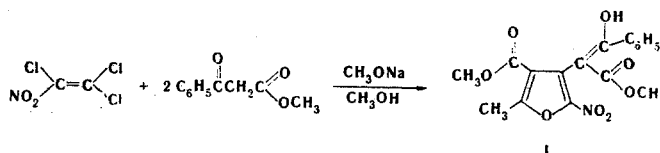


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We have developed a method for the preparation of 5-nitrofurans by reaction of the readily accessible trichloronitroethylene with  $\beta$ -keto acid esters, for example, with benzoylacetate ester.



Dimedone reacts similarly to give a nitro derivative (II) of tetrahydrobenzofuran.

2-Phenyl-3-carbomethoxy-4-(1-benzoylcarbomethoxymethyl)-5-nitrofurane (I). A 3.56-g (0.02 mole) sample of methyl benzoylacetate in 3 ml of methanol was added to a solution of 0.69 g (0.03 g-atom) of sodium in 15 ml of absolute methanol, and a solution of 1.77 g (0.01 mole) of trichloronitroethylene in 3 ml of methanol was then added dropwise with stirring and cooling (from  $-20$  to  $-25^\circ$ ) in the course of 15 min, during which sodium chloride precipitated. The mixture was stirred at the same temperature for 1 h, after which the cooling bath was removed, and the mixture was acidified with concentrated hydrochloric acid at  $10^\circ$  until the color changed from bright-red to light-yellow. The mixture was then poured over ice, and the resulting oil was worked up to give 1.8 g (43%) of lemon-yellow crystals with mp  $133-134^\circ$  [from methanol-chloroform (1:1)].

3-(4,4-Dimethyl-2,6-dioxocyclohexyl)-4-oxo-6,6-dimethyl-2-nitro-4,5,6,7-tetrahydrobenzofuran (II). This compound was obtained from 2.8 g (0.02 mole) of dimedone, 1.76 g (0.01 mole) of trichloronitroethylene, and 0.46 g (0.02 g-atom) of sodium in 40 ml of absolute methanol. The reaction was carried out at room temperature ( $20-25^\circ$ ). Workup gave 1.02 g (30%) of lemon-yellow crystals with mp  $213-214^\circ$  (from methanol). The results of the complete elementary analysis of I and II were in good agreement with the calculated values.

The reaction apparently consists of several successive steps: substitution of two chlorine atoms by residues of the  $\beta$ -carbonyl compounds and intramolecular cyclization through cleavage of the third chlorine atom. The presence of  $\beta$ -dicarbonyl residues in the side chain considerably expands the synthetic possibilities in the area of 5-nitrofurans derivatives.

The IR spectra (chloroform solutions) of I and II contain bands at 1730 (ester group), 1700 (keto group) 1660 and 1640 (keto-enol), and 1520 and  $1350\text{ cm}^{-1}$  (nitro group). The first and third maxima in the UV spectra (in alcohol) of I [ $\lambda_{\text{max}}$  (log  $\epsilon$ ) 260 (4.32), 275 (4.30), and 335 nm (4.28)] and II [225 (4.00), 263 (4.22), and 321 nm (3.90)] correspond to a nitro-substituted furan, and the second maximum corresponds to a keto-enol.

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