RELATIVE REACTIVITIES OF DOUBLE BONDS IN COMPOUNDS WITH FUNCTIONAL GROUPS TOWARDS THE DIMETHYLCYANOMETHYL RADICAL

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It is known that the decomposition of azobisisobutyronitrile (AIBN) in saturated hydrocarbons results in the preferential formation of the recombination product of dimethylcyanomethyl radicals, viz., tetramethylsuccinodinitrile R—R [1, 2]. When the decomposition is carried out in solution in an α-olefin (isobutylene or 1-heptene), the yield of R—R is substantially reduced with a corresponding increase in the products of the addition of $R^{\bullet}$ to the double bond of the olefin. The reactivity of the double bonds in olefins towards dimethylcyanomethyl radicals may be assessed by the decrease in the yield of R—R when the decomposition of AIBN is effected in the presence of an olefin [1, 2].

We have now examined the reactivity of some unsaturated compounds, most of which contained functional groups of various types, towards the dimethylcyanomethyl radical. The compounds examined were cyclopentene, norbornene, cyclopentadiene (CPD) condensation products, furfural, maleic anhydride (MA), and glycidyl methacrylate (GMA) (Tables 1 and 2).

The reactions of unsaturated compounds with AIBN were carried out at 80-90°C until it had decomposed completely, in solution in toluene, a mixture of toluene and dimethylformamide (DMF), or in DMF, depending on the solubility of the starting material. The proportion of dimethylcyanomethyl radicals reacting by addition to the double bonds was assessed by the decrease in the yield of the recombination product R—R as measured by chromatography. The molar ratio of the unsaturated compound to AIBN was in most cases 3—5. In the case of the adduct (V), it was shown that changing this ratio from 3 to 5 had little effect on the yield of R—R (65 and 60% respectively).

The experimental yields of R—R are given in Tables 1 and 2.

TABLE 1. Yields of R—R in the Decomposition of AIBN in the Presence of Unsaturated Compounds (1 mmole of AIBN in 5-10 ml of solvent, 80°C, 8-13 h)

Compound; mmoles	Solvent	Yield of R—R, %
-	Heptane, 4 mmoles	94*
-	Toluene	80
-	DMF	84
1-Heptene; 4	-	55*
1-Heptene; 5	Toluene	60
Isobutylene; 4	-	50*
2-Butene; 4	-	79*
Cyclooctene; 3.7	Chlorobenzene	82
Cyclopentene; 3.6	Chlorobenzene	80
Norbornene; 4	Toluene	72.5
Norbornene; 4	DMF	70.5
Maleic anhydride; 5	Toluene	23
Maleimide; 4	DMF	41
N-Phenylmaleimide; 3	Toluene + DMF (1:1)	42.5
Furfural; 5	Toluene	30

*Data from [1, 2].

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TABLE 2. Yields of R—R in the Decomposition of AIBN in the Presence of Unsaturated Adducts with Functional Groups (4 mmoles)* [1 mmole of AIBN in 5-10 ml of solvent, 80-90°C, 13 h]

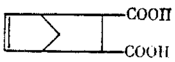
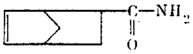
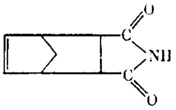
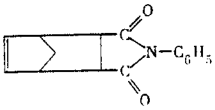
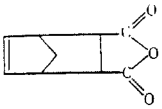
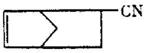
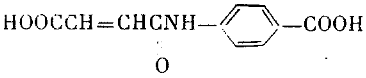
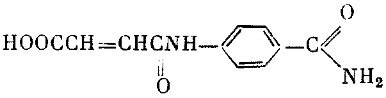
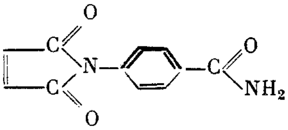
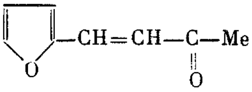
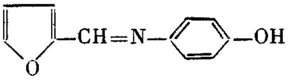
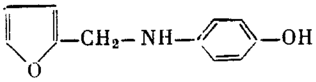
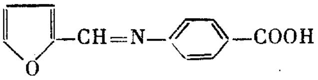
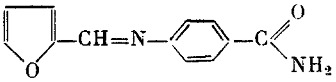
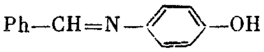
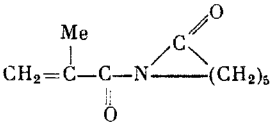
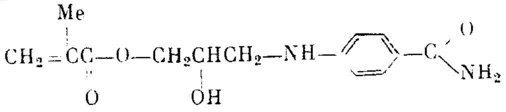
Adduct		Solvent	Yield, R-R,** %
number	formula		
(I) ***		Toluene-DMF (1 : 1)	44.5
(II)		DMF	51
(III)		Toluene-DMF	54
(IV)		Toluene-DMF	55
(V)		Toluene	60.5
(VI)		Toluene	65
(VII)		DMF	34
(VIII)		DMF	40.5
(IX)		DMF	35
(X)		Toluene	25
(XI)		Toluene-DMF	24
(XII)		Toluene-DMF	36
(XIII)		DMF	26
(XIV)		DMF	29
(XV)		DMF	63
(XVI)		Toluene—DMF	19.5

TABLE 2 (continued)

Adduct		Solvent	Yield, R—R,*** %
number	formula		
(XVII)		DMF	31

*Compounds (V), (VI), and (X) were taken in amounts of 5 mmoles, and (II) 3 mmoles.
**Mean of 2-3 experiments.
***Adducts (I)-(VI) have the endo-configuration.

When the decomposition of AIBN was carried out in heptane or CCl_4, the yields of R—R were 94-96% [1-3], and in toluene, 87% [3]. According to our results, the yield in chlorobenzene was 96%, and in toluene or DMF, 80-84%. Cyclopentene and cyclooctene were of low reactivity in trapping dimethylcyanomethyl radicals, being similar to 2-butene in this respect. The greatest reactivity was shown by norbornene, and this activity was increased even further when electron-acceptor substituents were introduced into the molecule [Table 2, (I)-(VI)], but the increased reactivity does not appear to be due to the inductive effect of the functional groups, since they are fairly remote from the double bonds. Wasserman [4], in a study of the mechanism of formation of the Diels-Alder adduct, took into account the definite contribution of nonvalent (dispersive and deformational) interactions in favoring the stability of the transition state. This facilitates the endo-orientation of the reaction components, favoring the formation of the endo-adduct, which is usually the main product in the diene synthesis. It may be assumed that it is this type of interaction of the functional groups which is responsible for their activating effect on the double bond in the adducts. Evidence for this assumption is provided by our observation that the double bonds in the exo-adducts of cyclopentadiene with maleic acid and N-phenylmaleimide are less reactive towards AIBN than the endo-adducts (in brackets): yield of R—R 56 (44) and 69 (52) %, respectively. Maleic anhydride and furfural (Table 1) trap dimethylcyanomethyl radicals almost quantitatively. The yield of R—R found in this case (20-30%) results from the 'cell' effect [2]. The high reactivity of the double bonds in furfural is in accordance with the results of an examination of the reactions of furans (including furfural) with AIBN in order to establish the reason for the inhibitory effects of these compounds on the radical polymerization of monomers [5]. As will be seen from Table 2, the adducts (VII)-(XIV), obtained from maleic anhydride and furfural, show high reactivity in trapping dimethylcyanomethyl radicals, like the starting materials. In the case of the condensation products of furfural with p-aminophenol (XI), p-aminobenzoic acid (XIII), and p-aminobenzamide (XIV), the radical can add either to the double bonds of the furan ring or to the azomethine bond —CH═N—. The product (XV) demonstrates the ability of the latter to react with AIBN. α-Olefins bearing electron-acceptor polar groups adjacent to the double bond (XVI and XVII) have much more reactive double bonds towards free radicals than the unsubstituted α-olefins (1-heptene and isobutylene) (Table 1).

EXPERIMENTAL

Bicyclo[2.2.1]-5-heptene-2,3-dicarbonic anhydride (V) and bicyclo[2.2.1]-5-heptene-2-carbonamide (II) were obtained as described in [6]. Mp of (V), 164-165°C [6]. Yield of (II) 55%, mp 186-188°C. Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid (I) was obtained by hydrolyzing the anhydride (V) with boiling water, yield 85%, mp 184-186°C. Bicyclo[2.2.1]-5-heptene-2,3-dicarbonimide (III) was obtained in 85% yield by treating (V) with an excess of 28% aqueous ammonia, followed by boiling for 3 h, mp 188°C [7]. Bicyclo[2.2.1]-5-heptene-2-carbonitrile (VI) was synthesized as in [8].

Furfurylideneacetone (X) was obtained as in [9], and furfurylidene-p-aminophenol (XI), furfurylidene-p-aminobenzoic acid (XIII), and furfurylidene-p-aminobenzamide (XIV) as described in [10]. Reaction of maleic anhydride with p-aminobenzoic acid and p-aminobenzamide in boiling acetone gave the acids (VII) and (VIII) respectively. The N-arylmaleimide (IX) was obtained from (VIII) as described in [11]. Benzylidene-p-aminophenol (XV) was obtained as for the Schiffs base from furfural [10], mp 186-187°C.

Reaction of GMA [12] with p-aminobenzamide in boiling water with the addition of hydroquinone as polymerization inhibitor gave (XVII), mp 104-107°C.

The reactions of unsaturated compounds with AIBN were carried out in solution in sealed glass ampuls, under argon. The ampuls were thermostatted at 80°C for 8-13 h. Tetramethylsuccinodinitrile (R–R) was determined quantitatively on an LKhM-80 chromatograph, column length 2.5 m, carrier Chromaton N-super, liquid phase 5% SE-30, evaporator temperature 300°C, carrier gas nitrogen, flow rate 1.8 liter/h. The accuracy of determination of R–R was 5%.

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CONCLUSIONS

1. The relative reactivities of the double bonds in some unsaturated compounds towards dimethylcyanomethyl radicals have been determined.

2. Norbornenes with electron-acceptor substituents (bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid and its anhydride and imide, and bicyclo[2.2.1]hept-5-ene-2-carbonamide) were more reactive towards these radicals than unsubstituted norbornene.

3. The condensation products of maleic anhydride and furfural with p-aminobenzoic acid and its amide, p-aminophenol, etc. are as reactive as acceptors of dimethylcyanomethyl radicals as the original maleic anhydride and furfural.

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