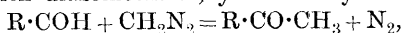


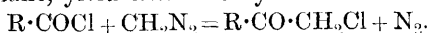
CLXV.—*The Action of Diazomethane on Some Aromatic Acyl Chlorides.*

By DOUGLAS ARTHUR CLIBBENS and MAXIMILIAN NIERENSTEIN.

THE reaction described in this communication is an extension of the observations made by Schlotterbeck (*Ber.*, 1907, **40**, 479), and to some extent also by Hans Meyer (*ibid.*, 847)—that aldehydes, when treated with diazomethane, yield methyl ketones:



as we have found that some aromatic acyl chlorides, when treated with diazomethane, yield chloromethyl ketones: *



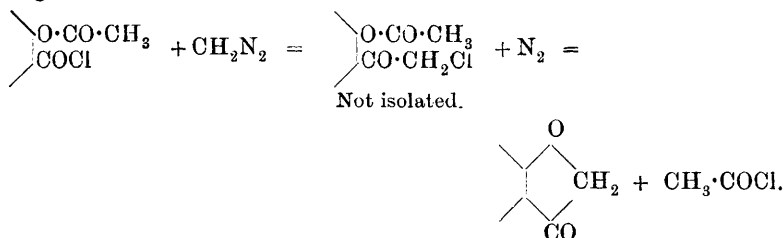
EXPERIMENTAL.

The following general technique was adopted by us in the preparation of the products described here. The chlorides were dissolved in ether (as used in the Grignard reaction) and treated in molecular proportion with an ethereal solution of diazomethane prepared according to Staudinger and Kupfer's method (*Ber.*, 1912, **45**, 501), and quantitatively tested by Marshall and Acree's benzoic acid method (*Ber.*, 1910, **43**, 2323; compare also Nierenstein, this vol., p. 870). The ether was removed after cessation of the evolution of nitrogen, and the residue distilled under diminished pressure. The first fraction generally contained some unchanged chloride, the second one consisted of the chloromethyl ketone, which solidified, whereas the third fraction consisted of a small amount of a nitrogenous by-product. In two cases where

* [With ARTHUR GEAKE.]—This reaction suggested to us the possibility that a more or less mobile hydroxyl group such as the one in triphenylcarbinol (compare Schmidlin, *Das Triphenylmethyl*, p. 120) would, if acted on with diazomethane in molecular proportion, probably yield triphenylethanol. This, however, is not the case, and our experiments have shown that neither in triphenylcarbinol nor in the other carbinols used by us are the hydroxyl groups methylated by diazomethane.

Triphenylcarbinol, benzhydrol, benzyl alcohol, and benzoylcarbinol were recovered unchanged and identified by their melting points, mixed melting points, and also tested in the Zeisel apparatus for methoxy-groups. Benzoic acid, on the other hand, gave methyl benzoate (m. p. 76°. Found, OMe=12.92. $C_{13}H_{11}O \cdot CO_2Me$ requires OMe=12.18 per cent.). When hydrolysed with alkali, benzoic acid was recovered (m. p. 149—150°, mixed m. p. 150°). Mandelic acid gave methyl mandelate (b. p. 257—259°/752 mm., m. p. 51—53°. Found, OMe=18.11. $C_7H_7O \cdot CO_2Me$ requires OMe=18.69 per cent.). On hydrolysis with alkali, mandelic acid was recovered (m. p. 117—118°, mixed m. p. 118°).

o-acetoxyacyl chlorides had been used, the first fraction contained, in addition to some unchanged chloride, mostly acetyl chloride, which had been eliminated during the formation of the corresponding coumaranone:



Blom and Tambor (*Ber.*, 1905, **38**, 3590) have already directed attention to the ease with which the five-membered ring is formed in the case of *o*-bromo-*o*-methoxyacetophenone, which results are more fully described by Blom (*Diss.*, Berne, 1907). Only in one case did we use a carbomethoxy-derivative (tricarbomethoxygalloyl chloride). The product obtained by us was a nitrogenous substance of high melting point, which we have so far not investigated.

o-Chloroacetophenone.

Fraction II boiled at 139—141°/14 mm., and the solidified product crystallised from light petroleum in leaflets, which melted at 58—59° (*Ber.*, 1871, **4**, 35). The yield was 72 per cent. of the theoretical. (Found, C=61.55; H=5.13; Cl=22.98. C₈H₇OCl requires C=61.85; H=4.53; Cl=22.98 per cent.)

o-Bromoacetophenone.

This ketone was prepared from benzoyl bromide and diazomethane. Fraction II passed over at 135°/18 mm., and solidified in the condenser. It crystallised from light petroleum in small needles, melting at 51° (*Ber.*, 1891, **27**, 550). The yield was 28 per cent. of the theoretical. (Found, Br=40.68. C₈H₇OBr requires Br=40.17 per cent.)

Benzyl Chloromethyl Ketone, C₆H₅·CH₂·CO·CH₂Cl.

The phenylacetyl chloride (b. p. 102—103°/16—17 mm.) was prepared by the method described by Anschütz and Berns (*Ber.*, 1887, **20**, 1389). Fraction II passed over at 159—161°/17 mm., and solidified. It crystallised from chloroform in star-shaped needles, which melted at 72—73°. The yield was 84 per cent. of the theoretical:

0.1396 gave 0.3282 CO₂ and 0.0692 H₂O. C=64.11; H=5.54.

0.1606 „ 0.1382 AgCl. Cl=21.27.

C₉H₉OCl requires C=64.09; H=5.34; Cl=21.06 per cent.

β-Phenylethyl Chloromethyl Ketone, C₆H₅·CH₂·CH₂·CO·CH₂Cl.

The phenylpropionyl chloride (b. p. 115—116°/11—12 mm.) was prepared according to Kipping's method (T., 1894, **65**, 484). Fraction II passed over at 153—156°/11—12 mm., and crystallised from benzene in long needles, melting at 84—85°. The yield was 82 per cent. of the theoretical:

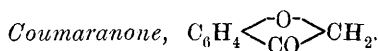
0.1822 gave 0.4398 CO₂ and 0.0986 H₂O. C=65.82; H=6.06.

0.1774 „ 0.1402 AgCl. Cl=19.55.

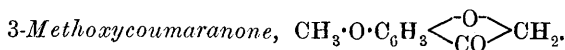
C₁₀H₁₁OCl requires C=65.75; H=6.03; Cl=19.45 per cent.

Anisyl Chloromethyl Ketone, CH₃·O·C₆H₅·CO·CH₂Cl.

The anisyl chloride (b. p. 262—263°/743 mm.) was prepared according to Ullmann and Goldberg's method (*Ber.*, 1902, **35**, 2814). Fraction II passed over at 179—181°/16—18 mm. It crystallised from alcohol in needles, which melted at 104—105°, as found by Kunckell and Johannssen (*Ber.*, 1897, **30**, 1715). The yield was 86 per cent. of the theoretical. (Found, Cl=19.64. C₉H₉O₂Cl requires Cl=19.24 per cent.)



The *o*-acetoxybenzoyl chloride (m. p. 41—42°) was prepared according to the method described by Anschütz (*Annalen*, 1909, **367**, 172). Fraction II passed over at 152—154°/15—17 mm. It crystallised from alcohol in needles, melting at 101—102°. The melting points found for coumaranone are 97° (Friedländer and Neudörfer, *Ber.*, 1897, **30**, 1081) and 101—102° (Störmer and Bartsch, *Ber.*, 1900, **33**, 3177). The product gave the colour reactions described by Friedländer and Neudörfer. The yield was 92 per cent. of the theoretical, which is in every way better than that found by other observers. (Found, C=71.84; H=4.93. M.W.=149, 136. C₈H₆O₂ requires C=71.64; H=4.48 per cent. M.W.=134.)



For the preparation of the *β*-resorcylic acid required for the chloride, a modification of Bistrycki and Kostanecki's method (*Ber.*, 1885, **18**, 1985) was used, in which carbon dioxide was

constantly passed through the solution of hydrogen carbonate (both potassium and sodium hydrogen carbonates were tried, and were found to yield the same results) and resorcinol during the heating process. The product obtained by us was snow-white, and when crystallised from water without the use of animal charcoal melted at 216–217°, carbon dioxide being evolved. The yield is 92–95 per cent. of the theoretical, and exceeds that obtained by Bistrycki and Kostanecki by 30 per cent. The acid was converted into *p*-methoxysalicylic acid according to Kostanecki and Tambor's method (*Ber.*, 1895, **28**, 2309), which crystallised from benzene in needles melting at 154° (Tiemann and Parrisius, *Ber.*, 1880, **13**, 2379). It was acetylated with acetyl chloride and pyridine to 2-acetoxy-4-methoxybenzoic acid, which crystallised from alcohol in perfect cubes, melting at 145–147°. This melting point is higher than the one given by Nagai (*Ber.*, 1891, **24**, 2852), who found 140° for a preparation obtained in a different way.

2-Acetoxy-4-methoxybenzoyl chloride, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OAc})\cdot\text{COCl}$, was prepared by warming 10 grams of the acid with a slight molecular excess of phosphorus pentachloride, and the phosphoryl chloride removed at 35–40°/10–12 mm. The residue was dissolved in light petroleum and filtered, when the product separated in long, prismatic needles, which melted at 81–82°. The yield was theoretical:

0.2060 gave 0.1306 AgCl. Cl=15.68.

$\text{C}_{10}\text{H}_9\text{O}_4\text{Cl}$ requires Cl=15.54 per cent.

The chloride was converted in the usual way into the 3-methoxycoumaranone. Fraction II passed over at 182–184°/11–12 mm., and crystallised from alcohol in colourless needles which melted at 125°, as found by Blom and Tambor (*Ber.*, 1905, **38**, 3590), who, however, describe 3-methoxycoumaranone as crystallising from alcohol in pale yellow needles. The yield was 88 per cent. of the theoretical. (Found, C=65.45; H=4.92. $\text{C}_9\text{H}_8\text{O}_3$ requires C=65.85; H=4.88 per cent.)

In conclusion, we wish to thank Cpl. C. W. Spiers, R.E., and Lieut. F. S. Wallis, for carrying out some of the analyses mentioned in this paper.

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