

Deuteration of Diazoacetone

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Summary Reaction of $\text{CD}_3\cdot\text{COCl}$ with CH_2N_2 gives $\text{CD}_3\cdot\text{CO}\cdot\text{CHN}_2$; exchange of $\text{CH}_3\cdot\text{CO}\cdot\text{CHN}_2$ with D_2O in the presence of sodium azide gives $\text{CH}_3\cdot\text{CO}\cdot\text{CDN}_2$.

VIBRATIONAL-SPECTROSCOPIC work under way in this laboratory¹ on aliphatic diazo-carbonyl compounds required deuteration of the methyl and/or methine groups of diazoacetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CHN}_2$.

Both synthesis and exchange were attempted for deuteration of the methyl group. Exchange did not proceed satisfactorily; in fact, under experimental conditions similar to those for effecting exchange in acetone,² decomposition was complete at 70° within about $\frac{1}{2}$ hr., and at 50° the extent of decomposition was too high for a convenient preparation.

Synthesis of $\text{CD}_3\cdot\text{CO}\cdot\text{CHN}_2$ was achieved by the method of Arndt and Amende,³ from $\text{CD}_3\cdot\text{COCl}$ and CH_2N_2 . $[\text{H}_4]$ Malonic acid, obtained⁴ by exchange at room temperature with 99.75% D_2O (repeated six times), was thoroughly dried by warming under vacuum for about 3 hr. at 90° in the presence of P_2O_5 . It was converted into $\text{CD}_3\text{CO}_2\text{D}$ and, by standard methods,⁵ into CD_3COCl . Diazomethane was prepared by the method of de Boer.⁶ Under these conditions the yield of $\text{CD}_3\cdot\text{CO}\cdot\text{CHN}_2$ was almost quantitative. The final purification of the deuterated compound met with some difficulties, because partial decomposition took place both on silica-gel t.l.c. and alumina column chromatography; repeated distillations under vacuum gave better results.

A mass-spectrometric purity check indicated a content

of <0.1% of totally or partially non-deuteriated material; the only impurity present to an appreciable extent (*ca.* 3–4%) in the mass spectrum was probably the species $\text{CD}_3\cdot\text{CH}_2\cdot\text{COCl}$. The i.r. spectrum of the sample did not show interference from this impurity and, when recorded at different times, did not show any evidence for methine-methine exchange; *e.g.*, the relative peak intensity of the 3108 cm^{-1} methine C–H stretching band (CS_2 soln.) did not change appreciably with time.

Synthesis was considered unsuitable for methine deuteration, because of the large number of steps involved.⁷

Direct exchange with D_2O was more convenient and, considering the acidic character of the methine proton,⁸ allowed considerable reduction of the reaction time, even at room temperature. The exchange was performed in basic medium, slightly modifying the conditions suggested by Morrison and Yates⁹ for 2-diazo-2',4',6'-trimethylacetophenone. Diazoacetone (500 mg.), prepared by the method of Wilds and Meader,¹⁰ was exchanged overnight at room temperature with 99.75% D_2O (0.9 ml.) in the presence of sodium azide (10 mg.). From the water-diazoacetone reaction mixture, separated from the catalyst by vacuum

distillation, $\text{CH}_3\cdot\text{CO}\cdot\text{CDN}_2$ was recovered by repeated extractions with small portions of anhydrous ether, drying over magnesium sulphate, and distillations.

The i.r. spectrum of liquid $\text{CH}_3\cdot\text{CO}\cdot\text{CDN}_2$ thus obtained was remarkably different from that of the undeuteriated material in the "fingerprint" region; it showed, moreover, a characteristic C–D stretching band at 2312 cm^{-1} . A single exchange sufficed to leave a very weak methine C–H stretching band at 3108 cm^{-1} (CS_2 soln.), which disappeared after two exchanges. The mass spectrum of the exchanged sample did not permit in this instance a check on its purity; in fact, exchange occurred in the inlet system of the mass spectrometer, presumably catalysed by previously deposited transition-metal films, giving back $\text{CH}_3\cdot\text{CO}\cdot\text{CHN}_2$.

The presence of $\text{CH}_3\cdot\text{CO}\cdot\text{CDN}_2$ is further supported by the reappearance of the 3108 cm^{-1} band on repeating the i.r. spectrum of the solution after a few days; this indicates that $\text{CH}_3\cdot\text{CO}\cdot\text{CDN}_2$, unlike $\text{CD}_3\cdot\text{CO}\cdot\text{CHN}_2$, undergoes fairly rapid exchange in the air even in the absence of catalysts.

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