Tetrahedron Letters No. 25, pp 2101 - 2104, 1976. Pergamon Press. Printed in Great Britain.

THE REACTION OF FURAN DERIVATIVES WITH AZO-BIS-ISOBUTYRONITRILE

A. Gandini* and J. Rieumont

Centro Nacional de Investigaciones Científicas, Apartado 6990, Habana, Cuba

(Received in USA 9 September 1975; received in UK for publication 10 May 1976)

The interaction of free radicals with furan has been studied previously, but only with alkoxy (1), benzoyl (2) and aromatic radicals (3-5). The addition reactions to give 2,5-dihydrofurans predominate, but in the case of the phenyl radicals (3-5) substitution at C-2 has been reported.

The mechanism of autoinhibition displayed by vinyl monomers containing the furan ring, such as vinyl 2-furoate (6-8), vinyl 2-furyl acetate (8), vinyl 2-furylpropionate (8) and vinyl 2-furyl acrylate (8), is not well understood. Neither is the strong retarding effect shown by these monomers (6-9) and by other furan derivatives such as furan itself, 2-methyl furan, phenyl 2-furoate and 2-furaldehyde (7-11) on the radical polymerization of common monomers, nor the role of 2-furfuryliden carbonyl compounds as radical inhibitors (12).

In order to gain a closer insight into these problems, we carried out a study of the reaction of several furan derivatives with azo-bis-isobutyronitrile (AIBN), one of the most widely used initiators in radical polymerization.

Reactions were conducted by dissolving the AIBN in the furan derivative (molar ratio 1:4 to 1:1), purging the solution with nitrogen and heating it at 70°C for 40-60 hours. The experiments with furan and with 2-methyl furan were carried out in a steel bomb, the others in a glass vessel provided with a reflux condenser. Products were isolated by standard procedures after eliminating the unreacted furan derivatives and the tetramethylsuccinodinitrile in a vacuum line. The compounds studied were furan (F), 2-methyl furan (MF), 2-furaldehyde (FA), ethyl 2-furoate (EF), vinyl 2-furoate (FV), 2-vinyl furan (VF) and vinyl 2-(5-methyl) furoate (MVF).

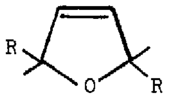
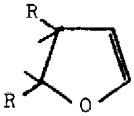
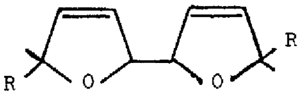
---

*Present address: Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6

Global yields varied from 40 to 70% depending on the derivative used and on the reaction time. The common feature of these systems, with the exception of that involving VF, was the production of 4,5- and 2,5-dihydrofuranic structures, the latter being favoured.

An example of the products obtained is given in the following Table:

F + AIBN (R = 2-cyano-2-propyl; yields and analysis are average of 3 runs)

PRODUCT (yield)	CHARACTERIZATION
 (32%)	m/e 204, 136, 68; ν (KBr, cm^{-1}) 2950 (CH$_3$), 2240 (CN), 1085 (C-O-C), 750 (C=C-H); δ (CDCl$_3$, TMS, ppm) 6.20 (s, H-3 and H-4), 4.80 (s, H-2 and H-5), 1.35 (d, C$\underline{H}_3$), 1:1:6; analysis: found C 70.63, H 7.95, N 13.66 (calc. C 70.59, H 7.84, N 13.72). Two stereoisomers observed by glc.
 (10%)	m/e 204, 136, 68; ν (liq., cm^{-1}) 2950 (CH$_3$), 2240 (CN), 1620 (C=C), 1200 (C-O-C); δ (CDCl$_3$, TMS, ppm) 6.50 (t, H-2), 5.05 (t, H-3), 4.28 (d, H-5), 2.96 (m, H-4), 1.37 (d, C$\underline{H}_3$), 1:1:1:1:12; analysis: found C 70.48, H 7.80, N 13.79 (calc. C 70.59, H 7.84, N 13.72). Two stereoisomers observed by glc.
 and other "dimers" (17%)	m/e 272, 204, 136, 68; the IR and NMR spectra indicate the presence of both 2,5- and 4,5-dihydrofuranic rings (see above) but the former predominate. The integrated nmr signals always gave H$_{ring}$: H$_R$ = 2:3. Analysis: C 70.66, H 7.29, N 10.12 (calc. C 70.59, H 7.35, N 10.29).

MF, FA and EF behaved similarly, no substitution product being obtained in any of the reactions studied.

FV only gave oligomers ($\overline{M}_n$ = 600-900, vapour pressure osmometry), consisting of vinyl-type and dihydrofuranic units, sealed at each end by a 2-cyano-2-propyl group (R). After four reprecipitations the product contained appreciable amounts of residual vinyl double bonds (ν 1640 cm^{-1} and characteristic pattern around δ 5 ppm for $=CH_2$) and of dihydrofuranic structures (δ 6.0 ppm for H-3 and H-4 in 2,5- and weaker signals for protons in 4,5-dihydrofuran rings). The "normal" furanic units were more frequent in the product: δ 7.4 (H-5), 7.0 (H-3), 6.35 (H-4), 5.2 ($C\underline{H}$) and 2.0 (CH_2) ppm, 1:1:1:1:2. The end groups give ν 2240 cm^{-1} (CN) and δ 1.3 ppm ($C\underline{H}_3$) integrating to give ∿ 2R *per* oligomer molecule. This structural interpretation disagrees with that given by Morita *et al*. (7), who claimed a simple vinyl-type propagation in the polymerization of this monomer with up to 25% AIBN. To substantiate their conclusion they reported IR and NMR spectra (which coincide with ours) which are not consistent with the normal structure they proposed, but rather confirm our alternative suggestion. We prepared a standard polyFV by esterifying polyvinylalcohol with furoyl chloride. As expected, this polymer did not show any anomalous features, i.e. its spectra did not indicate the presence of any residual double bond or of any dihydrofuranic rings.

VF, on the other hand, gave oligomers whose structure bore no evidence of dihydrofuranic units or of residual vinyl groups, *i.e.*, in this system the propagation only took place through the vinyl bond. It appears that the presence of this conjugated double bond "protects" the ring as long as there is monomer present, by diverting the radicals' attack towards itself.

MVF polymerized to give products ($\overline{M}_n$ = 2000-4000) which did not contain detectable amounts of double bonds or of dihydrofuranic structures. Probably,the presence of a methyl group at C-5 hindered somewhat the entrance of the attacking radicals onto the ring making the vinyl polymerization easier and the concentration of dihydrofuranic units lower.

The present findings are in agreement with previous work (1-5) as to the formation of 2,5-dihydrofurans and extend the validity of this observation to a series of 2-substituted furans. However, the 2-cyano-2-propyl radicals are less specific in their mode of addition to the furan ring since they can also give 4,5-dihydrofurans.

We also carried out experiments with *t*-butyl peroxide as a radical source, but the products obtained were brown resins with no detectable presence of either furan or dihydrofuran rings.

As for the autoinhibition and retardation by furan derivatives in radical polymerization, it seems plausible to conclude that the C-5 ring position constitutes a very competitive addition site for the propagating species because it can produce the stabilized allylic-type radical I which will deter normal propagation and couple with another radical to form dihydrofuranic structures.

(I)

1) K.E. Kolb and C.L. Wilson, Chem. Comm., 1966, 272.
2) K.E. Kolb and W.A. Black, ibid., 1969, 1119.
3) L. Benati, N. La Barba, M. Tiecco and A. Tundo, J. Chem. Soc. B, 1969, 1253.
4) L. Benati, M. Tiecco, A. Tundo and F. Taddei, ibid., 1970, 1443.
5) L. Benati, C.M. Canaggi, M. Tiecco and A. Tundo, J. Het. Chem., 9, 919 (1972).
6) G. Hardy and J. Szita, Acta Chim. Acad. Sci. Hung., 15, 339 (1958).
7) I. Morita, Y. Kato, B. Kamo and S. Furusawa, Chuo Kaygaku Rikag. Kiyo, 16, 139 (1973).
8) A. Gandini and J. Rieumont, unpublished results.
9) G. Hardy, Acta Chim. Acad. Sci. Hung., 17, 121 (1958).
10) J.T. Clarke, R.D. Howard and W.H. Stockmayer, Makromol. Chemie, 44/46, 427 (1961).
11) S.D. Savranskaya, S.N. Trubitsyna and M.A. Askarov, Vysokomolekul. Soedin., Karb. Vysokomolekul. Soedin., Sb. Statei, 1963, 20.
12) C. Hernandez, N. Galego, N. Llerandi and A. Gandini, Rev. CENIC, Cienc. Fis. (Cuba), 5, 217 (1974).