H 4.79. Calculated for $C_{12}H_{13}N_7O_2$, %: C 50.17; H 4.56. IR spectrum: 3370, 3233, 3128, 1708, 1673, 1629, 1603, 1553, 1466, 1416, 1378, 1358, 1336, 1318, 1257, 1192, 1162, 1128, 1108, 1053, 1000, 948, 863, 798, 773, 740 cm^{-1}. After recrystallization from formamide, a sample of **Ic** had a somewhat different IR spectrum: 3460, 3380, 3290, 1726, 1650, 1631, 1605, 1542, 1466, 1405, 1380, 1358, 1332, 1308, 1255, 1202, 1168, 1151, 1110, 1070, 1000, 955, 906, 870, 825, 800, 780, 740 cm^{-1}.

The IR spectra were taken in paraffin oil on a UR-10 spectrometer in the physical chemistry laboratory (Director B. S. Kikot). The microanalyses were carried out in the analytical laboratory of the Institute (Director A. D. Chinaeva).

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SOME REACTIONS BASED ON 4,4-DICHLORO-2,6-PYRANDICARBOXYLIC ACID

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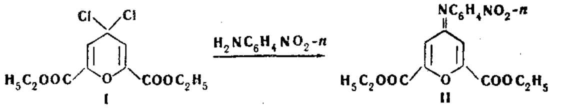
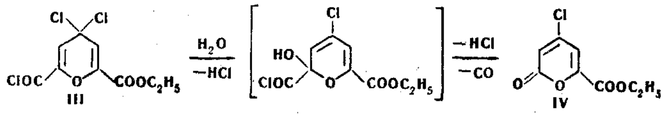
It has been shown, with the reaction of p-nitroaniline with 2,6-diethoxycarbonyl-4,4-dichloropyran (I) as an example, that, as in the case of the reaction of 4,4-dichlorobenzopyrans with aromatic amines [1], in this gem-dichloropyran system no allyl rearrangement takes place.



Conversely, the reaction of 4,4-dichloro-2-chloroformyl-6-ethoxycarbonylpyran (III) with water is accompanied by an allyl rearrangement and subsequent decarbonylation with the formation of 4-chloro-6-ethoxycarbonyl-2-pyrone (IV).



Consequently, the conversion of 4,4-dichloro-2-chloroformylchromenes into 4-chlorocoumarins observed previously [2] is not specific for benzopyrans and can be extended to monocyclic systems as well.

A mixture of 2.4 g (0.01 mole) of diethyl chelidonate and 20 ml of $SOCl_2$ was heated for 10 hr, the excess of $SOCl_2$ was distilled off in vacuum, the residue was dissolved in 20 ml of benzene, and the resulting solution was treated with a hot solution of 1.38 g of p-nitroaniline in 70 ml of benzene. The reaction mixture was left for 3 hr and was then heated to the boil and the hydrochloride of the imine II was filtered off. By treatment with aqueous bicarbonate solution, the hydrochloride was converted into the base II, yield 2.5 g (72%), mp 150.5–151° C (from ethanol). Found, %: C 56.88, 56.89; H 4.64, 4.57; N 7.94, 7.95. Calculated for $C_{17}H_{16}N_2O_7$, %: C 56.66; H 4.48; N 7.78.

A mixture of 4.9 g of monoethyl chelidonate and 50 ml of $SOCl_2$ was boiled for 10 hr, after which distillation yielded 2.5 g of III, bp 128–130° C (1 mm), to which water was added; after 18 hr, the mixture was treated with $NaHCO_3$ and extracted with benzene to give 0.68 g (38 %) of substance IV, mp 59.5–60° C (it sublimed at 100° C at 20 mm). Found, %: C 47.52, 47.39; H 3.36, 3.44; Cl 17.44, 17.28. Calculated for $C_8H_7ClO_4$. %: C 47.42; H 3.38; Cl 17.50. IR spectrum (CCl_4): 1760, 1736 cm^{-1} (ester and pyrone carbonyls). The NMR spectra confirms the structure IV.

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