

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESTERN ILLINOIS STATE TEACHERS COLLEGE]

## Structures of Some Nitrated Fluorene Derivatives

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This investigation was undertaken in order to clear up the structure of a dinitro derivative of 9-acetaminofluorene reported by the senior author of this paper and the late W. A. Noyes.<sup>2</sup> Since it obviously was not the mononitro-9-acetaminofluorene they were seeking it was not further studied at that time except for an analysis and the tentative suggestion that it might be the 1,8-dinitro-9-acetaminofluorene. It has since been shown by Huntress and Cliff<sup>3</sup> that the supposed 1,8-dinitrofluorenone of Kuhn and Jacob<sup>4</sup> and of Schmidt and Stutzel<sup>5</sup> prepared under more drastic conditions from 9-acetaminofluorene, was actually a mixture of 2,7-dinitrofluorenone and an unknown dinitrofluorenone, m. p. 213–214°. In fact no 1,8-dinitro derivatives of fluorene are known since the orienting groups seem to favor the 2-position in mononitration and the 2,7 and the 2,5 positions in dinitration.<sup>6</sup>

Langecker's<sup>7</sup> *unnecessarily oxidized* 2,7-dinitrofluorene melting above 270° is evidently 2,7-dinitrofluorenone which also melts above 270°. Various temperatures ranging from 275 to 300° had been given prior to 1943 for the m. p. of 2,7-dinitrofluorene. Courtot and Moreaux<sup>8</sup> reported 333–334° for their product recrystallized extensively from nitrobenzene. We were not able to obtain a higher m. p. than 310° (uncor.) even after dozens of recrystallizations. Langecker's other dinitrofluorene which he "oxidized" to a dinitrofluorenone, m. p. 236°, is evidently 2,5-dinitrofluorenone. Goldschmiedt and Schranzhofer<sup>9</sup> had obtained a mixture of 2,7-dinitrofluorenone and a more soluble, less abundant isomer m. p. 220°<sup>10</sup> by nitration of fluorenone. We have been able to show, after repeating these two preparations, that the substance melting at 220° of Goldschmiedt and Schranzhofer and that melting at 213–214° of Huntress and Cliff<sup>3</sup> are in fact impure forms of 2,5-dinitrofluorenone, very tenaciously contaminated with some of the 2,7-isomer.

The procedure used by Bennett and Noyes<sup>2</sup> in which 9-acetaminofluorene was added to a mixture of concentrated sulfuric and nitric acids at room temperature was much milder than that used by the other authors reviewed above. The

present authors after repeating this nitration several times were able to isolate two new compounds, 2,7-dinitro-9-acetaminofluorene and 2,5-dinitro-9-acetaminofluorene, which take the place of the tentatively reported 1,8-dinitro-9-acetaminofluorene.<sup>2</sup>

## Experimental

**Preparation of 2,7-Dinitrofluorene and 2,5-Dinitrofluorene.**—Fluorene was nitrated according to the directions of Courtot and Moreaux<sup>8</sup> using fuming nitric acid at room temperature. The 2,7-dinitrofluorene, recrystallized from nitrobenzene melted at 310° (uncor.). The 2,5-dinitrofluorene melted at 207–208° (uncor.) after recrystallization from glacial acetic acid. Oxidations of these isomers readily yielded the 2,7- and 2,5-dinitrofluorenones.

**Nitration of Fluorenone.**—Fluorenone prepared by oxidation of fluorene following the method of Huntress, Hershberg and Cliff<sup>11</sup> was nitrated according to Goldschmiedt and Schranzhofer.<sup>9</sup> Ten grams of fluorenone was added to 180 ml. of fuming nitric acid (sp. gr. 1.50). After solution was complete, ice water was added and the yellow mass filtered, washed and dried. The product was then refluxed with 1300 ml. of alcohol and filtered while hot. The insoluble residue after recrystallization from glacial acetic acid produced long yellow needles of 2,7-dinitrofluorenone, m. p. 296°. The alcoholic filtrate upon cooling yielded crystals melting at 201° which upon recrystallization from glacial acetic acid reached the 220° melting point given by Goldschmiedt and Schranzhofer. Further recrystallizations eventually yielded a product melting at 240° which was evidently 2,5-dinitrofluorenone. Its phenylhydrazone melted at 258° (uncor.) (Ray and Francis<sup>12</sup> had reported 252–253°). Goldschmiedt and Schranzhofer<sup>9</sup> gave 227–228° for the m. p. of their phenylhydrazone which was evidently impure.

**Nitration of 9-Acetaminofluorene According to Huntress and Cliff.**—Fluorenone oxime prepared according to Moore and Huntress<sup>13</sup> was reduced to the 9-amino-fluorene according to Ingold and Wilson's directions<sup>14</sup> using acetic acid and zinc dust. The crude amine was acetylated according to Kerp<sup>15</sup> with acetic anhydride. Eight grams of the 9-acetaminofluorene, m. p. 261°, was refluxed over a steam-bath with 48 ml. of nitric acid (sp. gr. 1.42) for thirteen hours. The reaction mixture was cooled and the bright yellow mass filtered. The dried product was extracted with hot alcohol as in the case of the fluorenone nitration product and the more abundant, less soluble fraction proved to be 2,7-dinitrofluorenone. The alcoholic solution upon cooling again yielded similar crystals to those obtained before. They melted at 216° and were evidently the same as the dinitrofluorenone described by Huntress and Cliff.<sup>3</sup> After several recrystallizations, yellow needles of 2,5-dinitrofluorenone, m. p. 240° (uncor.) were obtained. In both nitrations, in at least one run, brown feathery crystals were isolated which on recrystallization from glacial acetic acid had the expected m. p. of 240° and lost their color. In other cases these did not appear but a second alcoholic extraction removed the occluded impurity which was no doubt 2,7-dinitrofluorenone.

**Nitration of 9-Acetaminofluorene According to Bennett and Noyes.**<sup>2</sup>—Ten grams of the acetyl derivative was

(1) Abstracted from the theses of Mr. Jewsbury and of Mrs. Dupuis presented in partial fulfillment of the requirements for the M. S. degree.

(2) Bennett and Noyes, *THIS JOURNAL*, **52**, 3437 (1930).

(3) Huntress and Cliff, *ibid.*, **54**, 826–828 (1932).

(4) Kuhn and Jacob, *Ber.*, **58**, 1440 (1925).

(5) Schmidt and Stutzel, *Ann.*, **370**, 1–40 (1909).

(6) Anantakrishnan and Hughes, *J. Chem. Soc.*, 1607 (1935).

(7) Langecker, *J. prakt. Chem.*, **132**, 146 (1931).

(8) Courtot and Moreaux, *Compt. rend.*, **217**, 453 (1943).

(9) Goldschmiedt and Schranzhofer, *Monatsh.*, **16**, 807 (1895).

(10) The xx-dinitrofluorenone of Beilstein, V11, 271, 4th ed.

(11) Huntress, Hershberg and Cliff, *THIS JOURNAL*, **53**, 2721 (1931).

(12) Ray and Francis, *J. Org. Chem.*, **8**, 52–59 (1943).

(13) Moore and Huntress, *THIS JOURNAL*, **49**, 2621 (1927).

(14) Ingold and Wilson, *J. Chem. Soc.*, 1492–1505 (1933).

(15) Kerp, *Ber.*, **29**, 231 (1896).

added with stirring to a mixture of 18 ml. of concentrated sulfuric acid and 37 ml. of concentrated nitric acid at room temperature. As soon as all had dissolved, the solution was poured into cracked ice. The resulting solid was filtered, washed and dried. After several fractional crystallizations from glacial acetic acid two isomers were obtained. The more abundant, less soluble one, obtained in about 40% yield, consisted of cream colored shining disks, m. p. 256° (uncor.). Oxidation by chromic acid yielded quantitatively long yellow needles of 2,7-dinitrofluorenone, m. p. 293° (uncor.); oxime, m. p. 289° (uncor.); phenylhydrazone, m. p. 259° (uncor.); semicarbazone, m. p. above 338° (uncor.). It was therefore 2,7-dinitro-9-acetaminofluorene.

*Anal.* Calcd. for  $C_{15}H_{11}O_5N_3$ : C, 57.5; H, 3.5; N, 13.4. Found<sup>16</sup>: C, 57.27; H, 3.76; N, 13.39.

The more soluble fraction after several recrystallizations from glacial acetic acid melted at 243° (uncor.) and consisted of cream colored needles which usually formed a roset pattern. It was shown to be 2,5-dinitro-9-acetaminofluorene by its oxidation to 2,5-dinitrofluorenone, m. p. 240° and its analysis.<sup>16</sup> Calculated for  $C_{15}H_{11}O_5N_3$ : C, 57.5; H, 3.51; N, 13.4. Found: C, 56.30; H, 3.99; N, 13.05. These acetyl derivatives are very resistant to hydrolysis, long boiling with sodium hydroxide and with dilute acids having no effect.<sup>17</sup> Heating with nitric acid

(16) The actual analyses were performed by Dr. Carl Tiedcke of New York, N. Y.

(17) Popkin, Peretta and Selig, *THIS JOURNAL*, **66**, 833 (1944), have reported a similar resistance to hydrolysis in the biphenyl series.

(sp. gr. 1.42) for one hour on the steam-bath also produced no change.

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### Summary

1. The unknown dinitrofluorenone, m. p. 220°, of Goldschmiedt and Schranzhofer (the xx-dinitrofluorenone of Beilstein) is in reality an impure 2,5-dinitrofluorenone.

2. Huntress and Cliff's dinitrofluorenone, m. p. 213–214°, is this same 2,5-dinitrofluorenone as is Langecker's compound, m. p. 236°.

3. Mild nitration of 9-acetaminofluorene yields two new dinitro-derivatives. The more abundant 2,7-dinitro-9-acetaminofluorene melts at 256° uncor. while the other isomer, 2,5-dinitro-9-acetaminofluorene, melts at 243° uncor.

4. Dinitration of fluorene or its derivatives seems always to yield a mixture of the 2,7- and the 2,5-dinitro derivative, the former more abundant and less soluble.

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## The Reaction of $\alpha,\alpha,\beta$ -Trichlorobutyraldehyde with a Number of Grignard Reagents

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Jocicz<sup>1</sup> found that phenylmagnesium bromide and  $\alpha,\alpha,\beta$ -trichlorobutyraldehyde, commonly called butyl chloral, react normally and give a good yield of the secondary alcohol. One might expect other simple Grignard reagents to react with this aldehyde in a similar manner to give corresponding alcohols. Inasmuch as a search of the literature revealed no information in this connection, the research project here reported was undertaken to investigate further the reaction of  $\alpha,\alpha,\beta$ -trichlorobutyraldehyde with typical Grignard reagents. The study was conducted with *n*-hexylmagnesium bromide, cyclohexylmagnesium bromide,  $\beta$ -phenylethylmagnesium bromide and benzylmagnesium chloride, and the results of reaction with butyl chloral show that with these Grignard reagents products other than the anticipated carbinols are formed. Each of the first three mentioned reagents reacts to give 2,2,3-trichlorobutanol-1, and in addition hexene-1, cyclohexene or styrene, respectively, as main products. The last mentioned, benzylmagnesium chloride, reacts with butyl chloral to yield dibenzyl as the principal product.

It is evident that in the reaction of Grignard reagents,  $RMgX$ , with butyl chloral reduction of this aldehyde to the corresponding alcohol pre-

dominates in those cases where the Grignard reagent can be oxidized by the loss of two hydrogen atoms from adjacent carbons, with the resulting formation of a carbon to carbon double bond. For phenylmagnesium bromide and benzylmagnesium chloride such an oxidation is not possible.

In order to secure data for comparison purposes the synthesis reported by Jocicz<sup>1</sup> was repeated, with certain changes in reaction conditions.

### Experimental<sup>2</sup>

**$\alpha,\alpha,\beta$ -Trichlorobutyraldehyde and Phenylmagnesium Bromide.**—One-fourth mole portions of reactants were used and the procedure employed for the preparation of the Grignard reagent and its reaction with the aldehyde was essentially that outlined in the section which follows. Unreacted aldehyde was recovered and weighed as the hydrate. The secondary alcohol, 2,2,3-trichloro-1-phenylbutanol-1, was obtained as a colorless, viscous liquid which distilled at 160–163° at 8 mm. Weights of substances isolated as averaged from two runs were as follows, 2,2,3-trichloro-1-phenylbutanol-1, 45 g. (71.1%); diphenyl, 1.3 g.; hydrate of unreacted aldehyde, 5 g.; undistillable residue, 2 g. These results verify those of Jocicz's experiments.

**$\alpha,\alpha,\beta$ -Trichlorobutyraldehyde and *n*-Hexylmagnesium Bromide, Cyclohexylmagnesium Bromide and  $\beta$ -Phenylethylmagnesium Bromide.**—In the preparation of each of these Grignard reagents a 1-liter, three-necked flask fitted with a stirrer, dropping funnel and condenser was

(1) Jocicz, *J. Russ. Phys.-Chem. Soc.*, **34**, 97 (1902).

(2)  $\alpha,\alpha,\beta$ -Trichlorobutyraldehyde (butyl chloral) was furnished through the courtesy of the Westvaco Chlorine Products Corporation.