

heating should not exceed three days, as otherwise dark syrupy products are formed which refuse to crystallise.

The crystalline product which had separated was collected, recrystallised from alcohol, and analysed with the following result:

0.1116	gave 0.2056 CO ₂ and 0.0642 H ₂ O.	C = 50.24 ; H = 6.39.
0.2051	„ 0.3780 CO ₂ „ 0.1192 H ₂ O.	C = 50.26 ; H = 6.42.
0.1136	„ 10.05 c.c. moist nitrogen at 20.4° and 739.6 mm.	N = 9.78.
0.1097	„ 9.85 c.c. „ „ 19.2° „ 739.6 mm.	N = 9.78.
C ₁₂ H ₁₈ O ₆ N ₂ requires C = 50.30 ; H = 6.35 ; N = 9.81 per cent.		

The molecular weight was determined by the lowering of the freezing point in benzene.

Solvent.	Substance.	$\Delta t.$	M.W.
17.35	0.2357	0.2325	286
16.12	0.1267	0.1325	291

C₁₂H₁₈O₆N₂ requires M.W. = 286.

The compound is slightly soluble in water, but readily so in ether, alcohol, acetone, and chloroform; from alcohol it separates in colourless needles melting at 97.5° (uncorr.).

From this it becomes evident that the compound is the ethyl ester of 4:5-dihydropyrazole-3:4:5-tricarboxylic acid, a compound first obtained by Buchner and von der Heide (*Ber.*, 1901, **34**, 345) by the action of ethyl α -dimethylacrylate on ethyl diazoacetate at 100°. Its identity was further confirmed by the analysis of its silver salt, which is precipitated by the addition of silver nitrate to a neutral solution of the sodium salt, the latter being obtained by saponifying the ester with alcoholic soda. The silver salt ignites with explosive violence on heating, hence it was found necessary to carry out the analysis under special precautions. This was done by heating a weighed quantity in a tube, one end of which had been previously drawn out and closed with glass wool, the other being securely plugged with an india-rubber stopper. The silver salt was then decomposed by cautious heating and subsequently ignited in a current of pure air until the weight became constant.

0.2291	gave 0.1418 Ag.	Ag = 61.89.
0.2530	„ 11.5 c.c. moist nitrogen at 18° and 772.4 mm.	N = 5.31.
C ₆ H ₈ O ₆ N ₂ Ag ₃ requires Ag = 61.92. N = 5.37 per cent.		

On the addition of calcium chloride to the neutral solution, the calcium salt is produced as a white precipitate, soluble in acetic acid. Mercuric chloride slowly forms a white, crystalline precipitate insoluble in dilute hydrochloric acid.

ETHYL DIAZOACETATE.

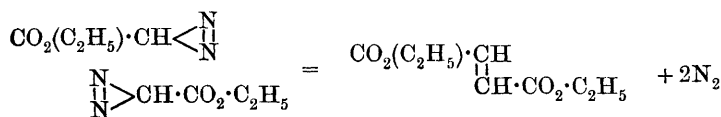
Action of Copper Dust on Ethyl Diazoacetate.—It seemed probable that in Buchner and von der Heide's experiments in which they obtained ethyl dihydropyrazoletricarboxylate by heating a mixture of ethyldiazoacetate and ethyl α -dimethylacrylate that the latter ester acted in some way catalytically. It therefore became of interest to ascertain whether the same acceleration could not be brought about by mere contact action, and to this end the action of copper dust on ethyl diazoacetate was investigated.

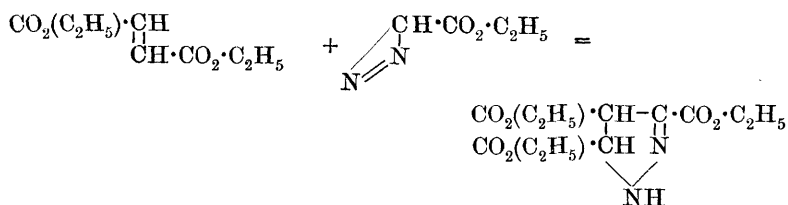
When the diazoacetate is added to copper dust, no reaction appears to take place below 80° , but above that temperature the addition of the first drop of ester is accompanied by an explosion of sufficient violence to shatter the flask. In order to moderate the violence of the reaction, the ester was diluted with absolute ether and after several experiments the following procedure was found to give satisfactory results. Two hundred grams of copper powder are placed in a flask heated in a water-bath and fitted with a dropping funnel and a tube connecting the flask with two wash-bottles filled with cold alcohol for the collection of the volatile products of the reaction. Fifty grams of ethyl diazoacetate, diluted with an equal volume of absolute ether are then cautiously added. The first addition is accompanied by a lurid green flash, which, however, may be avoided by previously displacing the air in the flask by means of carbon dioxide. The reaction is accompanied by a stormy evolution of thick white fumes, which condense readily in the alcohol wash-bottles. After allowing the flask to cool down to the ordinary temperature, the alcoholic solutions are added, the whole filtered, the alcohol removed, and the residue distilled under diminished pressure. In this manner, three fractions are obtained, of which the last, boiling at $220\text{--}254^\circ/2\text{ mm.}$, consists chiefly of ethyl 4:5-dihydro-3:4:5-tricarboxylate, which slowly solidifies to a crystalline mass which on recrystallisation melts at $97\cdot5^\circ$ (uncorr.).

0.1134 gave 9.95 c.c. moist nitrogen at 21° and 760.5 mm. $N = 9.95$.

$C_{12}H_{18}O_6N_2$ requires $N = 9.81$ per cent.

The lower fractions consisted chiefly of unaltered ethyl diazoacetate. The reaction is evidently due to the intermediate formation of ethyl fumarate (or maleate) and may be expressed as follows :





This view is further confirmed by the work of Buchner and Witter, who prepared the methyl ester by the action of the corresponding ester of fumaric or maleic acid on methyl diazoacetate (*Annalen*, 1893, 273, 239).
