m.p. 140°.

*$\delta$ -(p-Tolyl)valeric Acid* (II:  $R_1=Me$ ;  $R_2=R_3=H$ ).— $\gamma$ -(p-Tolyl)butyric acid (10 g.), amalgamated zinc (40 g.) and HCl (conc., 40 ml) were boiled gently for 24 hours. The product was extracted with ether, the extract washed with water, and the ether distilled; the residue was extracted with hot dilute sodium carbonate solution and acidified with HCl, when the reduced acid separated as a thick pasty mass. It was extracted with ether, dried with sodium sulphate, and distilled. It was collected as a colorless oil, b.p. 140-42°/2 mm; yield 6 g. (Found: C, 74.86; H, 8.2.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.33%).

*2'-Methyl-6,7-benzsuberone-1* (III:  $R_1=Me$ ;  $R_2=R_3=H$ ).— $\delta$ -(p-Tolyl)valeric acid (10 g.) was mixed with polyphosphoric acid ( $P_2O_5$ , 35 g. and 89%  $H_3PO_4$ , 15 ml) and the mixture was heated on steam bath for 1 hour with stirring. The product was poured on crushed ice and extracted with ether. The ethereal solution was washed with ammonia and then with water; it was dried with sodium sulphate and distilled. The ketone is a light straw-coloured liquid, b.p. 170-72°/15 mm, yield 6.5 g. (Found: C, 82.64; H, 7.9.  $C_{12}H_{14}O$  requires C, 82.75; H, 8.04%).

*2,4-Dinitrophenylhydrazone* of the ketone was crystallised from ethyl acetate as fine red needles, m.p. 205-206°. (Found: C, 60.81; H, 5.0.  $C_{18}H_{18}O_4N_4$  requires C, 61.01; H, 5.08%).

*2'-Methyl-6,7-benzsuberan* (IV:  $R_1=Me$ ;  $R_2=R_3=H$ ).—2-Methyl-6,7-benzsuberone-1 (6 g.) was gently boiled with amalgamated zinc (25 g.) and HCl (conc., 25 ml) for 24 hours. The product was extracted with ether, the extract washed with water, dried with sodium sulphate, and distilled. It is a colorless liquid with fragrance, b.p. 104-105°/10 mm, yield 4 g.;  $d_4^{20}$  0.9490,  $n_D^{20}$  1.5300,  $[R_L]_D$  52.07 (calc. 51.87). (Found: C, 89.72; H, 9.91.  $C_{12}H_{16}$  requires C, 90.0; H, 10.0%).

*Catalytic Dehydrogenation of 2'-Methyl-6,7-benzsuberan*.—The hydrocarbon (2.5 g.) was heated with 10% Pd-C catalyst (0.25 g.) in a sealed pyrex tube at 380-400° for 15 hours. When opening the sealed tube, the issuing gas burnt with a blue flame. The product was extracted with ether, the solvent removed, and the residual oil was subjected to chromatographic fractionation on Brockmann alumina with hexane. Eluates, each 10 ml, were collected. The first and second eluates left no solute on removal of the solvent. The third, fourth, and fifth eluates, each, contained a small quantity of oil with characteristic odour. The oils were separately converted into picrates in methanolic solution. Melting

point of each picrate obtained from different eluates was noted. They melted within a range of 108–114°. The picrates were mixed together and crystallised repeatedly from methanol when yellow needles melting at 115–16° were obtained. The mixed m.p. with the picrate of an authentic sample of 2-methylnaphthalene was not depressed. (Found: C, 54.8; H, 3.61. Calc. for  $C_{17}H_{13}O_7N_3$ : C, 54.98; H, 3.50%).

The hydrocarbon was regenerated from the picrate and solidified on cooling, m.p. 33–34°. Melting point of 2-methylnaphthalene is 34.4°. The UV absorption study also suggests that the hydrocarbon is an alkylated naphthalene. Five subsequent eluates left no solute on removal of the solvent.

### 3-Methyl-6,7-benzuberan

*$\beta$ -Methyl- $\gamma$ -benzoylbutyric acid* (I:  $R_1=R_2=H$ ;  $R_3=Me$ ) was prepared from the anhydride of  $\beta$ -methylglutaric acid (60 g.), benzene (100 ml), and aluminium chloride (132 g.) exactly as in the case of the keto-acid (I:  $R_1=Me$ ;  $R_2=R_3=H$ ). It was crystallised from dilute ethanol, m.p. 125–26°, yield 60 g. (Found: C, 69.72; H, 6.8.  $C_{12}H_{14}O_3$  requires C, 69.9; H, 6.79%).

The semicarbazone crystallised from dilute ethanol, m.p. 173–74° (decomp.). (Found: C, 59.2; H, 6.2; N, 16.1.  $C_{13}H_{17}O_3N_3$  requires C, 59.31; H, 6.46; N, 15.96%).

*$\beta$ -Methyl- $\delta$ -phenylvaleric Acid* (II:  $R_1=R_2=H$ ;  $R_3=Me$ ).—The keto-acid (I:  $R_1=R_2=H$ ;  $R_3=Me$ ; 50 g.) was reduced by heating with amalgamated zinc (200 g.) and HCl (conc., 200 ml) for 24 hours. The product was purified as in the case of the acid (II:  $R_1=Me$ ;  $R_2=R_3=H$ ), b.p. 161–62°/3 mm, yield 35 g. (Found: C, 74.7; H, 8.4.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.33%).

*3-Methyl-6,7-benzuberone-1* (III:  $R_1=R_2=H$ ;  $R_3=Me$ ).—The above reduced acid (28.8 g.) was mixed with polyphosphoric acid ( $P_2O_5$ , 105 g. and 89%  $H_3PO_4$ , 45 ml) and heated on the steam bath for 1 hour with stirring. The product was purified as in the case of the ketone (III:  $R_1=Me$ ;  $R_2=R_3=H$ ). It is a light straw-coloured liquid, b.p. 147°/9 mm, yield 15 g. (Found: C, 82.4; H, 8.1.  $C_{12}H_{14}O$  requires C, 82.75; H, 8.04%).

*2,4-Dinitrophenylhydrazone* of this cyclic ketone crystallised from ethyl acetate in red needles, m.p. 195–96°. (Found: C, 61.2; H, 5.1.  $C_{18}H_{18}O_4N_4$  requires C, 61.01; H, 5.08%).

*3-Methyl-6,7-benzuberan* (IV:  $R_1=R_2=H$ ;  $R_3=Me$ ).—The above cyclic ketone (14 g.) was reduced by heating with amalgamated zinc (60 g.) and HCl (conc., 60 ml) for 24 hours. It is a colorless oil with fragrance, b.p. 102–104°/10 mm;  $d_4^{25}$  0.9486,  $n_D^{25}$  1.5295,  $[R_L]_D$  52.05 (calc. 51.87). (Found: C, 89.9; H, 10.2.  $C_{12}H_{16}$  requires C, 90.0; H, 10.0%).

*Catalytic Dehydrogenation of 3-Methyl-6,7-benzuberan*.—The above hydrocarbon (3 g.) was heated with 10% Pd-C catalyst (0.3 g.) in a sealed pyrex tube at 380–400° for 15 hours. The product was purified through chromatographic fractionation on Brockmann alumina with hexane, as in the previous case. The first and second eluates, each, contained a little quantity of an oil with characteristic odour. The oils were separately converted into picrates in methanolic solution. They melted within a range of 108–14°. The picrates were

mixed together and crystallised repeatedly from methanol when yellow needles melting at 115-16° were obtained. The mixed m.p. with the picrate of an authentic sample of 2-methylnaphthalene was not depressed. (Found: C, 54.71; H, 3.41. Calc. for  $C_{17}H_{13}O_7N_3$ : C, 54.98; H, 3.50%).

### 3,3-Dimethyl-6,7-benzsuberan

*ββ-Dimethyl-γ-benzoylbutyric Acid* (I:  $R_1=H$ ;  $R_2=R_3=Me$ ).—*ββ*-Dimethylglutaric anhydride (45 g.), aluminium chloride (98 g.), and benzene (100 ml) were used. The product was worked up as in the case of the keto-acid (I:  $R=Me$ ;  $R_2=R_3=H$ ). This keto-acid had b.p. 196-99°/5 mm, yield 57 g. (Found: C, 70.65; H, 7.2.  $C_{13}H_{16}O_3$  requires C, 70.90; H, 7.27%).

The semicarbazone of this keto-acid crystallised from ethanol in plates, m.p. 177-78° (decomp.). (Found: C, 60.32; H, 6.7; N, 15.2.  $C_{14}H_{18}O_3N_3$  requires C, 60.64; H, 6.85; N, 15.16%).

*ββ-Dimethyl-δ-phenylvaleric Acid* (II:  $R_1=H$ ;  $R_2=R_3=Me$ ).—The keto-acid (I:  $R_1=H$ ;  $R_2=R_3=Me$ ; 50 g.) was reduced by heating with amalgamated zinc (200 g.) and HCl (conc., 200 ml) for 24 hours. It is a colorless oil, b.p. 185-87°/1 mm, yield 20 g. (Found: C, 75.8; H, 8.5.  $C_{13}H_{18}O_2$  requires C, 75.72; H, 8.73%).

3,3-Dimethyl-6,7-benzsuberone-1 (III:  $R_1=H$ ;  $R_2=R_3=Me$ ).—The valeric acid (II:  $R_1=H$ ;  $R_2=R_3=Me$ ; 20 g.) was cyclised with polyphosphoric acid ( $P_2O_5$ , 70 g. and 89%  $H_3PO_4$ , 30 ml). The ketone distilled at 135-36°/3 mm as a light straw-coloured liquid. The oil gradually crystallised in the form of needles, m.p. 52-53°, yield 10.5 g. (Found: C, 83.1; H, 8.42.  $C_{13}H_{16}O$  requires C, 82.97; H, 8.51%).

2,4-Dinitrophenylhydrazone of the cyclic ketone was crystallised from ethyl acetate as orange crystals, m.p. 220-21°. (Found: C, 61.62; H, 5.3; N, 15.33.  $C_{19}H_{20}O_4N_4$  requires C, 61.95; H, 5.43; N, 15.21%). The semicarbazone of the ketone crystallised from rectified spirit, m.p. 204-205°.

3,3-Dimethyl-6,7-benzsuberan (IV:  $R_1=H$ ;  $R_2=R_3=Me$ ).—The cyclic ketone (III:  $R_1=H$ ;  $R_2=R_3=Me$ ; 10 g.) was reduced by heating with amalgamated zinc (40 g.) and HCl (conc., 40 ml) for 24 hours. It is a colorless oil with fragrance, b.p. 105°/4 mm;  $d_4^{25}$  0.9329,  $n_D^{25}$  1.5215,  $[R_L]_D$  56.84 (calc. 56.52). (Found: C, 89.45; H, 10.1.  $C_{13}H_{18}$  requires C, 89.65; H, 10.34%).

*Catalytic Dehydrogenation of 3,3-Dimethyl-6,7-benzsuberan*.—The hydrocarbon (IV:  $R_1=H$ ;  $R_2=R_3=Me$ ; 3.07 g.) was heated with 10% Pd-C catalyst (0.31 g.) in a sealed pyrex tube at 380-400° for 15 hours. The product was purified through chromatographic fractionation exactly as in the previous case. The first and second eluates contained no solute. The third, fourth, and fifth eluates, each, contained a small quantity of oil with characteristic naphthalenic odour. The oils were separately converted into picrates in methanolic solution. They melted in the range of 108-14°. The picrates were mixed together and crystallised repeatedly from methanol when yellow needles melting at 114-15° were obtained. The mixed m.p. with the picrate of an authentic sample of 2-methylnaphthalene was not depressed. (Found: C, 54.68; H, 3.41. Calc. for  $C_{17}H_{13}O_7N_3$ : C, 54.98; H, 3.50%).

The hydrocarbon was regenerated from the picrate by passing benzenic solution of the picrate through Brockmann alumina and eluting with petroleum ether. It had m.p. 33-34°. The ultraviolet absorption spectra study also suggests that the hydrocarbon is an alkylated naphthalene compound.

Five subsequent eluates left no solute on removal of the solvent. Next the chromatographic column was eluted with hexane-benzene mixture (1:1). The eleventh, twelfth and thirteenth eluates, each, left on evaporation a small amount of a pale yellow solid. These were mixed together and crystallised repeatedly from ethanol when shining flakes were obtained, melting at 178-83°.

The UV absorption spectra study was made with the above substance. The absorption maxima suggest that it is a dinaphthyl compound or its alkyl derivative. An ethanolic solution of it showed maxima at 217 (log  $\epsilon$ , 4.2), 260 (log  $\epsilon$ , 4.8), 310 m $\mu$  (log  $\epsilon$ , 3.8). As the quantity of the substance was very small, no further study could be made.

### 3-Ethyl-3-methyl-6,7-benzsuberan

*$\beta$ -Ethyl- $\beta$ -methyl- $\gamma$ -benzoylbutyric Acid* (I:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ).—A solution of  $\beta$ -ethyl- $\beta$ -methylglutaric anhydride (77 g.) in benzene, aluminium chloride (132 g.), and dry benzene (150 ml) were used and worked up, following the same method as in the previous cases. The liquid keto-acid had b.p. 208-10°/6 mm, yield 90 g. (Found: C, 71.8; H, 7.61.  $C_{14}H_{18}O_3$  requires C, 71.79; H, 7.69%).

The semicarbazone of the keto-acid crystallised from ethanol in small needles, m.p. 165-66° (decomp.). (Found: C, 61.58; H, 7.4; N, 14.32.  $C_{13}H_{21}O_3N_3$  requires C, 61.85; H, 7.21; N, 14.43%).

*$\beta$ -Ethyl- $\beta$ -methyl- $\delta$ -phenylvaleric Acid* (II:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ).—The keto acid (I:  $R=H$ ;  $R_2=Me$ ;  $R_3=Et$ ; 85 g.) was reduced by heating with amalgamated zinc (250 g.) and HCl (conc., 250 ml) for 28 hours. The reduced acid is a colorless oil, b.p. 195-97°/6 mm, yield 56 g. (Found: C, 76.4; H, 9.24.  $C_{14}H_{20}O_2$  requires C, 76.36; H, 9.09%).

*3-Ethyl-3-methyl-6,7-benzsuberone-1* (III:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ).—The valeric acid (II:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ; 30 g.) was cyclised with polyphosphoric acid ( $P_2O_5$ , 105 g. and 89%  $H_3PO_4$ , 45 ml). The ketone distilled at 161-63°/6 mm as a light straw-coloured liquid, yield 22 g. (Found: C, 82.8; H, 8.7.  $C_{14}H_{18}O$  requires C, 83.16; H, 8.91%).

*2,4-Dinitrophenylhydrazone* of the cyclic ketone was crystallised from ethyl acetate as orange-red crystals, m.p. 217-18°. (Found: C, 62.53; H, 5.62; N, 14.54.  $C_{20}H_{20}O_4N_4$  requires C, 62.82; H, 5.75; N, 14.65%). The semicarbazone of the ketone crystallised from rectified spirit, m.p. 142-44°.

*3-Ethyl-3-methyl-6,7-benzsuberan* (IV:  $R_1=H$ ;  $R_2=Me$ ;  $R_3=Et$ ).—The previous cyclic ketone (20 g.) was reduced by heating with amalgamated zinc (80 g.) and HCl (conc., 80 ml) for 24 hours. It is a colorless oil with fragrance, b.p. 110°/1 mm;  $d_4^{25}$  0.9393,  $n_D^{25}$  1.5235,  $[R_L]_D$  61.18 (calc. 61.168). (Found: C, 89.2; H, 10.65.  $C_{14}H_{20}$  requires C, 89.36; H, 10.63%).

*Catalytic Dehydrogenation of 3-Ethyl-3-methyl-6,7-benzosuberan.*—The hydrocarbon (2.85 g.) was heated with 10% Pd-C catalyst (0.30 g.) in a sealed pyrex tube at 380-400° for 15 hours. The product was purified through chromatographic fractionation with hexane as in the former cases. The first and second eluates left no solute on removal of the solvent. The third, fourth, and fifth eluates, each, contained a small quantity of an oil with characteristic odour. The oils were mixed together and the picrate was prepared from methanolic solution. It was crystallised repeatedly from methanol in yellow needles, m. p. 115-16°. The mixed m. p. with the picrate of an authentic sample of 2-methylnaphthalene was not depressed. (Found: C, 55.1; H, 3.41. Calc. for  $C_{17}H_{15}O_7N_3$ : C, 54.98; H, 3.50%).

The hydrocarbon was regenerated from the picrate, as mentioned before, and solidified on cooling, m. p. 33-34°. The UV absorption spectra study suggests that the hydrocarbon is an alkylated naphthalene.

Five subsequent eluates left no solute on removal of the solvent. Next the chromatographic column was eluted with hexane-benzene mixture (1:1). The eleventh, twelfth, and thirteenth eluates, each, contained a small amount of a pale yellow solid. These were mixed together and crystallised from hexane containing a little benzene when shining flakes were obtained. UV absorption spectra study suggests that it may be a binaphthyl compound.

RAMAKRISHNA MISSION VIDYAMANDIRA,  
BELUR MATH, BELUR

AND

CHEMICAL LABORATORY,  
KRISHNAGAR GOVERNMENT COLLEGE,  
KRISHNAGAR, WEST BENGAL.

Received April 3, 1962.