sidered to behave as a sphere (so far as contacts in directions away from the carbon atom are concerned). This point of view has been especially emphasized by Mack[9] in connection with his interesting work on the packing of organic molecules. In metaldehyde, assuming rotation of methyl groups, the hydrogen–hydrogen distances corresponding to the methyl–methyl contacts mentioned above are 2.16 Å. (two), 2.15 Å. (four), and 2.11 Å. (two), giving for hydrogen the packing radius 1.07 ± 0.01 Å.

There may also be contact between oxygen and hydrogen atoms. Each oxygen atom is 2.68 Å. from two hydrogen atoms attached to ring carbons of the molecule below, and 2.70 Å. from a hydrogen atom in an adjacent column. These distances correspond to a packing radius for oxygen of 1.6 Å., which is somewhat larger than the ionic crystal radius 1.40 Å.

It is interesting to note that metaldehyde, like paraldehyde, contains no aldehyde groups, the oxygen atoms being ethereal in type.

We are indebted to Dr. S. Weinbaum for much assistance in the course of this investigation.

Summary

The tetragonal crystal metaldehyde is shown by x-ray examination to have a body-centered unit of structure with $a_0 = 10.40$ Å. and $c_0 = 4.11$ Å., containing two molecules of the tetramer, $(CH_3CHO)_4$. The atomic arrangement involves all atoms in general positions of the space group C_4^5–I_4, with the following parameter values: oxygen, $x = 0.074$, $y = 0.140$, $z = -0.163$; ring carbon, $x_1 = 0.151, y_1 = 0.047, z_1 = 0.000$; methyl carbon, $x_2 = 0.293$, $y_2 = 0.090$, $z_2 = 0.000$. The molecule contains an eight-membered –C–O–C– ring, with the carbon–oxygen distance 1.43 ± 0.03 Å., and methyl groups attached to ring carbon atoms, with the carbon–carbon distance 1.54 ± 0.03 Å. The bond angles of oxygen and carbon have the value 109.5 ± 3°. A discussion of the packing of the molecules and of the packing radii of the methyl group and hydrogen atom is given.

PASADENA, CALIF.
GENEVA, N. Y. RECEIVED MAY 11, 1936

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[9] E. Mack, Jr., THIS JOURNAL, **54**, 2141 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE B. F. GOODRICH COMPANY]

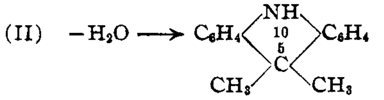
The Preparation of Acridanes by the Grignard Reaction

BY W. L. SEMON AND DAVID CRAIG

In previous publications[1a] *o*-*t*-butyldiphenylamine (III) has been identified as one of the two main products from the reaction of methylmagnesium iodide with methyl N-phenylanthranilate (I). The other product[1b] is shown here to be 5,5-dimethylacridane (IV) formed as indicated in reactions 1 and 3 by the dehydration of *o*-anilinophenyldimethylcarbinol (II).

$$C_6H_5\text{—}NH\text{—}C_6H_4\text{-}o\text{—}CO\text{—}OCH_3\ (I) + CH_3MgI \longrightarrow C_6H_5\text{—}NH\text{—}C_6H_4\text{-}o\text{—}C(OH)(CH_3)_2 \quad (II) \quad (1)$$

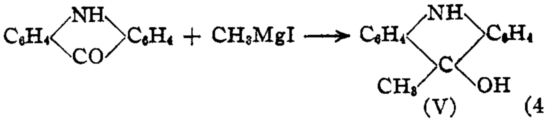
$$(II) + CH_3MgI \longrightarrow C_6H_5\text{—}NH\text{—}C_6H_4\text{-}o\text{—}C(CH_3)_3 \quad (III) \quad (2)$$



(IV) (3)

$$(II)\ -H_2O \longrightarrow C_6H_4 \langle {}^{NH}_{C(CH_3)_2} \rangle C_6H_4 \quad (IV) \quad (3)$$

The acridane (IV) has not previously been described and identified although some may have been contained in the material isolated following the action of sodium on commercial acridine.[2] The 5,5-diphenylacridane[3] and certain amino derivatives of acridane[4] have been prepared by reactions similar to the ones used here. While this method of formation is strong evidence for the accuracy of the formula assigned to IV, it is not beyond the realm of possibility that the product might have been *o*-isopropenyldiphenylamine. A more conclusive proof for the presence of an *o*,*o*′-carbon bridge was found in the synthesis of IV from compounds such as acridone or 5-methylacridine already containing the heterocyclic nucleus. This was accomplished by reactions 4 and 6



(V) (4)

$$C_6H_4 \langle {}^{NH}_{CO} \rangle C_6H_4 + CH_3MgI \longrightarrow C_6H_4 \langle {}^{NH}_{C(CH_3)(OH)} \rangle C_6H_4 \quad (V) \quad (4)$$

$$V + CH_3MgI \longrightarrow IV$$

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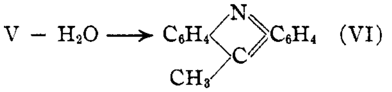
[1] (a) Craig, THIS JOURNAL, **57**, 195 (1935); (b) Semon, British Patent 405,797, Jan. 30, 1933, and French Patent 750,474, May 29, 1933.

[2] Bergmann and Blum-Bergmann, *Ber.*, **63**, 759 (1930).

[3] (a) Baeyer and Villiger, *ibid.*, **37**, 3191 (1904); (b) Gilman, THIS JOURNAL, **51**, 2260 (1929); (c) Kehrmann, and Tschui, *Helv. Chim. Acta*, **8**, 28 (1925).

[4] Goldstein and others, *ibid.*, **11**, 486 (1928), and previous papers especially *ibid.*, **11**, 478 (1928).



$$\mathrm{V - H_2O \longrightarrow C_6H_4}\left\langle{\mathrm{N} \atop \mathrm{C{-}CH_3}}\right\rangle\mathrm{C_6H_4}\ \mathrm{(VI)} \qquad (5)$$

$$\mathrm{VI + CH_3MgI \longrightarrow IV} \qquad (6)$$

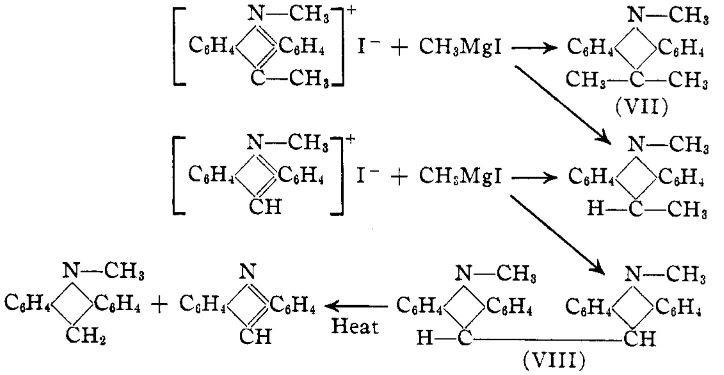
In some respects reaction 4 is similar to reaction 2 and might indicate the direct replacement of oxygen by Grignard reagent;[5] however, a two-stage reaction such as the 1,4-addition of methylmagnesium iodide to an unsaturated intermediate is not precluded[6] as a means for explaining the formation of III, or of IV from reaction 6.

Higher homologs of IV have been prepared by these same reactions. Thus ethylmagnesium bromide reacts with I to yield an oil analyzing satisfactorily for *o*-anilinophenyldiethylcarbinol. On dehydration there is obtained 5,5-diethylacridane and an isomer, possibly *o*-pentenyldiphenylamine. The formation of *o*-*t*-heptyldiphenylamine was not observed. The isolation of the two isomers emphasized the desirability for preparing the acridane by a reaction similar to reaction 4. Both the 5,5-diethylacridane and the 5,5-di-*n*-butylacridane were thus prepared from caridone and the appropriate alkylmagnesium halides.

In all of the cases discussed so far the alkylmagnesium halide has reacted with =NH or -N= to form N-magnesium halides. These have been hydrolyzed to the corresponding NH compounds as is usual in the process of working up such reaction mixtures.[7]

Where the nitrogen has an alkyl group attached as in the 5-alkylacridinium salts, the reaction with alkylmagnesium halide becomes more complex. Freund and Bode[8] reported 5,5-diethyl-10-methylacridane formed by the reaction of 5-ethylacridine methiodide with ethylmagnesium bromide and of 5,10-di-methylacridane by a similar reaction. Further, Stevens, *et al.*,[9] reported 5,5,10-trimethylacridane as a product from the reaction of methylmagnesium iodide with 5-methylacridine methiodide or with 5-cyano-5,10-dimethylacridane. However, the compounds reported were not well characterized and that described as trimethylacridane is probably, in the light of the present work, a mixture of this compound (m. p. 100–102°) and of 5,10-dimethylacridane (m. p. 140–141°). Freund and Bode[8a] failed to mention the formation of acridine from the reaction of methylmagnesium iodide and acridine methiodide and did not record the isolation of any high melting compound. We have subsequently isolated such a material and assigned formula VIII as it is probably the N,N′-dimethyl homolog of diacridane. The melting point of this compound, due to decomposition, varied with the rate of heating and the product of pyrolysis contained acridine and 10-methylacridane, thus behaving in a manner quite similar to the unsubstituted diacridane.[10]

Reaction 7 accounts for the products obtained when acridine methiodide and 5-methylacridine methiodide were treated with methylmagnesium iodide.



(7)

The further observation that the original acridine is reformed when the corresponding methiodide is treated with Grignard reagent indicates the reversible character of the formation of acridinium salts; thus the consumption of alkyl halide by some reagent such as the Grignard favors the decomposition and explains the formation of the ethane which is evolved as a gas in the course of the reaction.

The low yields and many products observed from the reaction of acridinium salts and Grignard reagent indicate that the products may not be formed in a single reaction but rather in a series of concurrent ones. If we generalize in re-

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(5) (a) See footnote 11, Ref. 1; (b) Maxim and Mavrodineanu, *Bull. soc. chim.*, [5] **2**, 591 (1935); (c) Aston, Ailman, Scheuermann and Koch, THIS JOURNAL, **56**, 1164 (1934); (d) Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

(6) Gilman, Kirby and Kinney, THIS JOURNAL **51**, 2252 (1929); Hoffman, Farlow and Fuson, *ibid.*, **55**, 2000 (1933).

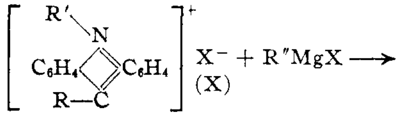
(7) For the formation of additive compounds of Grignard reagents with acridines, see Senier, Austin and Clarke, *J. Chem. Soc.*, **87**, 1469 (1905).

(8) (a) Freund and Bode, *Ber.*, **42**, 1746–1766 (1909); (b) see also Richter–Anschütz, "Chemie der Kohlenstoffverbindungen," Akademische Verlagsgesellschaft, Leipzig, 1931, Vol. III, p. 262.

(9) Stevens, *et al.*, *J. Chem. Soc.*, 2568–2572 (1931).

(10) Lehmstedt and Hundertmark, *Ber.*, **63**, 1239 (1930).

gard to a reaction such as reaction 8, it may be seen that the Grignard reagent may add in two


(8)

different ways in a 1,4-manner and in a larger number of ways if the less likely 1,2-addition is to be considered. The MgX portion may therefore be attached through N or through C. Where the attachment is to N there should be formed 5,5,10-trisubstituted acridane; where the attachment is to C there is formation of a new more complex Grignard reagent along with generation of alkyl halide which may occur in at least two ways. Further, the various Grignards now present may react with the alkyl halides and unsaturates to give a multiplicity of products which may account for the evolution of hydrocarbon noted. Specifically if the C attached MgX derivative reacts with X there is formed a complex salt which gives rise to a diacridane derivative of the type VIII already mentioned. Further, since acridines may be liberated from the acridinium salts by Grignard reagents as previously mentioned the possibility of these reacting further should not be overlooked. Pseudo-salt formation as an alternate for reaction 8 explains all of the products so far isolated but does not predict quite as many products in the case of higher homologs. The extent to which the formation of reduction products was due to unreacted magnesium was not determined.

Properties of 5,5-Dimethylacridane.—5,5-Dimethylacridane (IV) shows the typical reactions of a diarylamine. It dissolves readily in concentrated sulfuric acid and less readily in concentrated hydrochloric acid to form colorless solutions from which the free base precipitates on dilution with water. It forms N-acetyl, N-phenyl, N-methyl and N-metallic derivatives, showing the presence of a secondary amino group. One interesting reaction that indicates its similarity to many other hydrocarbon substituted diarylamines is the formation of 5-methylacridine by heating with hydrochloric acid, an essential reversal of the reaction by which it is formed from methylmagnesium iodide and 5-methylacridine. This reaction also occurs on refluxing IV with its N-sodium salt. The absence of an unsaturated side chain in the molecule is shown by the remarkable stability of IV on prolonged refluxing with aqueous potassium permanganate. 5,5-Dimethylacridane in a manner entirely similar to other diarylamines readily forms fairly stable yellow double compounds with acridine and 5-methylacridine.[11]

Experimental Part

5,5-Dimethylacridane (IV).—This compound prepared as previously described[1a] was reported as melting at 122–124°. After further recrystallization it was found to melt at 125–126°. Addition of 17 g. (0.088 mole) of 5-methylacridine to a solution of 0.3 mole of methylmagnesium iodide in 100 cc. of *n*-butyl ether at 100° produced no apparent reaction. When the mixture was heated to boiling, a vigorous reaction set in. After refluxing for thirty minutes the mixture was poured into ice water containing 30 cc. of glacial acetic acid. A solid precipitated which proved to be 5-methylacridine hydroiodide, yield 11.5 g. The butyl ether layer was separated, dried and upon distillation gave 3.5 g. of a product boiling at 155° at 1 mm. Recrystallization gave 2.5 g. of pure 5,5-dimethylacridane of the same melting point as the material prepared from methyl N-phenylanthranilate. This compound was also prepared by adding 18 g. (0.092 mole) of acridone to 0.3 mole of methylmagnesium iodide in di-*n*-butyl ether. Reaction began at 80° but, due to the insolubility of the acridone, it was not complete even after refluxing for thirty minutes. There were isolated from the crude reaction product, 6 g. of 5-methylacridine and 2.5 g. of 5,5-dimethylacridane or yields of 44 and 17%, respectively, of these compounds based upon the unrecovered acridone (14 g.).

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.07; H, 7.23; N, 6.70. Found: C, 86.0, 86.3; H, 7.28, 7.29; N, 6.96, 6.80.

The acetyl derivative was prepared by reaction of IV with acetyl chloride and crystallization from hexane. It melted at 153–154°. The benzoyl derivative was prepared by reaction with benzoyl chloride and, when crystallized from *o*-dichlorobenzene, melted at 294–297°.

5,5-Dimethylacridane is easily soluble in concentrated sulfuric acid from which it is precipitated by the addition of water. This property is useful for separating IV from other compounds which may be either less soluble in concentrated acid, or soluble and more strongly basic so that soluble, stable salts remain unhydrolyzed on dilution. 5,5-Dimethylacridane dissolves less readily in concentrated hydrochloric acid. A solid hydrochloride is not formed under these conditions. The free base precipitates on the addition of water. The solutions both in sulfuric and in hydrochloric acid are colorless, thereby distinguishing the compound from an acridine. The reaction of IV with iodobenzene according to Goldberg's[12] method gave an N-phenyl derivative, m. p. 123°, after crystallization from alcohol. The mixed melting point of this derivative and of the parent compound was lower than either. 5,5-Dimethylacridane reacted with sodium or sodamide much like diphenylamine and formed the N-sodium derivative.

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[11] Blum, *Ber.*, **62**, 891 (1929), described the corresponding double compounds of diphenylamine with these acridines as well as the double compound of 5-methylacridine with 5-methylacridane.

[12] Goldberg, *ibid.*, **40**, 4541 (1907).

Forty grams of 5,5-dimethylacridane and 0.5 g. of sodamide were heated gently until the evolution of ammonia was complete. The temperature was then raised to the refluxing point and maintained for forty-five minutes. A combustible gas was evolved slowly. The product was cooled and shaken with 100 cc. of benzene and the mixture extracted with three 50-cc. portions of 5% sulfuric acid. On making the extracts alkaline 2 g. of 5-methylacridine separated. After crystallizing from a mixture of benzene and hexane it melted at 117–119°. Heating a mixture of 5,5-dimethylacridane (0.3 mole), hydrogen chloride (0.15 mole) and diphenylamine (0.45 mole) in an autoclave for three hours at 250° gave 5-methylacridine and a combustible gas, presumably methane. The acid was neutralized and the non-aqueous portion distilled. The bright yellow double compound of 5-methylacridine with 5,5-dimethylacridane separated on crystallization from hexane. The melting point, 124°, was depressed not at all or only a few degrees by the addition of varying quantities of 5,5-dimethylacridane.

Anal. Calcd. for $C_{16}H_{15}N \cdot C_{14}H_{11}N$: C, 86.52; H, 6.52; N, 6.96. Found: C, 86.65; H, 6.51; N, 7.04.

The same compound was also prepared by mixing equimolecular quantities of the components dissolved in hot hexane or alcohol solution and cooling. Plates were secured from alcohol and needles from hexane. The corresponding double compound of 5,5-dimethylacridane with acridine melted at 135–136° when crystallized from hexane. The acridine components can be separated readily from these double compounds by repeated extraction with dilute sulfuric or nitric acid. Hydrochloric acid is less suitable because of the low solubility of the acridine hydrochlorides in water.

5,5-Dimethylacridane showed no signs of reaction with boiling aqueous potassium permanganate during four hours, the starting material being recovered unchanged.

During some experiments on the melting and freezing of 5,5-dimethylacridane it was found that a low melting (m. p. 92–93°) form could be obtained by careful cooling. It was unstable in the presence of the high melting form.

5,5,10-Trimethylacridane, 5,10-Dimethylacridane and Related Compounds.—The trimethyl derivative was prepared by treating the sodium salt of IV with methyl iodide in refluxing toluene. The sodium iodide was washed out with water and the oil fractionally distilled. Unreacted IV was then separated from its N-methyl derivative by crystallizing from a mixture of hexane and benzene. The N-methyl derivative melted at 100–102°.

Anal. Calcd. for $C_{16}H_{17}N$: C, 86.04; H, 7.68; N, 6.28. Found: C, 85.88; H, 7.64; N, 6.49.

In order to repeat the work of Stevens, *et al.*,[9] 0.072 mole of finely powdered 5-methylacridine methiodide[13] (m. p. 265–267°) was added to 0.30 mole of methylmagnesium iodide in 100 cc. of ether during five minutes. Reaction took place rapidly with the disappearance of the red color of the methiodide and with the evolution of a gas. The mixture was refluxed for forty minutes and then hydrolyzed with dilute acetic acid. Benzene (100 cc.) was added and the ether distilled. The residue was filtered, yielding 4.5 g. of solid material that was not identified. The benzene layer was distilled and yielded 10.5 g. of material at 160–170° (1.5 mm.). This on crystallization from a mixture of benzene and hexane gave 1.5 g. of crystals of m. p. 140–141° and 1.5 g. of less pure product of m. p. 138–140°. This product is 5,10-dimethylacridane.

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.07; H, 7.23; N, 6.70. Found: C, 86.05; H, 7.13; N, 6.99.

The mother liquor was extracted with dilute hydrochloric acid to remove colored by-products and on evaporation yielded 1 g. of crystals melting at 92–98°. These on crystallization from hexane melted at 100–102°, alone or mixed with the above described 5,5,10-trimethylacridane.

The 5,10-dimethylacridane just described was identified by mixed melting point with the compound prepared from the addition of 0.1 mole (32.1 g.) of acridine methiodide (m. p. 206–209°, dec.) to a well-cooled solution of 0.3 mole of methylmagnesium iodide in 100 cc. of ether. Reaction occurred with the evolution of a gas, presumably ethane, and precipitation of a solid. The mixture was hydrolyzed with ice and dilute acetic acid in the usual way. A considerable amount of solid (12 g.) was filtered off. From the filtrate there were obtained acridine and 5,10-dimethylacridane; yield 8.5 g. A small amount of impurity in the latter compound may have been 10-methylacridane.[14]

The solid after crystallizing twice from toluene melted with decomposition at about 280°.

Anal. Calcd. for $C_{28}H_{24}N_2$: C, 86.55; H, 6.23; N, 7.21. Found: C, 86.87; H, 6.08; N, 7.43.

Three grams of this solid was heated to reflux for three minutes, during which time the temperature reached 350°. The product was treated with 50 cc. of concentrated hydrochloric acid and filtered to remove a small amount of insoluble matter. Several volumes of water were added. The oil thus precipitated soon crystallized and was then filtered off. Four tenths gram of acridine was recovered from the filtrate by distilling the organic bases precipitated by the addition of sodium hydroxide. The product that was filtered off was dissolved in benzene. In order to remove traces of acridine the benzene solution was extracted repeatedly with dilute hydrochloric acid and finally with water. Distillation of the benzene solution produced 0.7 g. of crude 10-methylacridane. It melted at 91–93° after recrystallizing twice from petroleum ether.

Anal. Calcd. for $C_{14}H_{13}N$: C, 86.11; H, 6.72; N, 7.17. Found: C, 86.10; H, 6.82; N, 7.31.

A reaction of methylmagnesium iodide with acridine hydroiodide under the conditions used for acridine methiodide gave approximately a 15% yield of acridane along with some unreacted acridine. Attempts to isolate 5-methylacridine from the products were not successful.

5,5-Diethylacridane.—Thirty grams (0.132 mole) of methyl N-phenylanthranilate in 150 cc. of ether was added to 0.6 mole of ethylmagnesium iodide in 150 cc. of ether during twenty-five minutes. The heat of reaction caused the mixture to boil. A greenish-yellow color developed and a small amount of precipitate appeared. Stirring was continued for forty minutes during which time more of the precipitate formed. The mixture was allowed to stand at room temperature for three days, hydrolyzed with dilute

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[13] Hamer, *J. Chem. Soc.*, 1002 (1930).

[14] Bergmann, Blum-Bergmann and Christiani, *Ann.*, **483**, 80 (1930).

acetic acid in the usual way and distilled. The product boiled at 175° (2 mm.); yield 27 g. (79%).

Anal. Calcd. for $C_{17}H_{21}NO$: C, 79.94; H, 8.30; N, 5.49. Found: C, 79.76; H, 8.39; N, 5.66.

These values are in agreement with the empirical formula of *o*-anilinophenyldiethylcarbinol.

The product was dehydrated by dissolving in concentrated sulfuric acid and pouring into water. Distillation of the oil obtained and crystallization from hexane separated it into a white solid, m. p. 90–91°, and an oil, b. p. 150–155° (2 mm.).

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.02; H, 8.07; N, 5.91. Found for the solid: C, 85.99; H, 8.19; N, 6.08. Found for the oil: C, 86.01; H, 8.10; N, 5.89.

The oil contained a small amount of the solid and was probably largely an *o*-pentenyldiphenylamine. The solid was shown to be 5,5-diethylacridane by its synthesis as follows: 18 g. (0.092 mole) of acridone was added rapidly to 0.3 mole of ethylmagnesium bromide in 150 cc. of *n*-butyl ether at 100°. A vigorous reaction ensued causing the temperature to rise to 120°. The mixture was refluxed and stirred for two hours. When this was poured into water a greenish precipitate separated which was filtered off after the addition of 25 cc. of acetic acid and standing overnight; yield 7 g.; m. p. 250–270°. The ether layer was separated and distilled. A fraction, b. p. 150°(2 mm.)–165° (3 mm.), weighing 11 g. and a residue of 5 g. was obtained. The fraction, b. p. 150°(2 mm.)–165° (3 mm.) gave 7 g. (34% yield) of 5,5-diethylacridane which when recrystallized from hexane melted at 90–92° alone or mixed with the solid product obtained from methyl N-phenylanthranilate.

5,5-Di-*n*-butylacridane.—This compound was prepared in refluxing ethyl ether from 13 g. (0.067 mole) of acridone and 0.4 mole of *n*-butylmagnesium bromide. The initial reaction took place rapidly. After thirty minutes the ethyl ether was distilled off and the mixture refluxed in *n*-butyl ether for thirty minutes. The mixture was hydrolyzed in the usual manner with acetic acid and the product distilled and crystallized from hexane; m. p. 87–88°, b. p. 173–183° (2 mm.). The yield of pure product was 4 g. (24%).

Anal. Calcd. for $C_{21}H_{27}N$: C, 85.94; H, 9.28; N, 4.78. Found: C, 85.96; H, 9.16; N, 4.86.

Summary

1. The preparation of 5,5-dialkylacridanes by the reaction of acridines, acridinium iodides, acridone and methyl N-phenylanthranilate with Grignard reagents is described.

2. The following new compounds were prepared: 5,5-dimethylacridane, 5,5,10-trimethylacridane, 5,5-diethylacridane, *o*-anilinophenyldiethylcarbinol, 5,5-di-*n*-butylacridane and the double compounds of acridine and 5-methylacridine with 5,5-dimethylacridane.

3. The properties of 5,5-dimethylacridane are described in considerable detail.

AKRON, OHIO RECEIVED FEBRUARY 28, 1936

[CONTRIBUTION FROM THE LABORATORIES OF THE WM. S. MERRELL COMPANY]

The Synthesis of Dibenzoyl Disulfide

BY R. S. SHELTON AND T. H. RIDER

Amberg and Brunsting[1] recently investigated the use of dibenzoyl disulfide,[2] and found it of considerable value as an antipruritic. Their favorable preliminary clinical report suggested that a detailed study of the properties and methods of preparing dibenzoyl disulfide might be of interest and value, especially as applied to the commercial production of a medicinally pure product.

A check of the previous literature[3] on this product failed to give a method of preparation which was economically feasible.

It was found early in this investigation that sodium thiobenzoate is easily formed by the reaction of benzoyl chloride with 35% aqueous sodium hydrosulfide. The thiobenzoate was not, however, oxidized to any great extent in the reaction mixture to the desired disulfide. The reaction was tried in alcoholic solution, but without much better result, due to the reaction of the alcohol with the acid chloride.

A further investigation of the oxidation of the thiobenzoate yielded satisfactory results. Engelhardt, Latschinoff and Malyscheff[4] had previously studied the oxidation of thiobenzoic acid by the action of air, cupric sulfate, ferric chloride, potassium triiodide and potassium ferricyanide. These and other oxidation agents were investi-

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[1] S. Amberg and L. A. Brunsting, *Proc. Staff Meet. Mayo Clinic*, **8**, 443 (1933).

[2] Dibenzoyl disulfide was referred to in the original clinical report[1] as "benzoyl persulphide," an inaccurate nomenclature since it does not distinguish between the di-, tri- or tetra-sulfides, all of which are known [I. Block and M. Bergmann, *Ber.*, **53**, 961 (1920)].

[3] E. Fromm, *Ann.*, **348**, 144 (1906); A. Weddige, *J. prakt. Chem.*, **2**, 459 (1871); E. Moness, W. A. Lott, F. F. Berg and W. G. Christiansen, Portland Meeting, American Pharmaceutical Association, August, 1935; Wöhler and Liebig, *Ann.*, **3**, 267 (1832); A. Engelhardt, P. Latschinoff and S. Malyscheff, *Z. chem.*, **11**, 353 (1868); I. Block and M. Bergmann, *Ber.*, **53**, 961 (1920); J. v. Braun, *ibid.*, **36**, 2259 (1903); A. Binz and Th. Marx, *ibid.*, **40**, 3855 (1907); S. Mosling, *Ann.*, **118**, 305 (1861); L. Szperl, *Roczniki Chemji*, **10**, 510 (1930); *C. A.*, **25**, 503 (1931).

[4] A. Engelhardt, P. Latschinoff and S. Malyscheff, *Z. chem.*, **11**, 353 (1868).