An Unusual Reaction of 2,5-Dimethylfuran with Carbonyl Compounds: High-pressure Ene Reaction?

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High-pressure reaction of 2,5-dimethylfuran with various carbonyl compounds: butyl glyoxylate, chloral, methyl mesoxalate, methyl pyruvate, and 2,3-*O*-isopropylidene-D-glyceraldehyde, gives the adducts (**4**), probably the products of an ene reaction.

In the course of high-pressure studies of the Diels–Alder reaction with furan derivatives[1] it was found that the reaction of 2,5-dimethylfuran (**1**) with butyl glyoxylate (**2a**), an active carbonyl dienophile,[2] is inconsistent with a [4 + 2] cycloaddition pathway. The reaction of (**1**) with (**2a**) under high-pressure conditions† (8 kbar,‡ room temp., CH_2Cl_2 as solvent, 20 h) afforded only the product (**4a**) instead of the expected cycloadduct (**3**).

The structure of (**4a**)§ (determined from the ^{1}H n.m.r. and i.r. spectra and elemental analysis) suggested that the high-pressure reaction of (**1**) with (**2a**) is an ene type reaction.[4] A concerted mechanism is generally assumed for such reactions,[5] and this mechanism could apply to the investigated reaction, provided that 2,5-dimethylfuran can exist in form (**5**); in this case the transition state can be formulated as in (**6**).¶

If the reaction proceeds under high pressure according to the ene reaction pathway, then 2,5-dimethylfuran would be expected to react in form (**5**) with (**2a**) under atmospheric

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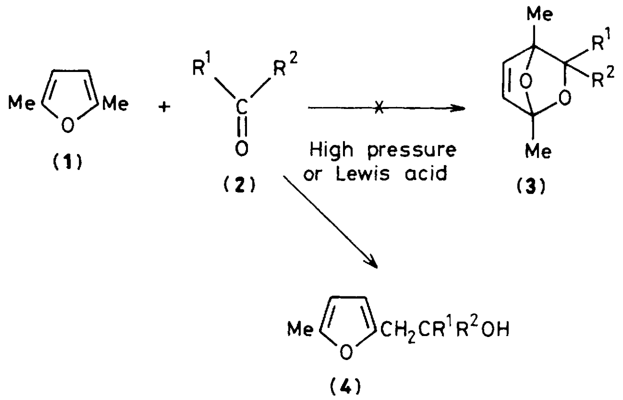
† For the high-pressure experiments we used the piston-cylinder type apparatus described earlier.[3]

‡ 1 bar = 10^5 Pa.

§ Satisfactory analyses and spectral data were obtained for all new compounds. ^{1}H N.m.r. (100 MHz, $CDCl_3$): (**4a**) δ 5.98 (m, 2H, *H*-furan), 4.45 (m, 1H, C*H*OH), 4.25 (t, 2H, CH_2O), 3.08 (d, 2H, C*H*$_2$-furan), 3.05 (d, 1H, OH), 2.27 (s, 3H, C*H*$_3$-furan), 1.80—1.15 (m, 4H, CH_2–CH_2), and 0.95 (t, 3H, C*H*$_3$–C).

¶ Preliminary results of the reaction of ethyl mesoxalate with 2,5-di[$^2H_3$]methylfuran, carried out in two different solvents (methylene chloride and toluene) under high pressure, are not inconsistent with the postulated mechanism. According to the ^{1}H n.m.r. spectra, deuterium atoms are distributed in the reaction product among all possible positions: 3 and 4 in the furan ring and in the hydroxy group; moreover there are signals derived from protons of the methylene and methyl groups. We found quantitative differences in deuterium and hydrogen distribution between reactions carried out in methylene chloride and toluene.



a; $R^1 = H, R^2 = CO_2Bu^n$
b; $R^1 = H, R^2 = CCl_3$
c; $R^1 = R^2 = CO_2Me$
d; $R^1 = Me, R^2 = CO_2Me$
e; $R^1 = H, R^2 = -\overline{CHCH_2OCMe_2O}$

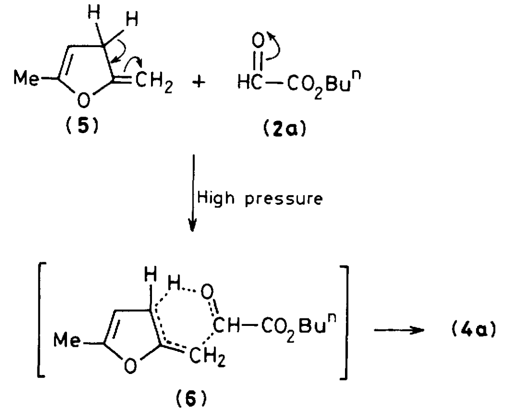
Table 1. High-pressure reactions of (**1**) with (**2a**—**e**).

Enophile	Solvent	Temp. /°C	Pressure /kbar	Yield[a] /%
(**2a**)	CH_2Cl_2	25	8	50
(**2a**)	PhMe	50	11	58
(**2b**)	CH_2Cl_2	25	10	38
(**2c**)	CH_2Cl_2	25	10	80
(**2c**)	PhMe	25	11	52
(**2d**)	CH_2Cl_2	55	20	30
(**2e**)	CH_2Cl_2	55	20	22

[a] Yield of isolated products.

pressure in the presence of Lewis-acid type catalysts. In fact, (**4a**) was obtained in reactions carried out at room temperature, in CH_2Cl_2, in the presence of $SnCl_4$ or $ZnCl_2$, in a yield of 39 and 29%, respectively.

Several high-pressure reactions were carried out using four other enophiles: chloral (**2b**),[6] dimethyl mesoxalate (**2c**),[2] methyl pyruvate (**2d**),[3] and 2,3-*O*-isopropylidene-D-glyceraldehyde (**2e**)[7] (Table 1).



In the case of the enophiles (**2d**) (steric hindrance) and (**2e**) (lack of the activating alkoxycarbonyl group), formation of the respective products, (**4d**) and (**4e**), required more drastic conditions of pressure and temperature. For these enophiles the product yields were low; it is stressed, however, that no reaction with (**1**) occurred under atmospheric pressure in the presence of Lewis-acid type catalysts.

Further work is needed to confirm that these are ene-type reactions, although we feel it is most likely that they are.

This work was supported by a Polish Academy of Sciences grant.

Received, 13th May 1983; Com. 610

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