

magnesium chloride to an excess of acetyl chloride in ether gives a 40% yield of pinacolone, b. p. 103–106° at 746 mm. pressure.

Somewhat lower yields are obtained with other combinations of tertiary Grignard reagents and acyl halides.

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PREPARATION OF SUBSTITUTED FLUORENONES

Sir:

The appearance of a paper by Langecker [*J. prakt. Chem.*, [2] **132**, 145–52 (1931)] citing certain attempts to prepare 1,8-dinitrofluorenone leads us to call attention to work of a similar nature which has for some time been in progress in this Laboratory. In May, 1927, Moore and Huntress [THIS JOURNAL, **49**, 1324–1334 (1927)] published a synthesis for both 2-nitro- and for 7-nitrophenanthridone. In November of the same year it was further shown [Moore and Huntress, *ibid.*, **49**, 2618–2624 (1927)] that 7-nitrophenanthridone could be prepared in almost quantitative yield by Beckmann rearrangement of 2-nitrofluorenone oxime. In pursuance of the studies of the phenanthridone series begun at that time, the present authors have been engaged since 1927 in attempting to obtain derivatives of fluorenone having substituents in one (or both) of the 1,8 positions. If an unsymmetrically substituted fluorenone oxime of this type could be obtained, it was hoped that stereoisomers might be isolated, and that by joint application of phenanthridone formation and of ring closure reactions involving the substituent and the oximino group, some additional light might be thrown upon the mode of interchange of radicals in the Beckmann rearrangement. Since Langecker's paper indicates its objective as the preparation of 1-substituted fluorenonenes, and since in dealing with the 2-nitrofluorenone oxime first reported by one of us it gives no evidence that the author was aware of our previous publications on fluorenone derivatives, it seems advisable that we reiterate the continuing interest of this Laboratory in this subject.

Of the few 1- or 1,8-substituted fluorenonenes on record in the literature (1-bromofluorenone, 1,3-dibromofluorenone, 1-hydroxyfluorenone, 1-amino-fluorenone, fluorenone-1,7-dicarboxylic acid, and 1,8-dinitrofluorenone), the alleged "1,8-dinitrofluorenone" of Schmidt and Stützel [*Ann.*, **370**, 22 (1909)] and of Kuhn and Jacob [*Ber.*, **58**, 1440 (1925)] is the only substance prepared by direct substitution. The structure assigned to this material is open to criticism upon several grounds. In the first place the nitrogen content given by Schmidt as 10.40% proves upon recalculation

of Schmidt's own experimental data to be in fact 8.08%, or about half-way between the theoretical value of 6.22% for a mononitrofluorenone and 10.36% for a dinitrofluorenone. In the second place, oxidation of the material yielded an acidic product whose observed melting point and nitrogen analysis suggested that it might be *o*-nitrobenzoic acid. Despite the proximity of the melting points of *o*- and of *m*-nitrobenzoic acids, no other derivatives of this oxidation product were prepared. Assuming for the moment that the product really was *o*-nitrobenzoic acid, the result accounts for only one of the nitro-substituted nuclei and does not necessarily imply that the same position in the other was involved. The supposed existence of stereoisomeric dinitrobenzidines and dinitrotolidines was based upon negative evidence of this kind. In the third place recent developments have shown that directly contrary to the assumptions prevalent at the time of Schmidt and Stützel's publication there is a strong tendency toward unsymmetrical nitration in the biphenyl series, in the phenanthraquinone series, and in the fluorene series.

In pursuance of our desire to obtain an appropriately substituted fluorenone oxime, we attempted to repeat the work of Schmidt and Stützel. In no case, however, was any material obtained possessing the properties ascribed to "1,8-dinitrofluorenone." In four separate experiments using Schmidt's conditions we obtained instead a 70% yield of 2-nitrofluorenone. The identity of this substance was established in four ways: (1) by analysis for nitrogen; (2) by its melting point and its failure to depress the melting point of a sample of authentic 2-nitrofluorenone; (3) by the identity of its phenylhydrazone with that of authentic 2-nitrofluorenone as shown by comparison and by mixed melting point determinations; and (4) by its reduction to 2-aminofluorenone. We can confirm Langecker, therefore, in stating that nitration of 9-acetylaminofluorene by the method of Schmidt and Stützel gives 2-nitrofluorenone as the only tangible product.

In examining the effect of varying the stated conditions, we have observed that when 9-acetylaminofluorene is treated with concentrated nitric acid (*d* 1.42) for two hours at 100° there results a mixture from which we have isolated a 30% yield of 2,7-dinitrofluorenone, together with 13% of a new dinitrofluorenone, m. p. 213–4° uncorr. This substance contains 10.57% of nitrogen as compared with the theoretical of 10.60% for a dinitrofluorenone. It depressed the melting points of both 2,7-dinitro- and 2,4-dinitrofluorenes. Its structure is being examined.

The melting point of Langecker's 2-nitrofluorenone oxime is given as 249°. Moore and Huntress [THIS JOURNAL, 49, 2622 (1927)] obtained a value of 262.5–263.0° uncorr., with decomposition. Since the former material was prepared from the ketone by means of hydroxylamine hydrochloride and barium carbonate in alcohol (*i. e.*, in neutral solution) while our product was prepared from hydroxylamine hydrochloride and an

alcoholic solution of the ketone (*i. e.*, in acid solution), it is possible that the two materials are stereoisomers. This point will be examined.

Our efforts to prepare fluorenones substituted in positions ortho to the carbonyl group are being continued.

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REACTION OF PHENYLACETONITRILE

Sir:

While investigating the action of sodium on benzyl cyanide, it was found that one mole of phenylacetone nitrile dissolved in liquid ammonia reacts almost quantitatively with one mole of sodium to form a salt, presumably sodium phenylacetone nitrile, which remains suspended in liquid ammonia. This when treated with ethyl bromide in liquid ammonia yields phenylethylacetone nitrile.

In previous work Rossolymo used sodium hydroxide, Hintikka, sodamide in toluene, Bodroux and Taboury, sodamide in ether, Rising, sodium in ether, Rising and Zee, sodamide in ether, as a means of forming sodium phenylacetone nitrile.

It is interesting to note that presumably only one of the hydrogen atoms on the carbon atom, alpha to the cyanide group, can be replaced at one time by sodium in liquid ammonia. If, after treatment with ethyl bromide to form phenylethylacetone nitrile, this latter nitrile is treated with sodium in liquid ammonia, a mole of sodium can be introduced per mole of nitrile.

This procedure can be utilized in the preparation of mono and dialkylated alkyl or aryl cyanides. It is being investigated further in these laboratories.

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THE CRYSTALLINITY OF OPALS AND THE EXISTENCE OF HIGH-TEMPERATURE CRISTOBALITE AT ROOM TEMPERATURE

Sir:

Opals have thus far been considered as outstanding examples of truly amorphous solids. The introduction of x-ray methods did not alter this result materially since Lehmann [W. M. Lehmann, *Z. Krist.*, **59**, 455 (1923)] reported that gem opal and ordinary opal give the Debye-Scherrer-Hull diagram of an amorphous solid; however, fire opal gives a faint in-