REACTION OF 2-ARYL-1,3-DIOXOLANES WITH NITROACETIC ESTER

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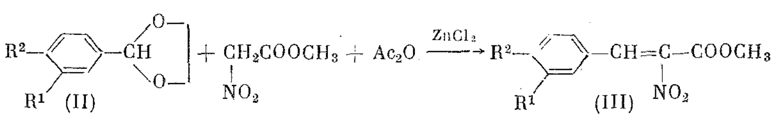
In the presence of Ac_2O the diethyl acetals of benzaldehydes (I) react with nitroacetic ester to give the C- and O-alkylation products [1, 2]. The more available cyclic acetals of benzaldehydes, namely the 2-aryl-1,3-dioxolanes, have not been used in reactions of this type [3, Chapter 2].

In the present paper we describe the preparation of a number of 2-aryl-1,3-dioxolanes (II) and the results of a comparative study of the reaction of acyclic (I) and cyclic (II) acetals with the methyl ester of nitroacetic acid (NAE). The (II) compounds were obtained from the corresponding benzaldehydes and ethylene glycol in the presence of TsOH. The reaction of the (II) dioxolanes with NAE goes with greater difficulty than with the (I) acetals, and requires the presence of an acid catalyst:



$R^1 = H$; $R^2 = H$ (a), OCH_3 (b), NO_2 (c); $R^1 + R^2 = OCH_2O$ (d).

The main reaction products in the case of the (IIb, d) acetals are the (III) esters. As can be seen from Table 1, the best results are obtained when $ZnCl_2$ is used as the catalyst. Transition to the unsubstituted 2-phenyl-1,3-dioxolane (IIa), as in the case of the acyclic acetals (I), lowers the yield of (III), while for the substituted acetal (IIc) the ester (IIIc) in general is not formed under the studied conditions. Here the main direction of the reaction is the acidolysis of (IIa, c) to ethylene glycol diacetate in harmony with [3, p. 95]. The cyclic ketal of acetone, namely 2,2-dimethyl-1,3-dioxolane (IIe), also does not react with NAE under these conditions. This ketal when heated for a long time in Ac_2O decomposes to give ethylene glycol diacetate, AcOH, and tar, the same as described in [4].

EXPERIMENTAL

The PMR spectra were taken on a Perkin–Elmer spectrometer (60 MHz) using HMDS as the internal standard, while the IR spectra were taken on a Hitachi EPI-S2 spectrometer.

The 2-aryl-1,3-dioxolanes (IIa, b) were obtained from the corresponding benzaldehydes and ethylene glycol in the presence of TsOH as described in [5]. 2-(3,4-Methylenedioxyphenyl)-1,3-dioxolane (IId) was obtained in a similar manner in 87% yield, bp 146-148°C (4 mm). Infrared spectrum (ν, cm^{-1}): 1030, 1070, 1090, 1120 (O–C–O). PMR spectrum (δ, ppm): 4.0 (4H, $O-CH_2$), 5.95 s (1H, CH), 6.2 s (2H, $O-CH_2-O$), 7.35 m (3H, Ar). Found: C 61.86; H 5.02%. $C_9H_{10}O_4$. Calculated: C 61.90; H 5.15%.

2-(4-Nitrophenyl)-1,3-dioxolane (IIc), yield 92%, mp 150° (from CCl_4). Infrared spectrum (ν, cm^{-1}): 1525, 1360 (NO_2); 1075 (O–C–O). PMR spectrum (δ, ppm): 4.0 s (4H, OCH_2), 5.8 s (1H, CH), 7.9 m (4H, Ar). Found: C 54.75; H 4.50; N 6.86%. $C_9H_9NO_4$. Calculated: C 55.38; H 4.65; N 7.18%.

2,2-Dimethyl-1,3-dioxolane (IIe), yield 55%, bp 91-92°, cf. [6].

Methyl Ester of α-Nitro-β-(3,4-methylenedioxyphenyl)acrylic Acid (IIIc). A mixture of 3.6 g (0.03 mole) of NAE, 5.8 g (0.03 mole) of (IIc), 7.65 g (0.075 mole) of Ac_2O, and 0.05 g of $ZnCl_2$ was heated for 14 h in a N_2 stream at 135°. The residue was diluted with 15 ml of CCl_4 and washed twice with water. The solution was dried over $MgSO_4$ and evaporated in vacuo to give 6.6 g of a viscous oil, which, based on the PMR data [1], is devoid of impurities and represents a 1.2 : 1 mixture of the Z and E isomers of (IIIc). The more stable Z isomer slowly crystallizes from this mixture, mp 133-134° ($CHCl_3$–hexane). Found: C 52.85; H 3.66; N 5.86%. $C_{11}H_9O_6N$. Calculated: C 52.77; H 3.57; N 5.90%.

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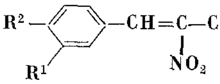
TABLE 1. α-Nitrocinnamic Esters  (IIIa-d)

Ester	Catalyst	Time, h	T., °C	Yield of (III), %*
(IIIa)	$ZnCl_2$	5	150	49 (33†)
(IIIa)	TsOH	10	150	(21†)
(IIIb)	$ZnCl_2$	16	110–135	89
(IIIb)	$AlCl_3$	18	135	81
(IIIb)	TsOH	20	135	Tarring
(IIIb)	–	7	110–160	99‡ [1]
(IIId)	$ZnCl_2$	14	140	93
(IIIc)	$ZnCl_2$	20	140	0

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*Crude mixture of Z and E isomers.

†After distillation (bp 140-145°C (3 mm)).

‡ 4-Methoxybenzaldehyde diethyl acetal [1] was used.

Esters (IIIa, b) were obtained in a similar manner (see Table 1), which in their properties are identical with the esters described in [1].

CONCLUSIONS

2-Phenyl-1,3-dioxolane, and its derivatives with donor substituents in the aromatic ring, react with the methyl ester of nitroacetic acid in Ac_2O medium and in the presence of acid catalysts to give the methyl esters of the corresponding α-nitrocinnamic acids.

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