nium chloride by means of *n*-butyl alcohol. The two products were dried to constant weight in a vacuum desiccator.

In the calculations the slight amount of ammonia in the monochloroamine solutions, as shown by the difference in analysis for nitrogen and chlorine, was subtracted from the amount of ammonium chloride obtained, to give the actual amount of ammonia formed in the reaction. Percentage yields were calculated on the basis of the chlorine analysis of the monochloroamine. These results are shown in Table I.

Monochloroamine with Dialkyl Magnesium Solutions (without Separation from Halide Precipitate).—The Grignard reagent was prepared and analyzed. The dioxane-ether precipitating solution was added. A slight increase over the usual amount was used to allow for dilution due to the addition of the monochloroamine solution. The amount of di-*n*-butylmagnesium in this mixture was calculated. Monochloroamine was added in the same proportion as before. The products were isolated in the usual manner. The results are shown in Table I.

The Addition of Anhydrous Magnesium Iodide to Organomagnesium Compounds and the Reactions of the Resulting Mixtures with Monochloroamine.—The ether solution of the Grignard reagent, or of di-*n*-butylmagnesium, was prepared with a minimum volume of ether and to this was added the ether solution of magnesium iodide in the calculated amount, based upon the analysis for iodine. Analysis before and after the addition of the magnesium iodide showed that there was no loss in the active reagent. This solution was cooled to 0° and stirred for an hour after which the ether solution of monochloroamine was added in the usual manner. The results are shown in Table I.

Summary

1. The reactions of monochloroamine with di-*n*-butylmagnesium and with Grignard reagents prepared from the *n*-butyl halides have been compared. A maximum yield of *n*-butylamine of 97% was obtained with di-*n*-butylmagnesium at −60°.

2. The effect on this reaction of adding various amounts of anhydrous magnesium iodide to the di-*n*-butylmagnesium has been determined.

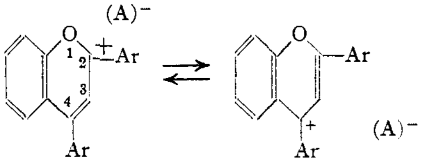
IOWA CITY, IOWA RECEIVED MARCH 31, 1941

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

Benzopyrylium Salts. III. Syntheses from Substituted Coumarins and Chromones

BY R. L. SHRINER AND ROBERT BRUCE MOFFETT

Previous studies of benzopyrylium salts[1] led to the suggestion that the carbon atoms 2, 3 and 4 in the heterocyclic ring represent a special case of the allylic three-carbon atom system and that these salts may tautomerize or resonate between the two structures I and II.



I II

(A = anion such as Cl^-, $FeCl_4^-$, ClO_4^-)

This viewpoint harmonized with the 2-carbonium salt structure proposed by Dilthey[2] and the 4-carbonium ion which Hill and Melhuish[3] pointed out must also be a possibility. Also, Löwenbein[4] had found that flavylium perchlorates undergo a coupling reaction with phenylmagnesium bromide, a reaction characteristic of allylic systems.[5]

Further evidence in favor of this viewpoint has now been obtained by demonstrating that the same benzopyrylium salt is obtainable from either a substituted coumarin or from a chromone by treatment with the appropriate Grignard reagent followed by reaction with an acid. The formation of flavylium salts by treatment of the carbinols obtained by the action of Grignard reagents on substituted coumarins is a well-known reaction introduced by Decker and Fellenberg[6] and used by Willstätter[7] for the synthesis of anthocyanidin salts. Heilbron and Zaki[8] prepared a 4-substituted benzopyrylium salt by the action of phenylmagnesium bromide on 2,3-dimethyl-7-methoxychromone but no comparison has been made of the salts obtained by these two different methods.

In the present work 3-phenyl-4-(*p*-tolyl)-6-

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[1] Shriner and Moffett, THIS JOURNAL, **62**, 2711 (1940).

[2] Dilthey, *J. prakt. Chem.*, **94**, 53 (1916); *ibid.*, **95**, 107 (1917); *Ber.*, **53**, 261 (1920); *J. prakt. Chem.*, **131**, 1 (1931); *ibid.*, **138**, 42 (1933); *Ber.*, **64**, 2082 (1931).

[3] Hill and Melhuish, *J. Chem. Soc.*, 1161 (1935); *Chem. Rev.*, **19**, 27 (1936).

[4] Löwenbein, *Ber.*, **57**, 1517 (1924); Löwenbein and Rosenbaum, *Ann.*, **448**, 223 (1926).

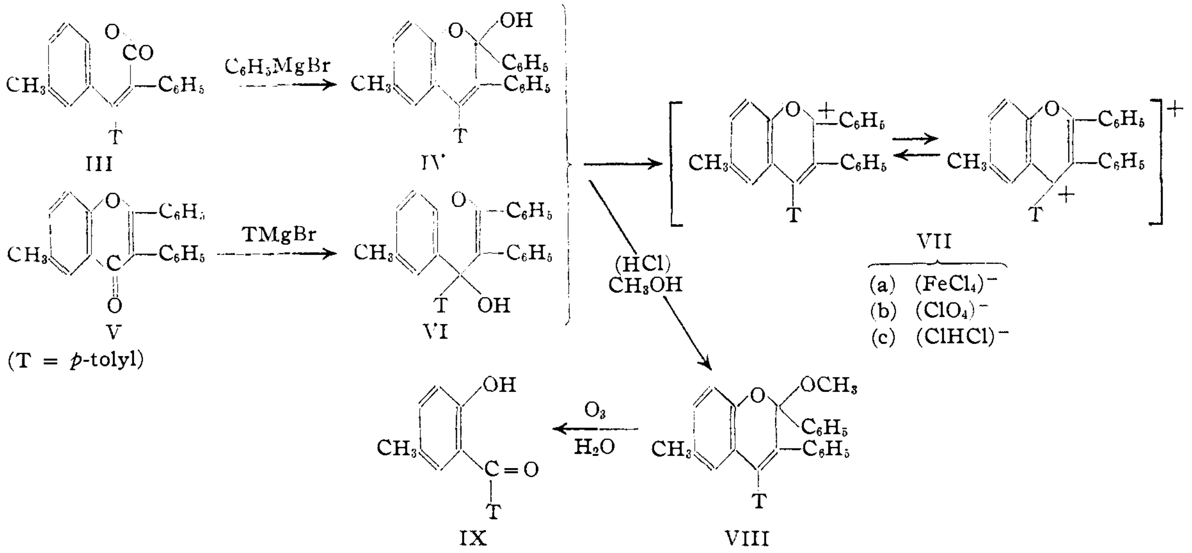
[5] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, Vol. I, p. 424.

[6] Decker and Fellenberg, *Ber.*, **40**, 3815 (1907); *Ann.*, **356**, 281 (1907).

[7] Willstätter and Schmidt, *Ber.*, **57**, 1945 (1924); Willstätter, Zechmeister and Kindler, *ibid.*, **57**, 1938 (1924).

[8] Heilbron and Zaki, *J. Chem. Soc.*, 1902 (1926).

CHART I



methylcoumarin (III) was treated with phenylmagnesium bromide (see Chart I). Decomposition of the reaction mixture with ammonium chloride solution yielded a carbinol (IV). Treatment of 2,3-diphenyl-6-methylchromone[9] (V) with p-tolylmagnesium bromide produced a carbinol (VI). The first carbinol (IV) melted with decomposition at 142–144° and the second one (VI) at 110–113°. Both were difficult to crystallize and to obtain pure. The carbinol (IV) is a hemiacetal and may be in equilibrium with the open chain substituted chalcone. Also, Ziegler, Fries and Sälzer[10] have shown that 2,3,4-triphenyl-6-methyl-1,4-benzopyran-4-ol is readily rearranged to the correspondingly substituted benzopyran-2-ol. In the present work it was also found that the low-melting carbinol (VI) could be converted to the higher melting carbinol (IV) by heating a ligroin (b. p. 90–120°) solution and fractional crystallization of the mixture.

Treatment of each of these carbinols separately with hydrogen chloride and ferric chloride yielded the flavylium ferrichloride (VIIa) which proved to be a homogeneous yellow crystalline salt. Exactly the same salt (VIIa) was obtained regardless of the carbinol used. Perchloric acid likewise reacted with each of the carbinols to produce identical flavylium perchlorates (VIIb). The production of the same salts (VII) from different carbinols (IV) and (VI) can only be accounted for on the basis of an allylic shift during the reaction.

When either of the carbinols was treated with methanol and a little hydrochloric acid, a single methoxy derivative (VIII) was obtained as colorless crystalline needles. Its structure is written as the 2-methoxy derivative (formula VIII) since ozonolysis produced the ketone (IX).

Attempts to prepare the flavylium chloride from the crude carbinols gave products which were difficult to purify. However, the methoxy derivative (VIII) was readily converted by hydrogen chloride to the flavylium chloride hydrochloride (formula VIIc), which analyzed correctly. This formation of chloride–hydrochlorides has been noted by other investigators[11] and is characteristic of flavylium salts when no free hydroxyl groups are present in any of the rings. During the present investigations a number of such compounds have been obtained and studies are now under way to determine the nature of such salts. It seems probable that the extra mole of hydrogen chloride may be involved in the anion but this point requires further proof.

Although the properties and reactions of the benzopyrylium salts described up to the present time[1,3,4] seem to require that the structures I and II be readily interconvertible, it should be pointed out that by properly choosing the substituents on carbon atoms 2 and 4, it may be possible to isolate both forms and demonstrate the interconversion. So far, the aryl substituents used have been phenyl, p-tolyl and p-bromophenyl. In

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(9) Wittig, Bangert and Richter, *Ann.*, **446**, 155 (1925).

(10) Ziegler, Fries and Sälzer, *ibid.*, **448**, 249 (1926).

(11) Decker and Fellenberg, *ibid.*, **346**, 1 (1909); Löwenbein and Rosenbaum, *ibid.*, **448**, 223 (1926); Hill, *J. Chem. Soc.*, 806 (1936).

each case only one salt has been obtained although three different methods of synthesis have been employed: *viz.*, (1) the action of the Grignard reagent on coumarin, (2) the action of the Grignard reagent on a chromone or (3) the condensation of salicylaldehyde with an ω-substituted acetophenone.[12]

Of particular interest in connection with the present work is the observation of Löwenbein[4] that 2,4-diphenyl-Δ^2- and -Δ^3-chromenes are oxidized by ferric chloride in acetic anhydride to the same 4-phenylflavylium salt. This reaction parallels the oxidation of the leuco base of a triphenylmethane dye to the color base and subsequent formation of the dye which is a salt. The

$$Ar_3CH \longrightarrow Ar_3C{-}OH \longrightarrow Ar_3C^+X^-$$

Δ^2-chromene contains a reactive hydrogen atom on the 4-carbon atom and the Δ^3-chromene has one on the 2-carbon atom. Hence, the 2- and 4-carbinol acetates are probable intermediates which form identical flavylium salts by an allylic shift. In the substituted triphenylmethane series this salt may tautomerize to a quinoid form. The anthocyanidin chlorides, which are polyhydroxy (and methoxy) flavylium salts also contain the allylic system in the heterocyclic ring and furthermore may tautomerize to a quinoid structure in a manner similar to that shown by the hydroxyl derivatives of triphenyl carbinol which undergo conversion to the aurin type dyes.

Experimental

6-Methyl-2,3-diphenylchromone (V).—A Fries rearrangement was carried out on *p*-tolyl phenylacetate and a 68% yield of 2-hydroxy-5-methyl-α-phenylacetophenone was obtained. It melted at 63.5–65° which checked the value reported by von Auwers.[13] Condensation of this ketone with benzoic anhydride and sodium benzoate, according to the procedure described by Wittig, Bangert and Richter,[9] gave a 70% yield of 6-methyl-2,3-diphenylchromone melting at 170.5–172°.

2,3-Diphenyl-4-(*p*-tolyl)-6-methyl-1,4-benzopyran-4-ol (VI).—The reaction between the chromone (V) and *p*-tolylmagnesium bromide was carried out at different temperatures and with different ratios of reactants. The procedure used to avoid rearrangements and to isolate the carbinol (VI) consisted in adding a solution of 12.5 g. of the chromone in 100 cc. of dry benzene to 0.05 mole of *p*-tolylmagnesium bromide in 50 cc. of absolute ether. The mixture was stirred at room temperature for two hours and then poured on a mixture of 500 g. of ice and water in which 50 g. of ammonium chloride had been dissolved. The benzene–ether layer was separated, dried with sodium sulfate and the solvents evaporated by suction. The residue was triturated with small amounts of petroleum ether repeatedly and finally a powdery compound was obtained. It was dissolved in a larger volume of petroleum ether at room temperature and cooled in a dry-ice–acetone mixture. A white amorphous powder was obtained which melted from 110–113° and analyzed for the carbinol (VI).

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 86.28; H, 6.18.

In order to obtain a higher yield of the product, an excess of the Grignard reagent (0.12 mole) may be used. A number of procedures were tried in an effort to purify this carbinol. If it is heated in a solvent such as ligroin (b. p. 90–120°) rearrangement takes place and fractional crystallization from ligroin then yields the carbinol (IV) melting at 142–144°. The use of an excess of the Grignard reagent gave the best yield of the carbinol (VI) (73% as judged from the yield of the perchlorate (VIIb)) and no compounds corresponding to 1,4-addition could be found. When only one equivalent of the *p*-tolylmagnesium bromide was used and the reaction mixture was not heated, a lower yield of the carbinol resulted and some unchanged chromone was present in the petroleum ether mother liquors from the above purification.

6-Methyl-3-phenyl-4-(*p*-tolyl)-flavylium Ferrichloride (VIIa).—The carbinol (VI) was dissolved in absolute ether, and dry hydrogen chloride was passed in. A yellow precipitate formed which redissolved as more hydrogen chloride was passed in. An excess of ferric chloride in absolute ether was added to this solution and the mixture was diluted with a large excess of absolute ether. The yellow crystalline ferrichloride separated and was removed by filtration. It was washed with absolute ether, and recrystallized from glacial acetic acid giving yellow crystals which melted at 183–184.5°.

Anal. Calcd. for $C_{29}H_{23}OFeCl_4$: C, 59.52; H, 3.96; Cl, 24.23; Fe, 9.54. Found: C, 59.37; H, 4.07; Cl, 24.15; Fe, 9.73.

6-Methyl-3-phenyl-4-(*p*-tolyl)-flavylium Perchlorate (VIIb).—The entire crude carbinol (VI) from one preparation was dissolved in absolute ether and 4.02 g. (0.04 mole) of 72% perchloric acid dissolved in 6 cc. of cold acetic anhydride was added. The perchlorate separated as crystals and was removed by filtration. It was washed with absolute ether and recrystallized from about 50 cc. of glacial acetic acid. The perchlorate weighed 14.3 g. (73.5%) and consisted of bright yellow crystals which melted at 235.5–238.5° with decomposition. Repetition of the procedure with the purified carbinol gave the same product.

Anal. Calcd. for $C_{29}H_{23}O_5Cl$: C, 71.53; H, 4.76. Found: C, 71.00; H, 4.96.

2-Methoxy-2,3-diphenyl-4-(*p*-tolyl)-6-methyl-1,2-benzopyran.—The carbinol (VI) was dissolved in 200 cc. of warm methanol. A few drops of hydrochloric acid was added which caused the immediate precipitation of a gummy solid. This was dissolved in the mother liquor by refluxing for several hours. By cooling overnight in the refrigerator the methoxy derivative was obtained in crystalline form. After recrystallization from methanol with the aid of Darco the methoxy derivative weighed 10.7 g.

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[12] Pratt and Robinson, *J. Chem. Soc.*, **121**, 1577 (1922); Shriner and Moffett, This Journal, **61**, 1474 (1939).

[13] Von Auwers, *Ber.*, **53**, 2251 (1920).

(64% of theoretical, based on the 6-methyl-2,3-diphenylchromone) and consisted of white crystals melting at 126–127°.

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.16; H, 6.44.

6-Methyl-3-phenyl-4-(*p*-tolyl)-flavylium Chloride Hydrochloride.—Ten grams of 2-methoxy-2,3-diphenyl-4-(*p*-tolyl)-6-methyl-1,2-benzopyran was dissolved in 75 cc. of absolute ether, and dry hydrogen chloride passed in. A gummy precipitate formed at first which soon crystallized. When no more precipitate formed the hydrogen chloride was stopped, the crystals removed by filtration and washed with absolute ether. By diluting the filtrate and washings with absolute ether an additional yield of crystals was obtained. The total yield was 10.5 g. (91.2%) of a yellow crystalline salt melting at 183–191° with decomposition.

Anal. Calcd. for $C_{29}H_{24}OCl_2$: Cl, 15.44. Found: Cl, 15.62.

2-Hydroxy-4′,5-dimethylbenzophenone.—In a 500 cc. three-necked round-bottomed flask fitted with a stirrer and reflux condenser with a gas trap, was placed 43.3 g. (0.4 mole) of anhydrous aluminum chloride and 45.2 g. (0.2 mole) of *p*-tolyl *p*-toluate (prepared from *p*-toluyl chloride and *p*-cresol in pyridine solution) dissolved in 150 cc. of dry carbon disulfide. The mixture was refluxed on a water-bath with stirring for forty-five minutes. The carbon disulfide was then removed by distillation and the mixture was heated on a boiling water-bath for two and one-fourth hours. By this time the mixture had become very viscous and the water-bath was replaced by an oil-bath and heated at 120° for three and one-fourth hours. After decomposition with ice and hydrochloric acid, the mixture was warmed on a steam cone. The oily layer crystallized on cooling. The ketone was recrystallized from methanol with the aid of Darco. The yield was 37 g. (82%) of yellow crystals melting at 89.5–90°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.63; H, 6.24. Found: C, 79.43; H, 6.44.

6-Methyl-3-phenyl-4-(*p*-tolyl)-coumarin (III).—A mixture of 50 g. (0.32 mole) of sodium phenylacetate (fused at 200° and powdered) and 20.9 g. (0.13 mole) of phenylacetyl chloride was heated in a 200 cc. round-bottomed flask in an oil-bath at 150° for one-half hour. To this mixture was added 13.5 g. (0.06 mole) of the above 2-hydroxy-4′,5-dimethylbenzophenone and the mixture heated with stirring in an oil-bath at 180–190° for three and one-half hours and then at 190–200° for three and one-fourth hours.

After cooling, 100 cc. of water was added and the mixture heated to boiling and placed in the refrigerator. The oily layer was separated from the water and an equal volume of alcohol added. The crystalline coumarin which separated was removed by filtration, washed with alcohol, and recrystallized from alcohol. A yield of 6.6 g. (33.8%) of light tan colored crystals melting at 181.5–183.5° was obtained. Repeated crystallization from alcohol yielded a pure white product melting at 183.5–184.5°.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.62; H, 5.56. Found: C, 84.73; H, 5.78.

Action of Phenylmagnesium Bromide on 6-Methyl-3-phenyl-4-(*p*-tolyl)-coumarin.—Phenylmagnesium bromide was prepared from 0.6 g. (0.025 g. atom) of magnesium, 3.9 g. (0.025 mole) of bromobenzene, and 25 cc. of dry ether, in a 200-cc. round-bottomed three-necked flask fitted with a stirrer, dropping funnel, and condenser protected by a calcium chloride tube. To this solution was added rapidly 6.5 g. (0.02 mole) of 6-methyl-3-phenyl-4-(*p*-tolyl)-coumarin dissolved in 50 cc. of dry benzene. The mixture was stirred for one hour and, after standing for two hours, was poured into 400 cc. of water and ice containing 35 g. of ammonium chloride. The benzene–ether layer was separated, dried, and the solvents evaporated by suction leaving the carbinol as a noncrystalline viscous mass. It was triturated with warm petroleum ether which was decanted. The powdery residue was recrystallized twice from ligroin and colorless crystals of the carbinol (IV) obtained which melted with decomposition at 142–144°. It was dried in a vacuum desiccator containing paraffin wax.

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 85.79; H, 6.02.

If the coumarin (IV) is treated with an excess of the Grignard reagent some of the product which would correspond to the addition of two moles of phenylmagnesium bromide could be isolated by fractional crystallization from ligroin. It melted at 141.5–143° but a mixed melting point determination with the carbinol (IV) gave a decided lowering to 120–126°. No flavylium salts could be made from this compound whose analysis corresponded to α,-β-diphenyl-β-(*p*-tolyl)-β-(2-hydroxy-5-methylphenyl)-propiophenone.

Anal. Calcd. for $C_{35}H_{30}O_2$: C, 87.11; H, 6.27. Found: C, 87.16; H, 6.47.

A sample of this compound was heated in an oil-bath at 140–150° for two hours. The glassy solid was recrystallized from ligroin. Colorless needles melting from 185–188° were obtained whose analysis corresponded to the cyclized dehydration product, 2,3,4-triphenyl-4-(*p*-tolyl)-6-methyl-1,4-benzopyran.

Anal. Calcd. for $C_{35}H_{28}O$: C, 90.49; H, 6.07. Found: C, 90.54; H, 6.34.

The yellow perchlorate prepared from carbinol IV by the procedure described above melted at 236–238° alone and when mixed with the perchlorate from VI. The ferrichloride from carbinol IV melted at 183.5–184.5° alone and when mixed with that from the carbinol VI. Likewise the methoxy derivative prepared from carbinol IV by the method described above melted at 127–128° and this melting point was not depressed by the sample prepared from the carbinol VI.

Ozonization of **2-Methoxy-2,3-diphenyl-4-(*p*-tolyl)-6-methyl-1,2-benzopyran.**—Ozonized oxygen (6.4% ozone) was passed at the rate of 250 cc. per minute into a solution of 9 g. of 2-methoxy-2,3-diphenyl-4-(*p*-tolyl)-6-methyl-1,2-benzopyran dissolved in 50 cc. of carbon tetrachloride. From time to time 0.1 cc. samples were withdrawn and tested by adding 0.5 cc. of concentrated hydrochloric acid and three drops of ferric chloride solution in concentrated hydrochloric acid. A yellow precipitate indicated the flavylium compound was not yet all destroyed. After two and one-half hours only a slight test was obtained, the ozone was stopped and 50 cc. of water was added with thorough shaking.

The carbon tetrachloride layer was separated and the solvent was removed by distillation at room temperature under reduced pressure. The gummy residue was dissolved in hot alcohol and cooled. By diluting with more alcohol a gummy precipitate formed. This was removed and the solution concentrated and allowed to stand in the refrigerator. After standing several weeks about 0.5 g. of needles of 2-hydroxy-4′,5-dimethylbenzophenone formed, which after recrystallization from alcohol melted at 88–90° and a mixed melting point with a known sample prepared as described above showed no depression. No other definite products could be isolated from the mother liquor.

Summary

Treatment of 2-phenyl-4-*p*-tolyl-6-methylcoumarin with phenylmagnesium bromide yielded a substituted pyranol-2 which was converted to 6-methyl-3-phenyl-4-(*p*-tolyl)-flavylium perchlorate, ferrichloride and chloride-hydrochloride. These same salts were also obtained from 2,3-diphenyl-4-(*p*-tolyl)-6-methyl-1,4-benzopyran-4-ol which was synthesized by the reaction between *p*-tolylmagnesium bromide and 6-methyl-2,3-diphenylchromone.

This formation of identical flavylium salts from a pyranol-2 and a pyranol-4 constitutes additional evidence in favor of the viewpoint that the flavylium salts contain a mobile allylic system.

URBANA, ILLINOIS RECEIVED MARCH 21, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

The Preparation and the Vapor Pressures of Cyclobutene and Cyclobutane*

BY G. B. HEISIG

Cyclobutene and cyclobutane have been prepared by the following series of reactions: (1) cyclobutanedicarboxylic ethyl ester from trimethylene bromide, ethyl malonate and sodium ethylate by the Perkin reaction, yield 25%[1]; (2) cyclobutane dicarboxylic acid from the ester, yield 25%[2]; (3) cyclobutane carboxylic acid by the decarboxylization of the dicarboxylic acid, yield 92%[3]; (4) acid chloride of the monocarboxylic acid by treatment with thionyl chloride, yield 84.7%[4]; (5) acid amide by the action of ammonia, yield 79%[2]; (6) cyclobutylamine by the Hoffman rearrangement of the acid amide, 22%[2]; (7) trimethylcyclobutylammonium iodide, yield 85%[5]; (8) trimethylcyclobutylammonium hydroxide, degradation to cyclobutene and butadiene, bromination, removal of the butadiene as tetramethyldiaminobutene, and distillation of the 1,2-dibromocyclobutene, yield 48%[5]; (9) cyclobutene, yield 85%[5]; (10) cyclobutane 100%.[5]

The small over-all yield (9.9%) is due largely to the low yields of cyclobutane dicarboxylic ester and to the difficulty in obtaining the amine from cyclobutane carboxylic acid.

Efforts to improve the yield of the dicarboxylic ester by changing the rate of the addition of the reagents, the temperature, the length of time of standing after mixing the reagents, and the rate of agitation were unsuccessful. It was found simpler to saponify the malonic and cyclobutyl dicarboxylic ethyl esters and to separate the malonic and cyclobutyl dicarboxylic acids by precipitating barium malonate according to the method of Sugden and Wilkens than to follow the directions of Perkin. The yield (23%) of pure acid was eventually the same in either case.[6]

A six-fold increase in the yield of amine from the monocarboxylic acid was obtained by carrying out a modified Curtius rearrangement according to the general method described by von Braun and modified by Oesterlin.[7]

To 28.4 g. of the monocarboxylic acid (0.284 mole) in a 500-cc. distilling flask were added 200 cc. of chloroform, 50 cc. of concd. sulfuric acid, and solid sodium azide (0.31 mole) in such portions as to maintain the mixture at 40–50°. After standing for two days at room temperature, water was added, and the aqueous layer was boiled to remove the chloroform. An aqueous solution containing 160 g. of potassium hydroxide was then added to render the solution alkaline, and the amine was distilled into 50 cc. of concd. hydrochloric acid. On evaporating the concentrated

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* Original manuscript received February 16, 1939.

[1] Perkin, *J. Chem. Soc.*, **51**, 1–28 (1887).

[2] Böeseken, *Rec. trav. chim.*, **37**, 261 (1919).

[3] Zelinsky and Cutt, *Ber.*, **40**, 4744 (1907).

[4] Perkin and Sinclair, *J. Chem. Soc.*, **61**, 41 (1892).

[5] Willstätter and Bruce, *Ber.*, **40**, 3979 (1907).

[6] Sugden and Wilkens, *J. Chem. Soc.*, 146 (1927).

[7] Von Braun, *Ann.*, **490**, 125 (1931); Oesterlin, *Angew. Chem.*, **45**, 536 (1932).