

dish and pouring in some bromine, again warming to volatilize the excess. The mixture glows and fumes and the product must be used immediately. Anhydrous aluminum chloride¹ has also been successfully employed a few times.

The method has not been applied to any of the very difficult preparations.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY,
DEPAUW UNIVERSITY,
GREENCASTLE, INDIANA

RALPH W. HUFFERD

RECEIVED APRIL 28, 1927
PUBLISHED JULY 5, 1927

The Chloromethylacetophenones.—In connection with some work on the condensation of benzil and substituted acetophenones, we have had occasion to prepare the 2-chloro-5-methyl and 4-chloro-3-methyl derivatives from *p*-chlorotoluene and *o*-chlorotoluene, respectively. These ketones have been reported once previously by Claus.¹ He made them by the action of acetyl chloride on the chlorotoluene in the presence of anhydrous aluminum chloride; his yields were very poor and the ketones boiled over a considerable range; furthermore, he did not analyze them because he realized they were impure. He made the oximes, however, and proved the structure of the ketones by oxidation to the corresponding chlorotoluic and chlorophthalic acids.

By the use of acetic anhydride instead of acetyl chloride² we have obtained the ketones nearly constant boiling after one distillation, the 3-chloro-4-methyl derivative in a yield of 70% and the 2-chloro-5-methyl derivative in a yield of 34%. Claus had great difficulty in preparing even small amounts of the latter. We have determined the boiling points and refractive indices of both the ketones; they distil without decomposition at atmospheric pressure, forming colorless oils that very slowly take on a yellow tinge in the light. They have a very faint odor suggestive of acetophenone.³

| Ketones | B. p., °C. | Press., mm. | n_D^{25} | Anal. | | | |
|-------------------------------|-------------|----------------|------------|--------|------|-------|------|
| | | | | Calcd. | | Found | |
| | | | | C, % | H, % | C, % | H, % |
| 2-Chloro-5-methylacetophenone | 245.8–246.0 | 760.1 | 1.5419 | 64.1 | 5.3 | 63.9 | 5.4 |
| 4-Chloro-3-methylacetophenone | 254.2–254.4 | 753.4 | 1.5521 | 64.1 | 5.3 | 64.0 | 5.3 |

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF TUFTS COLLEGE,
TUFTS COLLEGE, MASSACHUSETTS

CHARLES F. H. ALLEN
M. PHILBRICK BRIDGESS

RECEIVED MAY 10, 1927
PUBLISHED JULY 5, 1927

¹ Hesse, *Ber.*, **39**, 1127 (1906).

² Claus, *J. prakt. Chem.*, [2] **43**, 356 (1890); **46**, 26 (1892).

³ Noller with Adams, *THIS JOURNAL*, **46**, 1889 (1924).

⁴ The boiling points were determined with the mercury column of the thermometer wholly immersed in the vapor.