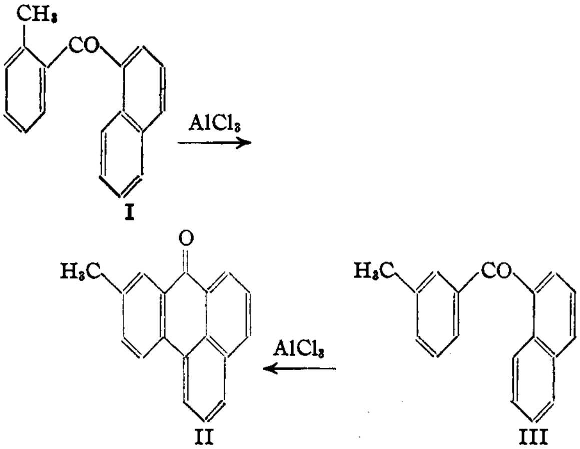
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conversion of Tolyl Naphthyl Ketones into Methylbenzanthrones

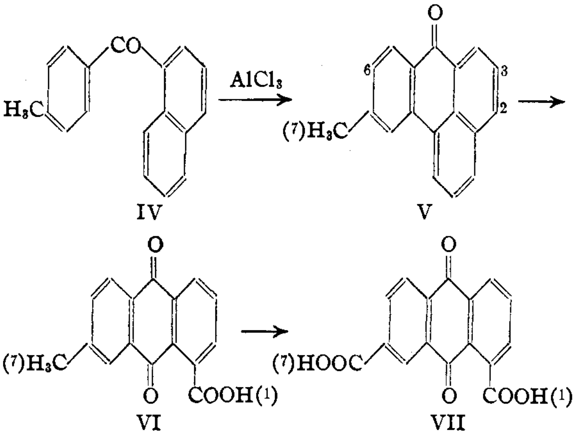
BY L. F. FIESER AND E. L. MARTIN

Among other instances of the migration of methyl groups in the course of the Scholl reaction reported by Mayer, Fleckenstein and Günther,[1] it was stated that both *o*-tolyl α-naphthyl ketone (I) and *m*-tolyl α-naphthyl ketone (III) yield the same (6)-methylbenzanthrone (II) on being heated with aluminum chloride. Scholl and Seer[2] had reported the reactions and established structure of the product from III by an independent synthesis of II, but had not recognized the identity of the substance obtained from the isomeric ketone, m. p. 64°, which they prepared from *o*-toluyl chloride and naphthalene and for which they assumed the structure I. In preparing a quantity of *o*-tolyl α-naphthyl ketone for a proposed study of the Elbs reaction we employed α-naphthylmagnesium bromide and *o*-tolunitrile and obtained a ketone, m. p. 52–53°, apparently different from that of Scholl and Seer, and since the observation cast some doubt on the reported rearrangement the matter was investigated further. Since a ketone having the melting point of the Scholl and Seer compound was obtained from *o*-tolylmagnesium bromide and β-naphthonitrile, it is probable that the purified product isolated by these investigators was *o*-tolyl β-naphthyl ketone. From the β-isomer we were unable to obtain a benzanthrone, while the pure α-isomer (I) was found to yield 6-methylbenzanthrone, II, which we also prepared from *m*-tolyl α-naphthyl ketone (III), synthesized by a method which establishes its structure. Although the original evidence was unsound, the conclusion of Mayer and co-workers is thus shown to be valid. It is probable that both earlier investigators employed the crude ketone mixture from the Friedel and Crafts reaction and that this contains a considerable proportion of the α-isomer (I) along with the substance actually isolated.



Samples of pure *m*-tolyl- and *p*-tolyl α-naphthyl ketone prepared by Grignard reactions corresponded in melting point and in their behavior with aluminum chloride to the descriptions of Scholl and Seer and of Mayer and co-workers. The corresponding β-isomers differ little in melting point but do not yield benzanthrones in the Scholl reaction.

The methylbenzanthrone obtained from pure *p*-tolyl α-naphthyl ketone (IV) corresponded to the earlier descriptions.[1,2] To test the assumption[1,2] that this is the 7-methyl derivative (V) and that no migration occurs in its formation, the substance was oxidized to a methylanthraquinone carboxylic acid and then to an anthraquinone dicarboxylic acid. The former substance yielded β-methylanthraquinone on decarboxylation, whence the original methyl group must be at the 2-, 3-, 6- or 7-position. Since 2- and 6-methylbenzanthrone are both known substances different from the compound in question, these positions are eliminated. The dicarboxylic acid could only be the 1,3- or the 1,7-derivative and on preparing the former substance[3] for comparison it was found to be different.



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(1) Mayer, Fleckenstein and Günther, *Ber.*, **63**, 1464 (1930).

(2) Scholl and Seer, *Ann.*, **394**, 111 (1912).

(3) Elbs and Günther, *Ber.*, **20**, 1364 (1887).

Therefore the oxidation products are the 1,7-derivatives VI and VII and the product of the Scholl reaction is 7-methylbenzanthrone (V). 6-Methylanthraquinone-1-carboxylic acid and anthraquinone-1,6-dicarboxylic acid were prepared for comparison from II.

Experimental Part

Preparation of the Ketones.—The components employed are indicated in Table I. The Grignard reagent was prepared under nitrogen from 3 g. of magnesium, 0.1 mole of the bromo compound and 120 cc. of dry ether, and to this was added a solution of 0.1 mole of the nitrile in 125 cc. of dry, thiophene-free benzene. A crystalline solid usually separated but when the ether was removed by slow evaporation in the nitrogen stream this dissolved. The reddish-brown benzene solution was refluxed for twenty-four hours and poured onto a mixture of water (100 cc.), ice (100 g.) and concentrated hydrochloric acid (30 cc.). The mixture was submitted to steam distillation for one hour both to remove the solvent and unreacted nitrile and to effect hydrolysis of the ketimine. The residual oil was taken up in ether, washed with sodium carbonate solution, and on vacuum distillation the ketone was obtained as a pale yellow oil which afforded a colorless, crystalline product when a fairly dilute solution in methyl alcohol was allowed to stand for some time. Further crystallization did not alter the melting points of the first crystallizates and the yields are reported for these products.

TABLE I

TOLYL NAPHTHYL KETONES

Ketone	Prepared from	Yield (pure) %	M. p., °C. Found	Lit.
o-Tolyl-α-naphthyl[a]	α-$C_{10}H_7MgBr$ + *o*-$CH_3C_6H_4CN$	57	52–53	
o-Tolyl-β-naphthyl	*o*-$CH_3C_6H_4MgBr$ + β-$C_{10}H_7CN$	53	63–64	64[2]
m-Tolyl-α-naphthyl	*m*-$CH_3C_6H_4MgBr$ + α-$C_{10}H_7COCl$	40	72–73	74–75[2]
m-Tolyl-β-naphthyl[b]	*m*-$CH_3C_6H_4MgBr$ + β-$C_{10}H_7CN$	55	76–77	
p-Tolyl-α-naphthyl	α-$C_{10}H_7MgBr$ + *p*-$CH_3C_6H_4CN$	65	83–84	85[2]
p-Tolyl-β-naphthyl[c]	*p*-$CH_3C_6H_4MgBr$ + β-$C_{10}H_7CN$	50	90–91	

[a,b,c] *Anal.* Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: (a) C, 87.97; H, 5.85; (b) C, 87.66; H. 5.56; (c) C, 87.66; H, 5.75.

The mother liquor often yielded 10–15% more material melting 2–3° low. The procedure was varied in some experiments by shaking the benzene solution with acetic acid (10 cc.), water (100 cc.) and ice (100 g.), discarding the water layer, and precipitating the ketimine hydrochloride as an oil by the addition of 100 cc. of concentrated hydrochloric acid. After decanting the liquor the oil was boiled with 200 cc. of water for one hour to effect hydrolysis, and the ketone was purified as above. The product was obtained in no better yield or purity than before and it seemed that the simpler procedure is preferable. In the experiment using β-naphthoyl chloride the Grignard reagent was added inversely to a solution of the chloride (0.1 mole) in 200 cc. of ether. The ketones were all obtained completely colorless, usually as needles, from methyl alcohol.

6-Methylbenzanthrone (II).—No difference was noted in the yield or quality of the material obtained from either *o*-tolyl α-naphthyl ketone or *m*-tolyl α-naphthyl ketone. When either ketone (3 g.) was heated with aluminum chloride (15 g.) at 150° the yield of pure product isolated was 0.5 g. (17%), but the yields were much improved by employing sodium aluminum chloride. To a melt prepared from 20 g. of aluminum chloride and 4 g. of sodium chloride 2.46 g. of either ketone was added and the temperature was raised from 90 to 150° in one and one-half hours and maintained at 150° for two hours. The red melt was stirred into ice and hydrochloric acid and the tarry product was extracted with acetic acid and precipitated with water and then crystallized to a constant melting point from alcohol; yield 1.4 g. (58%). The compound formed fine, bright yellow needles, m. p. 167–168°, in agreement with the literature.[1,2]

7-Methylbenzanthrone (V) was obtained from *p*-tolyl α-naphthyl ketone in 16–20% yield (pure) using aluminum chloride and in 50% yield with sodium aluminum chloride; fine, bright yellow needles, m. p. 158–159°.

6-Methyl- and 7-Methylanthraquinone-1-carboxylic Acid.—A solution of 1 g. of 6-methylbenzanthrone in 20 cc. of glacial acetic acid was prepared at 70° and treated slowly with 4 g. of chromic anhydride in 2 cc. of water diluted with 20 cc. of acetic acid, keeping the temperature at 60–70° by occasional cooling. Soon after the addition was complete the product was precipitated by adding water. The crude acid was dissolved in dilute ammonia solution, and after clarification with Norite the light yellow filtrate was acidified at the boiling point. On crystallization from dilute alcohol 6-methylanthraquinone-1-carboxylic acid (a) separated slowly as light yellow needles, m. p. 264–266°; yield 0.7 g. (64%). 7-Methylanthraquinone-1-carboxylic acid (b), obtained similarly from V in 55% yield, formed stout yellow needles, m. p. 310–312° from acetic acid. Mayer, *et al.*,[1] report 312–314°. The alkaline solutions of the acids are pale yellow, the vats are deep red.

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.15; H, 3.79. Found: (a) C, 72.20; H, 3.75; (b) C, 72.01; H, 3.82.

Each acid was decarboxylated in quinoline solution at 170° in the presence of Naturkupfer C, and the product was obtained by pouring the mixture onto water and adding hydrochloric acid. Crystallized from alcohol, the product in each case melted at 173–174° alone or when mixed with authentic β-methylanthraquinone; yield 90%.

Anthraquinone-1,6- and 1,7-Dicarboxylic Acids.—After heating 0.2 g. of 6-methylanthraquinone-1-carboxylic acid with 3 cc. of nitric acid, sp. gr. 1.1, in a sealed tube at 200–210° for five hours, there was obtained on cooling 0.21 g. of bright yellow needles of the 1,6-acid (a). This was purified by precipitation from a clarified ammonium hydroxide solution, by refluxing with a concentrated nitric acid (6 cc.)–water (1 cc.) mixture, which left the substance undissolved but less highly colored, and finally by crystallization from a large volume of alcohol; faintly yellow needles, m. p. 336–338°. Anthraquinone-1,7-dicarboxylic acid (b), similarly prepared and purified, formed light yellow, microscopic crystals, m. p. 346–348°. The alkaline solutions of the acids are nearly colorless, the vats are red.

Anal.[*] Calcd. for $C_{16}H_8O_6$: C, 64.84; H, 2.72. Found: (a) C, 64.90; H, 2.90; (b) C, 64.64; H, 2.73.

Anthraquinone-1,3-dicarboxylic Acid.—Phthalic[*] anhydride (7.4 g.) was condensed with *m*-xylene (25 cc.) by the addition of aluminum chloride (15 g.), heating the mixture on the steam-bath for one-half hour to complete the reaction. The keto acid precipitated from soda solution, yield 11.5 g. (91%), m. p. 130–133°, was heated with 55 cc. of concentrated sulfuric acid for one hour on the steam-bath, giving after one crystallization from alcohol 6.9 g. (63%) of 1,3-dimethylanthraquinone, m. p. 159–160°. For the oxidation 0.2 g. of material was heated with 3 cc. of nitric acid, sp. gr. 1.1, for six hours at 180–190°. The product formed pale yellow needles from dilute alcohol (0.15 g.). The substance decomposes at 320–325°.

Anal. Calcd. for $C_{16}H_8O_6$: C, 64.84; H, 2.72. Found: C, 64.60; H, 2.89.

Summary

On preparing the six possible tolyl naphthyl ketones by methods leaving no doubt as to their structures it was found that two of the isomers had been confused in the literature but that the previous conclusions regarding the formation of methylbenzanthrones by the action of aluminum chloride on the tolyl α-naphthyl ketones are substantiated by the results of experiments with the pure ketones and by more rigid evidence of the structure of one of the reaction products.

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The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. I. The Carbon–Hydrogen Bond in Methane and Methane-d_4

BY KIYOSHI MORIKAWA,[1] W. S. BENEDICT AND HUGH S. TAYLOR

In a preliminary communication[2] to THIS JOURNAL we have recorded the ready interaction of methane and deuterium at reduced nickel catalyst surfaces at temperatures of 184° and upward. At that time we suggested that the reaction must be determined in rate by the activated adsorption of methane and called attention to the fact that, if this were so, we have in the exchange reaction a more sensitive index of activated adsorption than is available in adsorption measurements of gases on catalytic surfaces. The evidence that we present in the following pages confirms these views and lays the foundations for a comprehensive program of research upon the activation of specific bonds in complex molecules, a central problem in the field of contact catalysis, that of specific activity.

We have studied the interaction of methane and deuterium, of methane-d_4 and hydrogen, of methane and methane-d_4 and of methane and deuterium oxide at surfaces of catalytic nickel through a range of temperatures. From the measurements of reaction velocity and the derived energy of activation of the processes we are able to show that the rate-determining step is to be ascribed to the activation of the C–H bond of the methane molecule. These studies represent an extension to saturated hydrocarbon molecules of the phenomenon of isotope exchange already demonstrated to occur with unsaturated hydrocarbon molecules by the researches of Farkas, Farkas and Rideal[3] and by Polanyi and his collaborators.[4] We shall show that our results with the saturated hydrocarbons are of material importance in view of the theories of the exchange reaction developed by the latter group of authors.[4b]

Experimental Details

Materials.—The deuterium gas employed was obtained by electrolysis of our purest heavy water d^{25}_{25} 1.1079 containing 0.5 *M* NaOD as electrolyte. It was freed from oxygen by passage over a glowing platinum wire and dried by passage through a dry-ice trap.

Methane was prepared catalytically from carbon monoxide and excess hydrogen over a nickel catalyst at 255°, the excess hydrogen being removed by passage repeatedly over granular copper oxide at 300° after which carbon dioxide and water vapor were removed by soda lime and a solid carbon dioxide trap. The product used was further purified by fractional condensation and evaporation.

Methane-d_4 was prepared in a similar manner from carbon monoxide and pure deuterium, care being exercised to remove all hydrogen from the reaction system by exhaustion and repeated flushing with deuterium gas. The product was a very pure methane of which 98% of the bonds were found by analysis to be C–D bonds.

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(1) Visiting Research Fellow of the South Manchuria Railway Co., Dairen, Japan.

(2) Morikawa, Benedict and Taylor, THIS JOURNAL, **57**, 592 (1935).

(3) Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (London), **A146**, 630 (1934).

(4) (a) Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663 (1934); (b) Horiuti and Polanyi, *ibid.*, **30**, 1164 (1934).