tion only) approximately doubled. The eluates and filtrates from the column and batch operations, respectively, required further processing to separate the mixtures of the mono and dibenzyl ethers formed.

Hydroquinone dibenzyl ether. The separation of the dibenzyl ether of hydroquinone was accomplished by treating the residues from evaporation of the eluate and filtrate with 0.1*N* sodium hydroxide solution and extracting the resulting alkaline-aqueous mixtures with several portions of ether. Evaporation of these ether extractives, first washed free of alkali, yielded hydroquinone dibenzyl ether which when crystallized once from ethanol melted at 128.5–129°; lit.[12,13] m.p. 128–129°, 130°. Yield: column technique, 1.6 g. (10%); batch technique, 4 g. (27%).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.82; H, 6.66.

Hydroquinone monobenzyl ether. The alkaline-aqueous portions from which the hydroquinone dibenzyl ether was removed were acidified with diluted hydrochloric acid and extracted with ether. These ether extractives washed free of acid and evaporated to dryness left crystalline residues. Crystallization of the residues from diluted ethanol yielded hydroquinone monobenzyl ether, m.p. 121–121.5°; lit.[14] m.p. 121–122°. A mixture melting point with an authentic sample of hydroquinone monobenzyl ether showed no depression. Yield: column technique, 0.96 g. (9%); batch technique, 1.46 g. (14%).

Resorcinol dibenzyl ether. Although both column and batch techniques were applied to the preparation of this ether, only the latter technique yielded the compound. The monobenzyl ether of resorcinol could not be obtained by either the column or the batch techniques.

The isolation of the resorcinol dibenzyl ether was accomplished in the same manner as described for the isolation of the dibenzyl ether of hydroquinone. The yield was 2.35 g. (16%), m.p. 73–74°; lit.[14] m.p. 73–74°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 83.06; H, 6.45.

Experiments are being continued to acertain whether any ethers of phenols other than benzyl can be prepared by the method herein described; and similarly, whether any benzyl or alkyl groups can replace non-carboxylic hydrogens on other types of compounds.

INDIANAPOLIS, IND.

---

(12) A. Colson, *Bull. soc. chim.*, **3**, 347 (1889).

(13) H. Schiff and G. Pellizzari, *Ann.*, **221**, 369 (1883).

(14) J. Druey, *Bull. soc. chim.*, **5**, 1740 (1935).

(15) F. Caujolle, C. Franck, and L. Girard, *Compt. rend.* **218**, 572 (1944).

(16) I. M. Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, 1946, Vol. II, p. 136.

(17) T. F. West, *J. Chem. Soc.*, 490 (1945).

(18) G. Kumpf, *Ann.*, **224**, 123 (1884).

(19) V. H. Dermer and O. C. Dermer, *J. Org. Chem.*, **3**, 291 (1938).

(20) W. Staedel, *Ber.*, **14**, 899 (1881).

(21) HLA, BAW, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926); *Chem. Abstr.*, **20**, 3695 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AIN SHAMS UNIVERSITY]

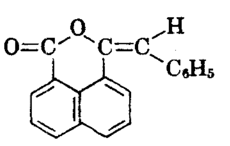
Comparative Study between Phthalides and Naphthalides. II[1]

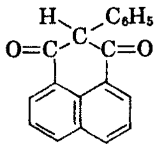
O. M. ALY, W. I. AWAD, AND A. M. ISLAM

Received March 27, 1958

In addition to the β-diketone (II), 3-benzalnaphthalide (I) was isolated from the product of interaction of naphthalic anhydride and phenylacetic acid. Infrared curves for the naphthalide (I) and the phthalide (VI) together with the β-diketones (II), (III) and (IV) are discussed.

Recently, Aly, Awad, and Islam,[1] investigated the condensation of naphthalic anhydride with phenylacetic acid in the presence of sodium acetate, and obtained a product (m.p. 214°) to which they assigned the benzalnaphthalide structure (I).


I


II

Cesaris[2] obtained from the same condensation a product which possessed no ketonic properties and to which he gave β-diketone structure (II). He claimed that in contrast to ortho-anhydrides such as phthalic anhydride, which gives only the phthalide, naphthalic anhydride gives directly the β-diketone (II).

In the light of the above controversial results, we decided to reinvestigate the whole problem in more detail.

We have now isolated from the reaction mixture of the above Perkin condensation, two products. The main product is orange in color, m.p. 214°, and is fairly soluble in cold dilute sodium hydroxide and dilute sodium carbonate solutions. Infrared measurements of this compound (Fig. 1) show a clear carbonyl stretching frequency (1570 cm.$^{-1}$) in the normal carbonyl group region (the carbonyl stretching frequency for β-diketones is 1640–1540 cm.$^{-1}$).[3] Similar carbonyl stretching frequencies are present in the infrared curves of the two β-diketones, III[4] (Fig. 2) and IV[1] (Fig. 3), being 1620

---

(1) Compare Comparative Study between Phthalides and Naphthalides, O. M. Aly, W. I. Awad, and A. M. Islam, *J. Org. Chem.*, **22**, 517 (1957).

(2) M. Cesaris, *Gazz. chim. ital.*, **42**, II, 453.

(3) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 114.

(4) G. Errera, *Gazz. chim. ital.*, **41**, I, 190.

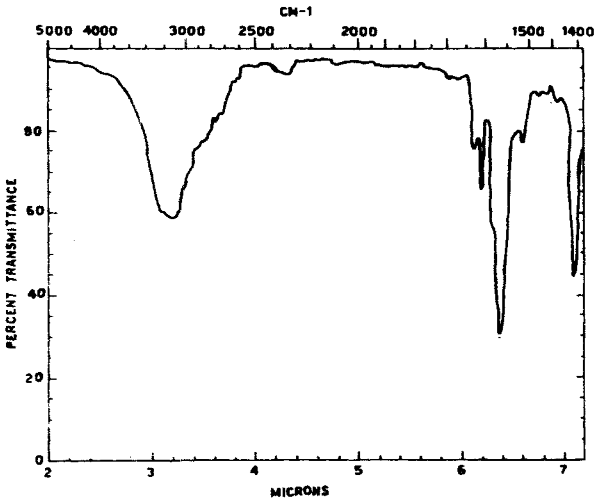


Fig. 1. 8-Phenyl-*peri*-naphthindan-7,9-dione (II)

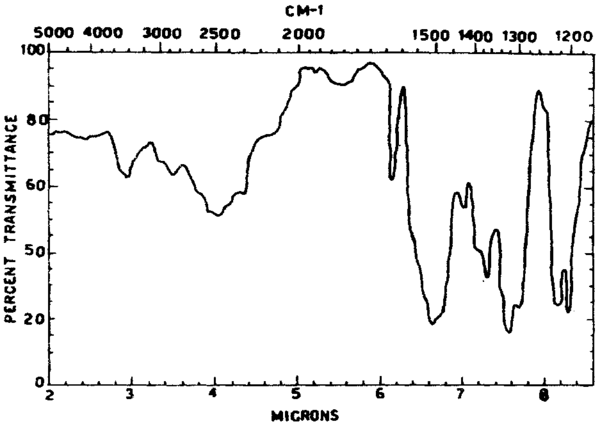
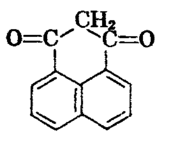
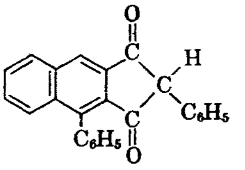


Fig. 2. *peri*-Naphthindan-7,9-dione (III)



III



IV

cm.$^{-1}$ and 1600 cm.$^{-1}$, respectively. The β-diketone structure (II) is therefore given for this compound which is in agreement with Cesaris's consideration.

Whereas the infrared curve of the diketone (IV) shows a free —OH stretching frequency at 3400 cm.$^{-1}$, it is remarkable that neither of the peridiketones (II and III) showed frequencies in the solid state or in solution which indicates a minimum contribution for the enol configuration.

The second product isolated from the reaction mixture of the above condensation is obtained in lower yield through extraction with petroleum ether, in which it is comparatively soluble. This compound is yellow in color, m.p. 146°, and is insoluble in both dilute sodium hydroxide and sodium carbonate solutions. The constitution of this compound as the naphthalide (I) is supported by the following facts: (*a*) on treatment with an alcoholic sodium methoxide solution, it is converted quantitatively to the β-diketone (II) (Nathanson[5] and Eibner[6]), (*b*) it reacts in sunlight with tetrabromo-*o*-quinone to give the photo-addition product (V),[1,7] (*c*) the infrared measurements show a

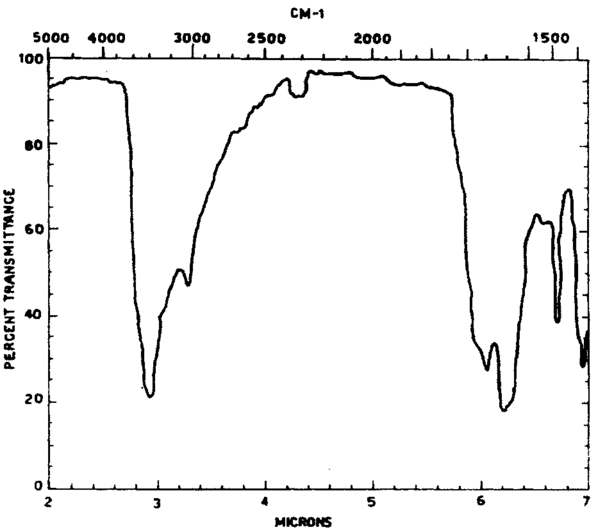
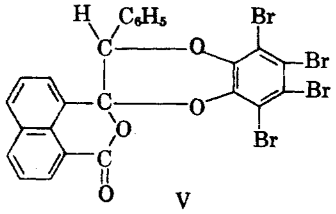


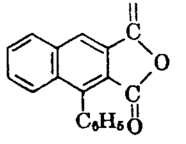
Fig. 3. 2,4-Diphenyl-5,6-benzindan-1,3-dione (IV)



V

carbonyl stretching frequency at 1710 cm.$^{-1}$ (Fig. 4) (δ-lactones have stretching frequency in the range 1750–1735 cm.$^{-1}$).[8] Unsaturated δ-lactones are expected to have a slightly higher stretching frequency than the saturated ones as is the case with saturated γ-lactones.

The infrared curve of the phthalide (VI)[1] shows also a carbonyl stretching frequency in the unsaturated γ-lactone region (1760 cm.$^{-1}$) (Fig. 5).



VI

---

(5) Nathanson, *Ber.*, 26, 2576 (1893).

(6) Eibner, *Ber.*, 39, 2203 (1906).

(7) A. Schönberg, and A. Mustafa, *Chem. Revs.*, 40, 190 (1948).

(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1956, p. 153.

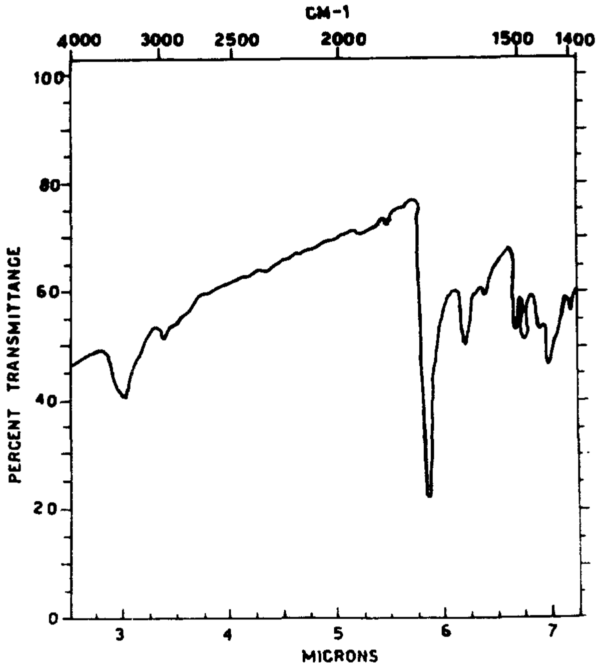
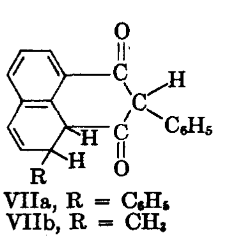


Fig. 4. 3-Benzalnaphthalide (I)

The non-isolation of the naphthalide (I) as reported in our previous publication[1] was due to the fact that I is easily adsorbed during the purification of the reaction product, then leaving the β-diketone (II) as the sole product.

As II is the major product, it is feasible to suggest that the naphthalide (I) is first formed which then rearranges, in the presence of sodium acetate and at the high temperature of the reaction, to the β-diketone (II).

In the presence of excess phenylmagnesium bromide or excess methylmagnesium iodide, the β-diketone (II) reacts as a monoketone. It adds only one molecule of Grignard reagent. Koelsch and Rosenwald[9] reported the isolation of VIIa from the interaction of II and phenyllithium, the mode of interaction being a 1:4 addition. They were unable, however, to obtain this compound, VIIa, by the direct interaction of II and phenylmagnesium bromide. Our product from II and phenylmagnesium bromide proved to be identical with VIIa by a mixture melting point.



VIIa, R = C_6H_5
VIIb, R = CH_3

In accordance with the above considerations, the product from II and methylmagnesium iodide should have structure VIIb. VIIa was previously described[1] as a hemiketal, owing to the fact that the diketone II was erroneously given the benzalnaphthalide structure.

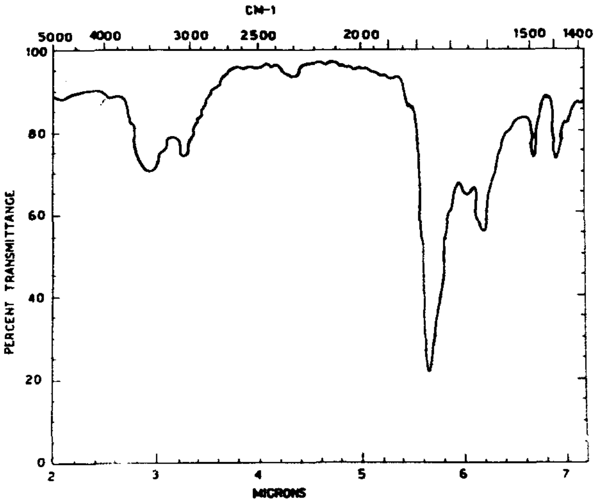
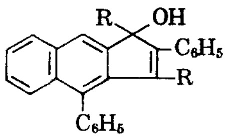
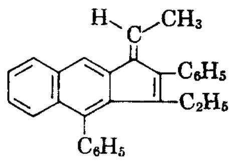


Fig. 5. Benzal-7-phenyl-5,6-benzophthalide (VI)

On the other hand, the five-membered compound IV reacted with Grignard reagents as a diketone. With excess methylmagnesium iodide or excess phenylmagnesium bromide, IV gives colorless or almost colorless products which possess carbon and hydrogen figures corresponding to VIIIa and VIIIb, respectively, which results from the addition of two molecules of the Grignard reagent followed by the loss of one molecule of water.



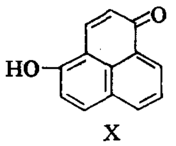
VIIIa ; R = C_6H_5
VIIIb ; R = CH_3



IX

With excess ethylmagnesium iodide, however, IV gives rise to an oxygen-free compound IX.

On the constitution of perinaphthindan-7,9-dione. The non-appearance of ketonic properties for the diketone II, as reported by Cesaris[2] and as confirmed by the authors, was unusual, since compounds of structure similar to X[10] and XI[11] are reported to give carbonyl derivatives.



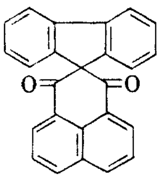
X

---

[9] C. F. Koelsch and R. H. Rosenwald, *J. Am. Chem. Soc.*, 59, 2166 (1937).

[10] J. London and R. Razdan, *J. Chem. Soc.*, 4299 (1954).

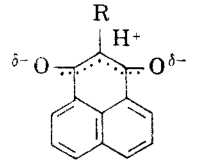
[11] E. J. Greenhow, E. N. White, and D. McNeil, *J. Chem. Soc.*, 3099 (1953).



XI

By comparing the infrared curves (in the solid state and in solution) for the three diketones II, III, and IV, the following facts are observed. While they all show a clear absorption in the normal carbonyl stretching frequency range, compounds II and III show no free OH stretching frequency as found for the diketone IV.

Among the different unperturbated structures for II or III, it is not unreasonable to consider structure XII as a possible representative. Such a structure would then explain the empirical facts such as the non-appearance of normal ketonic properties, the strong acidic character of the hydrogen atom at position (8) (II being soluble in dilute sodium carbonate solution) and the non-appearance of a free OH stretching frequency in the infrared curve.



XII

R = H or C_6H_5

EXPERIMENTAL[12]

Reaction of naphthalic anhydride with phenylacetic acid. A mixture of naphthalic anhydride (5 g.), phenylacetic acid (3.5 g.), and fused sodium or potassium acetate (0.2 g.) was heated to 230–240°, and maintained at that temperature for 1 hr. The hot melt was rubbed with 30 ml. of alcohol and allowed to cool. On filtration, a brownish orange product was obtained (6 g.). The crude product was boiled with 150 ml. of petroleum ether (70–80°) and filtered. The filtrate acquired a brownish yellow coloration and on concentration, brownish yellow needles separated out, m.p. 135–140°. This product was washed with a warm solution of sodium carbonate (100 ml. of 10% solution), to remove 8-phenyl-*peri*-naphthindan-7,9-dione. Recrystallization from petroleum ether (70–80°), yielded 3-benzalnaphthalide (I), 2.4 g. (34%), as yellow long needles, m.p. 146–148°.

This product could also be obtained in pure form, by chromatographing the petroleum ether extract on alumina. On elution by anhydrous benzene and concentration of the eluted benzene solution, 3-benzalnaphthalide (I) separated as yellow needles. The phenyl-*peri*-naphthindan-7,9-dione could not be eluted under these conditions.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.4. Found: C, 83.4; H, 4.4.

This compound was insoluble in a dilute solution of sodium hydroxide or sodium carbonate. It gave a brownish red coloration with concentrated sulfuric acid.

Recrystallization of the product which was insoluble in petroleum ether from boiling alcohol (charcoal) gave 3 g. (48%) of 8-phenyl-*peri*-naphthindan-7,9-dione as orange needles, m.p. 214–216° (previously[1] analyzed).

Rearrangement of 3-benzalnaphthalide (I). 3-Benzalnaphthalide (I) (0.3 g.) was boiled for 15 min. with a 2% methyl alcoholic solution of sodium methoxide (50 ml.). The reaction mixture was diluted with water, filtered, cooled, and acidified with ice cold dilute hydrochloric acid. Crystallization of the precipitated product from alcohol gave 0.25 g. (75%) of 8-phenyl-*peri*-naphthindan-7,9-dione (II).

Photo-addition of 3-benzalnaphthalide (I) *with tetrabromo-o-quinone.* A mixture of 3-benzalnaphthalide (I) (0.3 g.) and tetrabromo-*o*-quinone (0.4 g.) in dry thiophene-free benzene (30 ml.) was placed in Schlenck tube[13] under a carbon dioxide atmosphere and exposed to sunlight. After 48 hr. the red color disappeared and the solution acquired a pale yellow coloration. On concentration of the benzene solution, a colorless product was obtained. Recrystallization from benzene gave 0.2 g. (29%) of the adduct (V) as colorless needles, m.p. 273–275°.

Anal. Calcd. for $C_{25}H_{12}O_4Br_4$: Br, 45.9. Found: Br, 44.5.

Action of methylmagnesium iodide on (II). A solution of 8-phenyl-*peri*-naphthindan-7,9-dione (II) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of methylmagnesium iodide (from methyl iodide, 2.8 g., and magnesium, 0.5 g.) and the reaction mixture was heated under reflux for 2 hr., then left overnight. The reaction mixture was decomposed with an aqueous solution of ammonium chloride. On concentration of the washed and dried benzene extracts followed by addition of petroleum ether (40–60°), a yellowish product was obtained. Recrystallization from a benzene–petroleum ether mixture (1:1) gave 0.2 g. (20%) of 1-methyl-8-phenyl-1,9-dihydro-*peri*-naphthindan-7,9-dione (VIIb) as yellow needles, m.p. 138–140°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6. Found: C, 83.8; H, 5.1.

The product was soluble in a methyl alcoholic solution of sodium methoxide with an orange-red coloration and in sodium hydroxide solution with a yellowish orange coloration. In both cases the product was recovered unchanged on acidification.

Action of phenylmagnesium bromide on II. A solution of 8-phenyl-*peri*-naphthindan 7,9-dione (II) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 1.8 g., and magnesium, 0.3 g.) and the reaction mixture was heated under reflux for 4 hr. then left overnight. Decomposition with aqueous ammonium chloride solution, and concentration of the washed and dried benzene extracts followed by addition of petroleum ether (40–60°), gave a pale yellow product. Recrystallization from a benzene–petroleum ether mixture (1:1) gave 0.2 g. (17%) of 1,8-diphenyl-1,9-dihydro-*peri*-naphthindan 7,9-dione (VIIa) as pale yellow plates, m.p. 177–178°. The melting point of this product was undepressed on admixture with the product obtained by Koelsch and Rosenwald[3] by the action of phenyllithium on II.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.7; H, 5.2. Found: C, 85.5; H, 5.3.

The substance gave a pale yellow coloration with concentrated sulfuric acid.

Action of methylmagnesium iodide on IV. A solution of 2,4-diphenyl-5,6-benzindan-1,3-dione (IV) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of methylmagnesium iodide (from methyl iodide, 3 g., and magnesium, 0.5 g.) and the reaction mixture was heated under reflux for 3 hr. The reaction mixture was then decomposed with aqueous ammonium chloride solution and on concentration of the washed and dried benzene extracts followed by addition of petroleum ether (40–60°), gave a yellowish product.

---

(12) Microanalyses were carried out by Alfred Bernhardt, im Max-Plank Institut, Mülheim (Ruhr), Germany. Melting points are not corrected.

(13) Houben, *Die Methoden der Organischen Chemie*, 2nd. ed., Vol. 4, Georg Thieme, Leipzig, 1924, p. 960.

Recrystallization from benzene–petroleum ether mixture (1:1) gave 0.3 g. (30%) of VIIIa as pale yellow needles, m.p. 197–200°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.4; H, 6.1. Found: C, 88.9; H, 6.6.

Action of ethylmagnesium iodide on IV. A solution of 2,4-diphenyl-5,6-benzindan-1,3-dione (IV) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of ethylmagnesium iodide (from ethyl iodide, 3.5 g., and magnesium, 0.5 g.) and the reaction mixture was heated under reflux for 2 hr., then left overnight. Decomposition with aqueous ammonium chloride solution, and concentration of the washed and dried benzene extracts, gave a pale yellow product. Recrystallization from benzene gave 0.25 g. (24%) of IX as almost colorless needles, m.p. 182–184°.

Anal. Calcd. for $C_{29}H_{24}$: C, 93.5; H, 6.5. Found: C, 92.8; H, 6.4.

The product gave a rose red coloration with concentrated sulfuric acid.

Action of phenylmagnesium bromide on IV. A solution of 2,4-diphenyl-5,6-benzindan-1,3-dione (IV) (1 g.) in dry benzene (100 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 2 g., and magnesium, 0.5 g.) and the reaction mixture was heated under reflux for 3 hr. then left overnight. Decomposition with aqueous ammonium chloride solution, and concentration of the washed and dried benzene extracts followed by addition of petroleum ether (40–60°), gave a colorless product. Recrystallization from benzene–petroleum ether mixture (1:1) gave 0.4 g. (30%) of VIIIb as colorless prisms, m.p. 198–199°.

Anal. Calcd. for $C_{37}H_{26}O$: C, 91.3; H, 5.4. Found: C, 91.1; H, 5.4.

The product gave a bluish coloration with concentrated sulfuric acid.

Acknowledgment. The authors wish to express their thanks and gratitude to Messers. Samuel P. Sadtler & Son, Inc., Research Laboratories, Philadelphia, Pa., for kindly carrying out the infrared spectrograms of II, III, IV, and VI. The samples were vacuum dried and the spectrograms were carried out using the potassium bromide Wafer technique. The infrared measurements of I, II, and III were also carried out in solution by Mr. Nagib Doss, Chemistry Department, Ohio State University, U.S.A., to whom we are greatly indebted.

ABBASSIA, CAIRO, EGYPT

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

Higher Hydrocarbons. VI.[1] Polyalkylbenzenes and Polyalkylcyclohexanes[2]

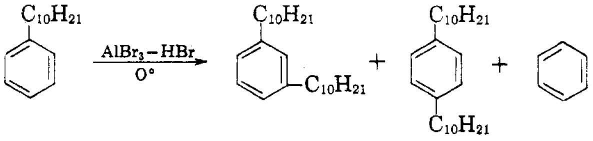
S. G. CLARK II AND J. A. DIXON

Received May 15, 1958

The syntheses of six new high molecular weight polyalkylbenzenes and polyalkylcyclohexanes are reported.

As a portion of a continuing study of high molecular weight hydrocarbons, the synthesis and physical properties of six new monocyclic hydrocarbons are reported. They are 1,3-didecylbenzene, 1,3-didecylcyclohexane, 2,5-dimethyloctadecylbenzene, 2,5-dimethyloctadecylcyclohexane, 2,4,6-trimethyloctadecylbenzene, and 2,4,6-trimethyloctadecylcyclohexane.

Three different synthetic routes were used for the preparations of the above hydrocarbons. The 1,3-didecylbenzene was prepared by the disproportionation of decylbenzene with aluminum bromide–hydrogen bromide catalyst.[3–6]



It has been found from studies of the hydrogen fluoride and aluminum halide catalyzed disproportionations of a series of lower alkylbenzenes that the dialkylbenzenes obtained are exclusively the meta isomers except in the case of isopropyl or tertiary butylbenzene.[3,4] It was believed that the increased branching of the alkyl group in these two cases decreased the differences in the stability of the isomeric hydrocarbon catalyst complexes.[5] In the present work it was observed that the disproportionation of decylbenzene catalyzed by aluminum chloride–hydrogen chloride yielded a four to one ratio of *meta-* to *para*-didecylbenzene while aluminum bromide–hydrogen bromide produced the isomers in a nine to one ratio. The ortho isomer was looked for but not found. Analysis was by infrared, density, and viscosity, after separation of the isomers by fractional distillation. The identity of the para isomer was unequivocally established by comparison with an authentic sample which had been prepared previously in this labora-

---

(1) For the previous paper in this series: R. W. Schiessler, A. W. Rytina, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 529 (1948).

(2) Taken from a portion of a dissertation submitted by S. G. Clark to the Graduate School of The Pennsylvania State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) A. P. Lien and D. A. McCaulay, *J. Am. Chem. Soc.*, **75**, 2407, 2411 (1953).

(4) R. D. Kinney and L. A. Hamilton, *J. Am. Chem. Soc.*, **76**, 786 (1954).

(5) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).

(6) R. M. Roberts and S. G. Brandenberger, *J. Am. Chem. Soc.*, **79**, 5485 (1957).