the added chlorine has been removed the rate returns to the uncatalyzed value. The slope of the curve during the period when the chlorine is being removed exceeds that of the maximum rate produced by the addition of acetanilide.

We are unable to harmonize the effects shown in Figs. 1 and 2 with the current theory of the rearrangement. On the other hand, we have no thoroughly satisfactory mechanism to offer as a substitute.

Summary

In glacial acetic acid containing sodium chloride and sodium acetate as buffers, the rearrangement of acetylchloro-aminobenzene is a first-order reaction. The rate of disappearance of the chloro-amine is accelerated by the addition of acetanilide or β-acetnaphthalide. In each case a maximum rate can be secured but the maximum rates produced by the two amides are not identical.

The addition of chlorine and of acetanilide have entirely different effects upon the rate of the reaction. These results are not in harmony with the view that the first step, and the slowest one, is the reversible production of chlorine and acetanilide from the chloro-amine and hydrochloric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TETRACYCLOHEXYLDIPHENYLETHANE

BY S. S. ROSSANDER, L. H. BOCK AND C. S. MARVEL

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In recent years it has been shown that the cyclohexyl group is effective in promoting the dissociation of hexa-substituted ethanes. Ziegler and Schnell[1] have prepared dicyclohexyltetraphenylethane and found that it forms a peroxide in the air. Conant and his students[2] have observed that dicyclohexyldixanthyl is dissociated into the free radical cyclohexylxanthyl to a considerable extent. These facts make it desirable to know the properties of ethanes which have more than two cyclohexyl groups in the molecule.

Some time ago Gray with Marvel[3] reported the preparation of a hydrocarbon, which they believed to be tetracyclohexyldiphenylethane, by the action of silver on a boiling toluene solution of dicyclohexylphenylchloromethane. Later Conant, Small and Sloan[2b] showed that this hydrocarbon was in reality phenylcyclohexylidinecyclohexylmethane. In view

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[1] Ziegler and Schnell, *Ann.*, **437**, 252 (1924).

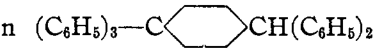
[2] (a) Conant and Small, THIS JOURNAL, **47**, 3068 (1925); (b) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

[3] Gray with Marvel, *ibid.*, **47**, 2796 (1925).

of the great interest in the properties of a hexa-substituted ethane containing two cyclohexyl groups on each ethane carbon, this preparation has been undertaken again.

It was found in the present work that dicyclohexylphenylchloromethane would react with 40% sodium amalgam to give a red metallic alkyl along with a hydrocarbon which from its analysis proved to be an isomer of the desired tetracyclohexyldiphenylethane. When the pure sodium alkyl was treated with tetramethylethylene bromide in ether solution according to the procedure developed by Ziegler and Schnell,[4] the color disappeared. The colorless ether solution reacted with either 1 or 40% sodium amalgam to give again the original metallic alkyl. The ether solution absorbed oxygen with some rapidity. When air was rapidly bubbled through the ether solution, a white crystalline solid separated and this on analysis proved to be dicyclohexylphenylmethyl peroxide. These reactions all indicate that tetracyclohexyldiphenylethane was present in this ether solution and that it was to some extent dissociated into a free radical.

In order to be certain of the structure of the compounds which were obtained, the dicyclohexylphenylmethyl sodium prepared from the dicyclohexylphenylchloromethane was converted into dicyclohexylphenylacetic acid. The same acid was obtained by cleavage of the unstable hydrocarbon with sodium amalgam and treatment of the alkali metal alkyl thus obtained with carbon dioxide. This acid on oxidation yielded benzoic acid. Hence there had been no rearrangement of the metal into the benzene ring as sometimes occurs with benzyl halides in reactions of this type. With water the metallic alkyl gave dicylohexylphenylmethane.

No method has yet been devised for the isolation of the unstable hydrocarbon in a pure condition. It readily rearranged on heating or on standing when exposed to the light. This rearrangement with heat produced the isomeric hydrocarbon which was obtained by the action of sodium amalgam on dicyclohexylphenylchloromethane. The stable rearranged hydrocarbon probably has a structure analogous to that of the hydrocarbon  $(C_6H_5)_3—C\langle\quad\rangle CH(C_6H_5)_2$ which is formed by the rearrangement of hexaphenylethane.[5]

The peroxide reacted with sulfuric acid to give dicylohexylphenylcarbinol. The carbinol was identified by converting it to dicyclohexylphenylchloromethane by treatment with acetyl chloride. This chloride had the proper melting point and showed no depression when a mixed melting point was taken with an authentic specimen of the chloride.

The reactions which have been carried out may be seen in the diagram.

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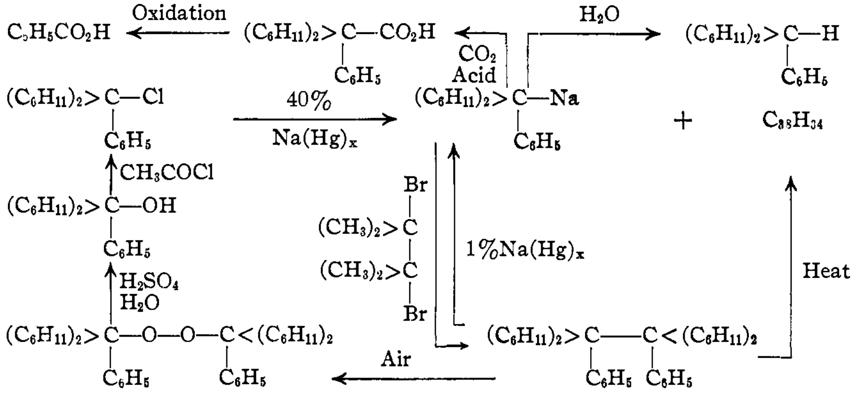
[4] Ziegler and Schnell, *Ann.*, **437**, 244 (1924).

[5] Gomberg, *Ber.*, **36**, 379 (1903); Tschitschibabin, *ibid.*, **37**, 4709 (1904); **41**, 2421 (1908); Schlenk and Marcus, *ibid.*, **47**, 1665 (1914).



Experimental Part

Dicyclohexylphenylchloromethane was prepared as described by Gray with Marvel.[3]

Dicyclohexylphenylbromomethane.—To a solution of 14 g. of dicyclohexylphenylcarbinol in 40 cc. of dry benzene was added 10 cc. of acetyl bromide. The solution was allowed to stand overnight and the solvent was removed by evaporation under reduced pressure until crystals began to appear. At this point 100 cc. of 95% alcohol was added and the mixture was cooled overnight in an ice box. After three crystallizations from benzene and alcohol there was obtained 10–12 g. of a product which melted at 104–105°.

Anal. Subs., 0.3321: 13.2 cc. of 0.07504 *N* $AgNO_3$. Calcd. for $C_{19}H_{27}Br$: Br, 23.86. Found: Br, 23.91.

An attempt to prepare the Grignard reagent from the bromide was unsuccessful. Silver would not remove the bromine from the molecule in cold toluene solution. It was observed that heating either the chloro compound or the bromo compound in toluene solution gave phenylcyclohexylidinecyclohexylmethane and halogen acid.

Sodium Dicyclohexylphenylmethyl and the Hydrocarbon $C_{38}H_{54}$.—A solution of 5 g. of dicyclohexylphenylchloromethane in 100 cc. of anhydrous ether was placed in a 500-cc. round-bottomed flask and the air was swept out with nitrogen. To this solution was added 40 cc. of 40% sodium amalgam. The flask was tightly stoppered, placed on a shaking machine and agitated for about eight hours. A red color developed in about an hour. At the end of the shaking period the excess amalgam was frozen by cooling the mixture in an ice-bath and the solution of the metallic alkyl was transferred to a second flask. During this process and subsequent operations an atmosphere of dry nitrogen was maintained over the reaction mixture. To the suspension 100 cc. of dry, oxygen-free petroleum ether (b. p. 25–65°) was added in order to precipitate any of the metallic derivative from the ether. A cloth filter was fitted into the neck of the flask and the flask was inverted. The ether solution was then filtered. The red metallic alkyl remained on the filter.

The ether solution which was filtered from this reaction mixture was evaporated. The residue was recrystallized with some difficulty from benzene and alcohol. It melted at 209–211°.

Anal. Subs., 0.1310: CO_2, 0.4283; H_2O, 0.1254. Calcd. for $C_{38}H_{54}$: C, 89.33; H, 10.67. Found: C, 89.17; H, 10.70. Mol. wt. (in benzene) Subs., 0.3893: benzene, 21.975; Δt, 0.191°. Calcd. for $C_{38}H_{54}$; mol. wt., 510. Found: mol. wt., 475.

This hydrocarbon was very stable. It could be heated to 220° at 1 mm. without decomposition. When 1 g. of hydrocarbon was boiled with 100 cc. of aqueous potassium permanganate solution for twelve hours, over half of it was recovered unchanged. Oxidation with potassium dichromate and sulfuric acid destroyed the compound entirely. The hydrocarbon was unaffected by liquid sodium–potassium alloy.

Dicyclohexylphenylacetic Acid.—The sodium dicyclohexylphenylmethyl obtained from 5 g. of the chloride as described above was suspended in 50 cc. of ether (freshly dried with ethylmagnesium bromide) and dry carbon dioxide was passed into the suspension for about ten minutes. To the mixture was slowly added, first, about 15 cc. of water and then a solution of 5 g. of sodium hydroxide in 30 cc. of water. The mixture was warmed on the water-bath to remove the ether and 10 cc. of alcohol was added. This solution was cooled to about $-5°$ and acidified with dilute hydrochloric acid. The acid which separated was recrystallized twice from glacial acetic acid and then melted at 242–244°. The yield was 0.9–1.1 g.

Anal. Subs., 0.1270: CO_2, 0.3738; H_2O, 0.1070. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.40. Found: C, 80.20; H, 9.43. Subs., 0.092: 9.75 cc. of 0.0312 N NaOH. Calcd. for $C_{20}H_{28}O_2$: neutral equivalent, 300.2. Found: 302.

Three and one-quarter grams of the acid was boiled under a reflux condenser with an aqueous solution of 20 g. of potassium permanganate for four hours. An additional 27 g. of potassium permanganate was then added and the solution was again boiled under a reflux condenser for eight hours. The excess permanganate was destroyed by alcohol and the reaction mixture was worked up as usual. From the mixture was obtained about 0.25 g. of benzoic acid, m. p. 119–120°. A mixed melting point with an authentic specimen of benzoic acid showed no depression.

Dicyclohexylphenylmethane.—The pure sodium dicyclohexylphenylmethyl from 30 g. of dicyclohexylphenylchloromethane was suspended in ether and treated with water from which the dissolved oxygen had been removed. The ether was evaporated and the remaining oil was distilled under reduced pressure. The product boiled at 145–148° at 5 mm. The yield was 10 g., n_D^{20} 1.5390.

For comparison the same hydrocarbon was prepared by the reduction of phenylcyclohexylidenecyclohexylmethane. To a solution of 17 g. of phenylcyclohexylidenecyclohexylmethane in 130 cc. of glacial acetic acid was added 0.3 g. of platinum-oxide platinum black and the mixture was reduced by hydrogen under pressure as described by Adams and Marshall.[6] The reduction product boiled at 146–148° at 5 mm.; n_D^{20} 1.5391; d_4^{20} 0.9774; calcd. M_D, 81.96; found, M_D, 82.07.

Anal. Subs., 0.1551: CO_2, 0.5067; H_2O, 0.1570. Calcd. for $C_{19}H_{28}$: C, 88.98; H, 11.02. Found: C, 89.09; H, 11.33. Mol. wt. (cryoscopic in benzene). Subs., 0.1295: benzene, 13.1765; Δt, 0.203. Calcd. for $C_{19}H_{28}$: mol. wt., 256. Found: mol. wt., 248.

Godchot[7] has previously obtained this hydrocarbon in an impure condition by the catalytic hydrogenation of triphenylmethane over nickel.

Tetracyclohexyldiphenylethane.—The sodium derivative from 4 g. of dicyclohexylphenylchloromethane was prepared as described before and was then suspended in 50 cc. of dry, oxygen-free ether. To the cold (0°) suspension was added slowly an ether solution of tetramethylethylene bromide until the color of the metallic alkyl was no longer apparent. During the addition of this solution the reaction mixture was vigorously shaken. The mixture was filtered and the filtrate evaporated in an atmosphere of nitrogen. About 1 g. of an oil remained which could not be made to crystallize. This oil was apparently the desired hydrocarbon, as shown by the following reactions.

When about 1 g. of the oil was dissolved in 50 cc. of dry oxygen-free ether and the

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[6] Adams and Marshall, This Journal, **50**, 1970 (1928).

[7] Godchot, *Comp. rend.*, **147**, 1057 (1908).

mixture treated with 40 cc. of 40% sodium amalgam, the solution became red in about twenty minutes. Shaking was continued for six hours. Dry carbon dioxide was then admitted and the reaction mixture was worked up as described before for dicyclohexylphenylacetic acid. The yield of acid was 0.4 g., m. p. 242–244°. A mixed melting point with the acid prepared previously showed no depression. From the same reaction mixture there was obtained 0.15 g. of the hydrocarbon $C_{38}H_{64}$ which melted at 209°.

The crude oily hydrocarbon from 4 g. of dicyclohexylphenylchloromethane was prepared and treated in dry oxygen-free ether with 110 g. of 1% sodium amalgam. The deep red color characteristic of the metallic alkyl appeared in about two and a quarter hours.

Dicyclohexylphenylmethyl Peroxide.—A slow current of dry air was bubbled through a solution of 1 g. of the freshly prepared hydrocarbon in dry ether. A white precipitate separated from the solution. This product was recrystallized from ether or from benzene and alcohol. The purified product weighed 0.5 g.; m. p. 186–188° (with decomposition).

Anal. Subs., 0.1630, 0.1297: CO_2, 0.5011, 0.3982; H_2O, 0.1479, 0.1212. Calcd. for $C_{38}H_{54}O_2$: C, 84.07; H, 10.03. Found: C, 83.86, 83.80; H, 10.03, 10.03. Mol. wt. (Rast method). Subs., 0.0109; camphor, 0.1861; Δt, 4.5° (average of 3 detns.). Calcd. for $C_{38}H_{54}O_2$: mol. wt., 542. Found: mol. wt., 521.

Three-tenths of a gram of this peroxide was slowly dissolved in 10 g. of ice-cold sulfuric acid. The reaction mixture was stirred and allowed slowly to come to room temperature. It was then poured on cracked ice and extracted with ether. The ether was evaporated and the oil was dissolved in 6 cc. of benzene and treated with 2 cc. of acetyl chloride. After standing overnight the mixture was evaporated. A few crystals were obtained which melted at 122° and showed no depression in melting point when mixed with an authentic specimen of dicyclohexylphenylchloromethane. Some unsaturated material, probably phenylcyclohexylidenecyclohexylmethane remained in the mother liquors.

Attempts to follow quantitatively the absorption of oxygen by the crude hydrocarbon were not very successful. Using oxygen-free xylene as a solvent, a preparation was made starting with 4 g. of dicyclohexylphenylchloromethane. As soon as the color of the metallic alkyl had disappeared, the apparatus was connected with a eudiometer filled with oxygen. In the first seven minutes 18 cc. of oxygen was absorbed. In the next thirty minutes 7 cc. more was absorbed. No more oxygen was absorbed in the next eight hours. On evaporating the solution and recrystallizing the residue, 0.25 g. of the peroxide was obtained. In a duplicate run 17 cc. of oxygen was absorbed in the first five minutes, 7 cc. in the next fifteen minutes and 4 cc. in the next half hour. The peroxide found amounted to 0.3 g. In a third run a weighed sample of 0.9 g. of crude ethane was used and results of the same order were obtained. In the first five minutes 15 cc. of oxygen was absorbed, in the next fifteen minutes 6 cc. and in the next hour 3 cc. The amount of oxygen absorbed would be that required for only 0.54 g. of the ethane and the peroxide isolated weighed only 0.29 g.

Stability of Tetracyclohexyldiphenylethane toward Heat and Light.—One gram of the crude freshly prepared tetracyclohexyldiphenylethane was dissolved in 60 cc. of dry oxygen-free xylene and heated to 100° for ten minutes. No color developed. The xylene was removed and the residue was recrystallized from alcohol and benzene. There was thus obtained 0.2 g. of product which by a mixed melting point determination was found to be the same hydrocarbon as that obtained as a by-product in the preparation of sodium dicylohexylphenylmethyl. In the mother liquors there was present an oily material which probably was a mixture of phenylcyclohexylidenecyclohexylmethane and phenyldicyclohexylmethane produced by disproportionation of the tetracyclohexyldiphenylethane.

When another sample of the ethane was heated for the same length of time and then shaken with 40% sodium amalgam for four hours, no red color developed, showing the absence of the starting material.

Three runs of the ethane were prepared from 4 g. of dicyclohexylphenylchloromethane. The solutions of hydrocarbon in ether were allowed to stand for different times and then treated with 40% sodium amalgam and the amount of dicyclohexylphenylacetic acid which could be isolated was noted. One sample was treated at once with amalgam and from it 0.32 g. of the acid was isolated. The second solution stood in the light for eight hours before the amalgam was added. It yielded only 0.12 g. of acid. The third solution stood in the light for five days before the amalgam was added. The amount of acid formed was too small to isolate and weigh. Several other solutions of the hydrocarbon were allowed to stand in the light and some in the dark. The hydrocarbon apparently decomposed rather rapidly in either case.

Summary

1. Dicyclohexylphenylchloromethane has been found to react with 40% sodium amalgam to give sodium dicyclohexylphenylmethyl and a hydrocarbon, $C_{38}H_{54}$.

2. Sodium dicyclohexylphenylmethyl when treated with tetramethylethylene bromide gave tetracyclohexyldiphenylethane. This hydrocarbon absorbed oxygen to give a peroxide and was cleaved by 1% sodium amalgam, indicating that it dissociated to some extent into a free radical.

3. Solutions of tetracyclohexyldiphenylethane were not colored. When the hydrocarbon was heated in solution it rearranged at least in part to the same hydrocarbon that was obtained by the action of sodium amalgam on dicyclohexylphenylchloromethane. The ethane decomposed fairly rapidly at ordinary temperatures.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

CONDENSATION OF 3-PHENYL-2,4-THIAZOLIDIONE WITH AROMATIC ALDEHYDES[1]

BY KLARE S. MARKLEY[2] AND E. EMMET REID

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It has long been known that heterocyclic compounds containing the linkage —SCH_2CO— undergo condensation with aromatic aldehydes[3] and with substances like phthalic anhydride and nitrosodimethylaniline,[4] isatin,[5]

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[1] Presented in abstract before the Organic Division at the Columbus meeting, April, 1929.

[2] Part II of the Ph.D. dissertation of Klare S. Markley, June, 1929.

[3] Nencki, *Ber.*, **17**, 2277 (1884); Andreasch, *Monatsh.*, **8**, 407 (1887); Hann and Markley, *J. Wash. Acad. Sci.*, **16**, 169 (1926); Kingsbury and Markley, *ibid.*, **18**, 558 (1928).

[4] Kučera, *Monatsh.*, **35**, 137 (1914).

[5] Andreasch, *ibid.*, **38**, 135 (1917).