Initiation Mechanisms in Radical Polymerization: Reaction of t-Butoxy Radicals With Allyl Acrylate and with Diallyl Ether

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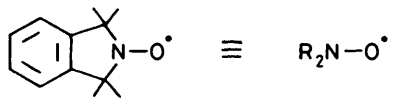
The radical trapping technique employing 1,1,3,3-tetramethyl-1,3-dihydroisoindol-2-yloxyl (**1**) as a scavenger has been used to study the reaction of t-butoxy radicals with allyl acrylate and with diallyl ether. With allyl acrylate, extensive H-abstraction as well as addition to both allyl and acryloyl double bonds was observed whereas with diallyl ether, the only products obtained were derived exclusively from H-abstraction.

In a previous paper[1] we described the use of the radical scavenger 1,1,3,3,-tetramethyl-1,3-dihydroisoindol-2-yloxyl (**1**) to study the complex pattern of reaction of t-butoxy radicals with allyl methacrylate (**2a**). In this paper we report the results obtained with the related monomers, allyl acrylate (**2b**) and diallyl ether (**2c**).



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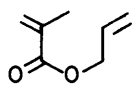

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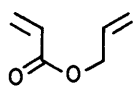

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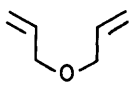


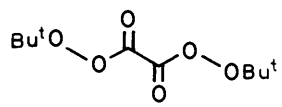
(2c)

Compounds (**2a**) and (**2b**) both have potential as monomers or comonomers for commercial two-stage polymerization in which linear polymers are produced in a preliminary process and, following fabrication, are later crosslinked to thermoset resins. Monomers (**2a**), (**2b**), and (**2c**) all have potential as crosslinking agents.[2] Attempted homopolymerization of monomer (**2b**) by conventional free-radical techniques generally leads directly to insoluble crosslinked polymers;[3] however, there are reports of a soluble polymer being produced by the bulk homopolymerization of monomer (**2b**) with benzoyl peroxide.[4] The product is thought to be a linear polymer containing some cyclized monomer units. Monomers (**2a**) and (**2b**) have frequently been recommended as comonomers with methyl and other alkyl methacrylates for the purpose of enhancing properties, such as impact resistance of coatings and contact lenses; indeed they copolymerize readily by free-radical initiation as evidenced by reactivity ratios, *e.g.* for the copolymerization of monomer (**2b**) with methyl acrylate (MA); $r_{(2b)} = 0.33$, $r_{MA} = 0.52$.[5] However, diallyl ether, (**2c**), has not been homopolymerized and even in free-radical copolymerization, very low reactivity ratios are exhibited, as with acrylonitrile (AN) $r_{(2c)} = 0.01$, $r_{AN} = 4.9$ and with 2-methyl-5-vinylpyridine (MVP), $r_{(2c)} = 0.0$, $r_{MVP} = 80$.[6] Brace has recently shown that both addition and cyclization can be induced in diallyl ether (**2c**) by free-radical initiation under special conditions.[7]

Clearly a better understanding of the reaction of these monomers with free radicals is desirable. In theory they are capable of undergoing a number of competing reactions, *e.g.* addition to the double bond, H-abstraction, cyclization; a detailed knowledge of the relative importance of these is necessary for a complete understanding of the defect groups and structure of polymers and copolymers produced from these monomers. The radical trapping method used in this work has been described previously.[8–10]

Results and Discussion

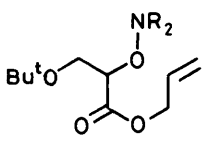
t-Butoxy radicals were generated by thermolysis of di-t-butyl peroxalate (**3**). Thus, treatment of monomer (**2b**) or (**2c**) with compound (**3**) (0.08M) in the presence of a 10% excess of radical



(3)

trap (**1**) (0.18M) at 60 °C afforded a mixture of alkoxy amines [see compounds (**4**)—(**15**) and Schemes 1 and 2] which was analysed quantitatively by h.p.l.c., separated, and characterised by ^{13}C and ^{1}H n.m.r. spectroscopy, by analytical data, and by comparison with similar products obtained from (**2a**) and described previously.[1] The reaction schemes and product yields for (**2b**) and for (**2c**) are illustrated in Schemes 1 and 2 respectively. A general comparison of product yields for monomers (**2a**),[1] (**2b**), and (**2c**) is given in Table 1.

The outstanding feature in the overall pattern of reactivity is the predominance of hydrogen abstraction. With monomer (**2c**) it constitutes the entire process and with monomer (**2b**) it constitutes over 80% of the reaction. In the allyl methacrylate system (**2a**), the corresponding percentage was 49%.[1] Abstraction is, of course, a favoured process at allylic groups *e.g.* Kwart *et al.*[11] found only hydrogen-abstraction products in the radical acetoxylation of allylbenzene and Sustmann *et al.*[12] could detect no addition products by e.s.r. spectroscopy in the reaction of t-butoxy radicals with crotononitrile. In addition, the presence of an adjacent ether-oxygen atom also enhances the ease of abstraction at a C–H group due to the donation of electron density from the oxygen lone pair into the antibonding orbital of the C–H bond (see Figure). This effect is well illustrated by the experimental investigation of hydrogen abstraction in a range of cyclic and linear ethers,[13,14] is in agreement with theoretical studies,[15] and is reflected in gas-phase bond-dissociation energies[16] which indicate that an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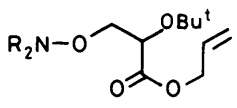
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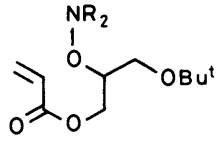
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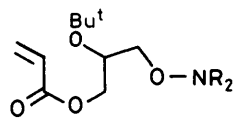
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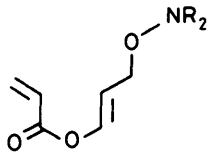
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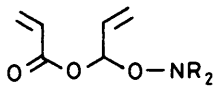
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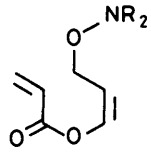
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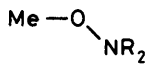
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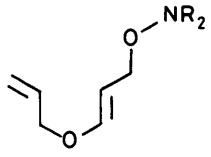
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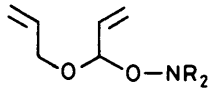
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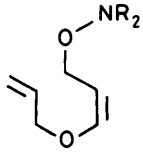
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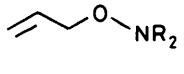

(15)

R_2N = 1,1,3,3-tetramethyl-1,3-dihydroisoindol-2-yl

adjacent ether-oxygen can weaken the C–H bond by as much as 40 kJ mol^{-1}. The importance of the dihedral angle between the C–H bond and the lone pair on the oxygen has been discussed by several groups.[13,17,18] Hydrogen abstraction will occur at a maximum rate when the angle is least (in practice, examples with angles of less than 30° are unlikely to be found) and at a minimum rate when the angle is 90°.

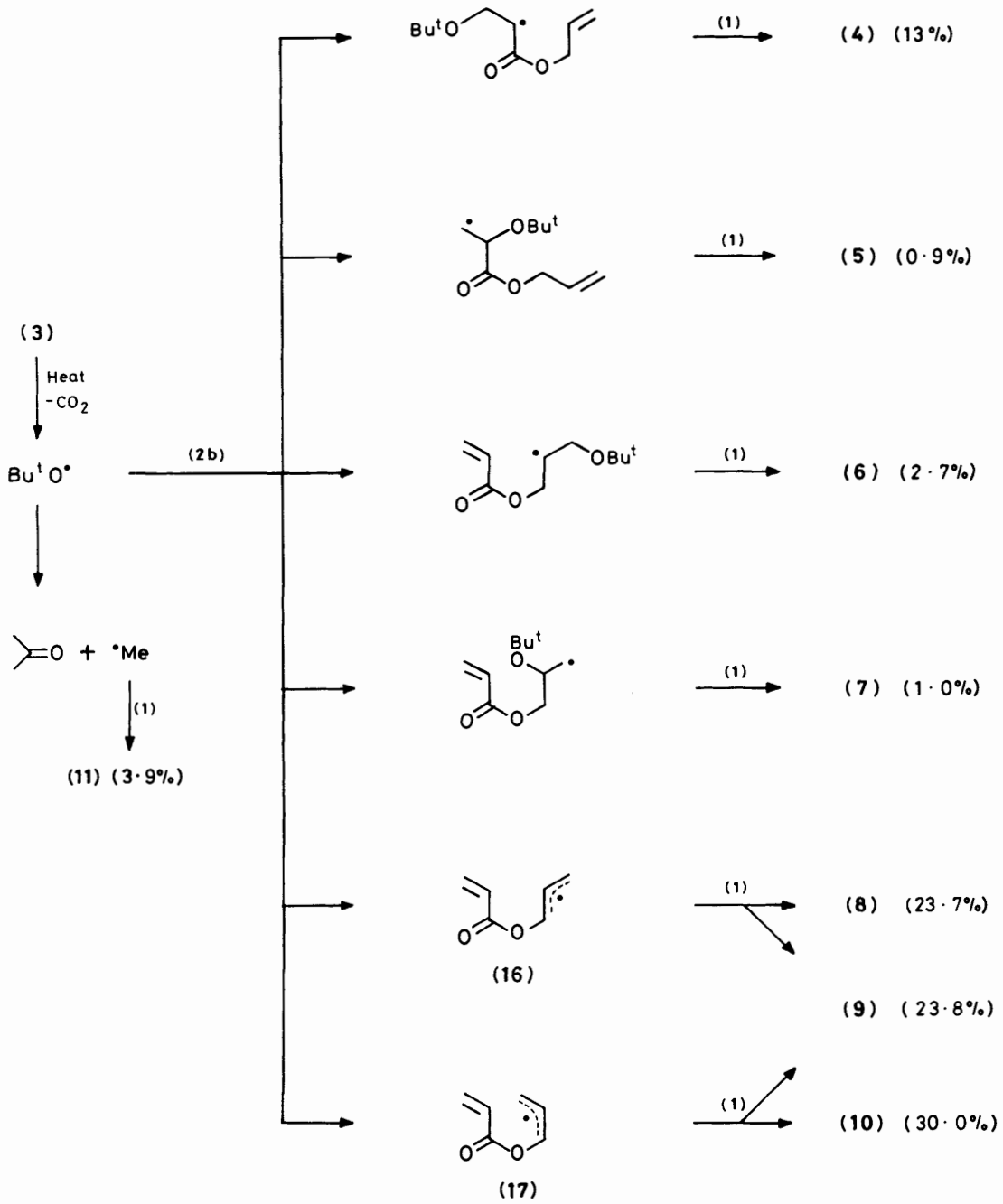
The relative reactivity of the various sites in the different substrates towards t-butoxy radicals can be obtained by comparing the yields of the various products with the yield of compound (**11**) plus any other product derived from methyl radicals. This assumes * negligible solvent effects on the rate of β-scission of t-butoxy radicals, a process that can serve as a common 'radical clock' for the three substrate reactions.[9] Rate constants for product formation, based on the rate constant for β-scission of t-butoxy radicals,[20] for monomers (**2a**) and (**2b**) and lower limits for monomer (**2c**) are given in Table 2 along with values calculated from previously published data for the reactions of the monomers methyl acrylate (MA)[21] and methyl methacrylate (MMA)[8] with t-butoxy radicals under similar reaction conditions. Only a minimum value can be recorded for monomer (**2c**) since none of product (**11**) was observed in the h.p.l.c. trace. The stated values, and those in Table 3, are based on our estimate of the maximum possible yield of (**11**) that could have escaped detection. The reactivity at the reactive sites in the acryloyl group of monomer (**2b**) and (MA) and in the methacryloyl group of monomer (**2a**) and (MMA) are remarkably independent of the replacement of methyl by allyl as the ester group. The values for the head addition process in (**2b**) and (MA) are comparable, within experimental error, since these products are in the low yield category (<1%). Similar independence is displayed by both addition and abstraction processes in the allyl group of monomers (**2a**) and (**2b**). However, reactivity at the allyl group of monomer (**2c**) is greatly enhanced and the only process observed is hydrogen abstraction; possible products from addition processes were below the limit of detection. This difference is presumably due to the donation of electron density from the ether-oxygen lone pair to the adjacent C–H bond being more important in the case of

Table 1. Product yields[a] from the reaction of t-butoxy radicals with allyl acrylate, allyl methacrylate,[1] and diallyl ether

Reaction mode	Allyl acrylate	Allyl methacrylate	Diallyl ether
Acryloyl position			
Tail addition	13.0	32.0	
Head addition	0.9	0	
α-Methyl abstraction		13.5	
Allyl position			
Tail addition	2.7	3.0	0
Head addition	1.0	1.0	0
Abstraction	77.5	48.0	100
Abstraction:addition	21	12	>300
Other processes			
β-Scission; trapped methyl	3.9	2.0	<0.3
Methyl tail addition	0	0.1	0

[a] Expressed as percentages except for abstraction:addition which is a ratio.

* Walling and Wagner have shown[19] that the rate of β-scission (relative to hydrogen abstraction) undergoes a small increase with increasing polarity. However, in the present study the solvents (substrates) have very similar polarities so that rate differences are expected to be extremely small.



Scheme 1. Reaction pathways for allyl acrylate

monomer (**2c**). The reduced electron density on the corresponding (ester) oxygen in monomers (**2a**) and (**2b**) leads to less C–H bond weakening and a lower reactivity.

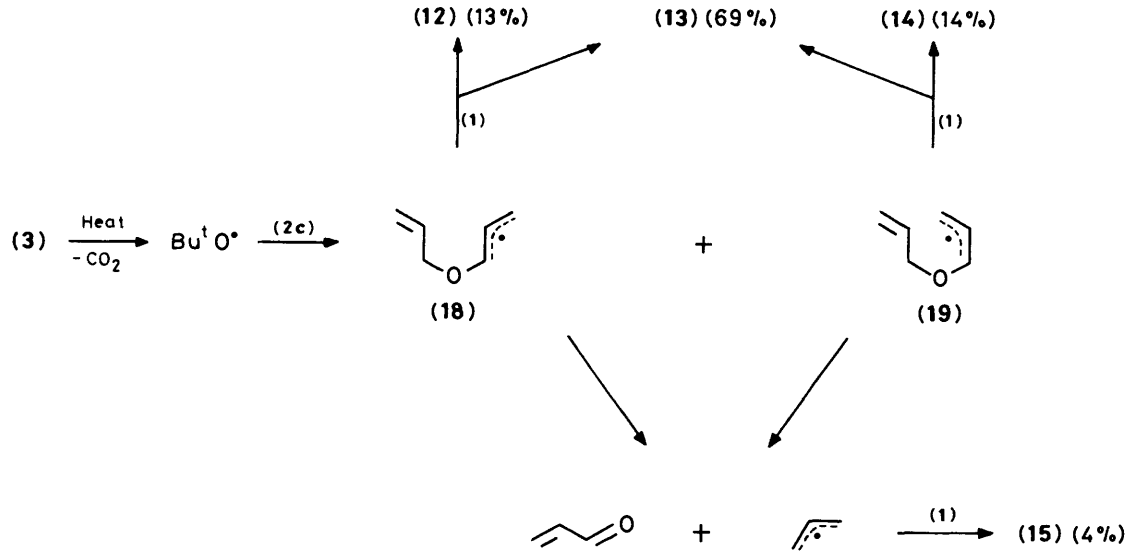
The slightly higher ratio of abstraction to addition in the allyl moiety of monomer (**2b**) compared with monomer (**2a**) (Table 1) may be due to a conformational effect. The presence of the methyl group in monomer (**2a**) may result in the dihedral angle between the ether-oxygen lone pair and the adjacent C–H bond of the allyl group being in a less favourable position for accelerating abstraction than in monomer (**2b**).

The pattern of the trapping process following hydrogen abstraction from the allyloxy moiety shows interesting variations. Product yields and some product ratios are shown in Table 3. The ratio of products arising from coupling of nitroxide (**1**) at the α-position to coupling at the γ-position [*e.g.* the ratio of compound (**9**) to compounds (**8**) and (**10**)] increases from 0.44 for monomer (**2b**) to 2.56 for monomer (**2c**). There are two factors which might affect this ratio. First, the oxygen atom in radicals (**18**) and (**19**), by virtue of its mesomeric effect, may increase the electron density on the adjacent (α) carbon atom thereby facilitating coupling with the electrophilic[22,23] nitroxide (**1**). Clearly this effect will be less important in radicals (**16**) and (**17**) where the mesomeric effect is weaker. Secondly, it is possible that the most stable rotamers for monomers (**2a**), (**2b**), and (**2c**) would have different spatial arrangements of the relevant atoms (we suggested above that even the very similar monomers (**2a**) and (**2b**) may differ in conformational preferences). This would result in different proportions of

Table 2. Rate Constants[a] for product formation using the β-scission of t-butoxy radicals as a radical clock[b]

Reaction mode	Methyl[13] acrylate	Allyl acrylate	Diallyl ether	Allyl[1] methacrylate	Methyl[8] methacrylate
	$k/10^3$ l mol^{-1} s^{-1}				
Acryloyl position					
Tail addition	32	39		203	170
Head addition	0.5	3		0	0
Ester Me abstraction	5				9
α-Me abstraction				81	74
Allyl position					
Tail addition		8	0	19	
Head addition		4	0	7	
Abstraction (total)		238	>4 000	311	
Other processes					
Dimerization	5	0	0	0	3

[a] Rate constants at 60 °C for the reaction of t-butoxy radicals with substrate to products according to reaction mode. [b] Using rate constant for β-scission of 1.0×10^5 s^{-1}, as discussed previously.[14]



Scheme 2. Reaction pathways for diallyl ether

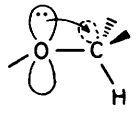


Figure.

initially formed allyl radicals as discussed previously.[1] Thus, the final ratio of (**12**):(**13**):(**14**) (for example) would depend on the ratio of (**18**):(**19**) and on the relative rates of trapping of these two radicals at the α- and γ-positions. This second factor is presumably also responsible for the variation in the observed *cis*:*trans* ratios (Table 3).

Allyl radicals (**18**) and (**19**) also underwent some β-scission to produce acrylaldehyde and allyl radicals, subsequently trapped as (**15**) (Scheme 2). In the absence of such an efficient radical trap as (**1**), this would clearly be an important reaction and may be part of the reason why monomer (**2c**) has not been homopolymerized with radical initiators.

Conclusion

Clearly, the radical trapping technique is an extremely powerful one for studying the initially formed radicals in the reactions of olefinic substrates with alkoxy radicals. Unfortunately, as discussed previously,[1] the highly efficient trapping of C-centred radicals by (**1**) precludes the simultaneous study of secondary radical reactions of interest such as cyclisations. In the present study, the radical trapping technique shows that the major reaction between t-butoxy radicals and monomers containing the allyloxy moiety is hydrogen abstraction. The range of products obtained illustrates the diverse initiation pathways, and reflects the possible end groups that may be produced in

Table 3. Products derived from allyl abstraction

Reaction mode	Allyl acrylate	Allyl[1] methacrylate	Diallyl ether
	%		
Trap add. α	23.8	26.0	69.0
Trap add. γ(*trans*)	23.7	8.5	13.0
Trap add. γ(*cis*)	30.0	13.0	14.0
Radical scission	0	0	4.0
cis:*trans*	1.3	1.6	1.1
α:γ(total)	0.44	1.17	2.56

polymers of allyl acrylate. With diallyl ether, hydrogen abstraction was the only reaction observed. The facile formation of an oxyallyl radical with a propensity to undergo radical scission, coupled with an expected slow rate of radical addition to double bonds, is suggested as a possible reason why diallyl ether cannot be homopolymerized by free radical means.

Experimental

Allyl acrylate and diallyl ether were obtained from Polysciences Inc. and Aldrich Chemical Co. Ltd. respectively. Allyl acrylate was purified by passage through a short column of basic alumina (activity I) followed by distillation under reduced pressure. Diallyl ether (99%) was used as received. General procedures for trapping experiments, details of h.p.l.c. and n.m.r. spectroscopic instrumentations and preparations of compounds (**1**) and (**3**) are given in our earlier report on the reaction of t-butoxy radicals with allyl methacrylate.[1]

The conditions used for h.p.l.c. analysis of both reaction mixtures were: flow 2.0 ml min^{-1}, 85% methanol in water over 45 min. However, for the reaction of diallyl ether, isolation of the products was carried out initially by reverse phase h.p.l.c. which afforded pure (**14**) and (**15**), and (**12**) and (**13**) as a mixture. These latter compounds were separated cleanly by flash column chromatography on Kieselgel 60, 230—400 mesh, using ethyl acetate–hexane, 1:24 as eluant.

2-Methoxy-1,1,3,3-tetramethyl-1,3-dihydroisoindole (**11**) was identified by comparison with an authentic sample. New compounds isolated (alkoxy amines) were characterized by the spectroscopic data listed below.

Allyl 3-t-Butoxy-2-(1,1,3,3-tetramethyl-1,3-dihydroisoindol-2-yloxy)propionate (**4**).—$\delta_C(CDCl_3)$ 25.1, 25.3, 29.7, 29.9 (4 × q, ring Me), 27.4 (q, Me_3C), 62.1 (t, Me_3COCH_2), 65.3 (t, $OCH_2CH{=}CH_2$), 67.7, 68.4 (s, C-1, C-3), 73.5 (s, Me_3CO), 85.8 (d, CHON), 118.5 (t, $OCH_2CH{=}CH_2$), 121.4, 121.6 (2 × d, C-4, C-7), 127.2 (d, C-5, C-6), 132.0 (d, $OCH_2CH{=}CH_2$), 144.9 (s, C-3a, C-7a), and 171.8 (s, C=O); $\delta_H(CDCl_3)$ 1.21 (s, 9 H, Me_3C), 1.40 (br s, 3 H), 1.42 (br s, 6 H) 1.58 (br s, 3 H, 4 Me), 3.62 (dd, 1 H, ^2J 9.4 Hz, ^3J 5.4 Hz, CH_2CHON), 3.71 (dd, 1 H, ^2J 9.4 Hz, ^3J 7.0 Hz, CH_2CHON), 4.61 (dd, 1 H, ^3J 5.4, 7.0 Hz, CH_2CHON), 4.67 (dt, 2 H, ^3J 5.8 Hz, ^4J 1.4 Hz, $OCH_2CH{=}CH_2$) 5.24 (ddt, 1 H, ^3J 10.4 Hz, $^2J = {}^4J$ = 1.4 Hz, $OCH_2CH{=}CH_2$), 5.37 (ddt, 1 H, ^3J 17.2 Hz, $^2J = {}^4J$ = 1.4 Hz, $OCH_2CH{=}CH_2$), 5.95 (ddt, 1 H, ^3J 5.8, 10.4, 17.2 Hz, $OCH_2CH{=}CH_2$), 7.08 (m, 2 H, 4-H, 7-H), and 7.22 (m, 2 H, 5-H, 6-H) (Found: C, 70.6; H, 9.0; N, 3.6. $C_{22}H_{33}NO_4$ requires C, 70.4; H, 8.9; N, 3.7%).

Allyl 2-t-Butoxy-3-(1,1,3,3-tetramethyl-1,3-dihydroisoindol-2-yloxy)propionate (**5**).—$\delta_C(CDCl_3)$ 25.0—29.0 (broad hump, ring Me), 27.9 (Me_3 C), 65.5 ($OCH_2CH{=}CH_2$), 67.1 (C-1, C-3), 71.0 (CH_2ON), 75.4 (Me_3CO), 78.6 (Me_3COCH), 118.7 ($OCH_2CH{=}CH_2$), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 132.0 ($OCH_2CH{=}CH_2$), 145.2 (C-3a, C-7a), and 172.4 (C=O); $\delta_H(CDCl_3)$ 1.26 (s, 9 H, Me_3C), 1.43 (v br s, 12 H, 4 Me), 4.10 (dd, 1 H, ^2J 9.4, ^3J 6.4 Hz, $NOCH_2CH$), 4.11 (dd, 1 H, ^2J 9.4, ^3J 5.3 Hz, $NOCH_2CH$), 4.33 (dd, 1 H, ^3J 5.3, 6.4 Hz, $NOCH_2CH$), 4.67 (dt, 2 H, ^3J 5.8 Hz, ^4J 1.4 Hz, $OCH_2CH{=}CH$), 5.26 (ddt, 1 H, ^3J 10.4 Hz, $^2J = {}^4J$ = 1.4 Hz, $OCH_2CH{=}CH_2$), 5.37 (ddt, 1 H, ^3J 17.2 Hz, $^2J = {}^4J$ = 1.4 Hz, $OCH_2CH{=}CH_2$), 5.95 (ddt, 1 H, ^3J 5.8, 10.4, 17.2 Hz, $OCH_2CH{=}CH_2$), 7.09 (2 H, 4-H, 7-H), and 7.23 (m, 2 H, 5-H, 6-H) (Found: C, 70.1; H, 9.0; N, 3.9. $C_{22}H_{33}NO_4$ requires C, 70.4; H, 8.9; N, 3.7%).

3-t-Butoxypropyl-2-(1,1,3,3-tetramethyl-1,3-dihydroisoindol-2-yloxy) Acrylate (**6**).—$\delta_C(CDCl_3)$ 25.3, 30.2 (ring Me), 27.5 (Me_3C), 60.5 (Me_3COCH_2), 64.1 (OCH_2CHON), 67.9 (C-1, C-3), 73.1 (Me_3CO), 81.0 (OCH_2CHON), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 128.6 ($CH_2{=}CH$), 130.5 ($CH_2{=}CH$), 145.2 (C-3a, C-7a), and 166.2 (C=O); $\delta_H(CDCl_3)$ 1.20 (s, 9 H, Me_3C), 1.36, 1.37, 1.52, and 1.54 (4 br s, 12 H, 4 Me), 3.48 (dd, 1 H, ^2J 9.3 Hz, ^3J 6.8 Hz, CH_2OCMe_3), 3.70 (dd, 1 H, ^2J 9.3 Hz, ^3J 5.1 Hz, CH_2OCMe_3), 4.16 (dddd, 1 H, ^3J 3.5, 5.1, 5.3, and 9.3 Hz, CHON), 4.36 (dd, 1 H, ^2J 11.8 Hz, ^3J 5.3 Hz, CO_2CH_2), 4.47 (dd, 1 H, ^2J 11.8 Hz, ^3J 3.5 Hz, CO_2CH_2), 5.85 (dd, 1 H, ^2J 1.5 Hz, ^3J 10.4 Hz, $CH_2{=}CH$), 6.18 (dd, 1 H, ^3J 10.4 and 17.3 Hz, $CH_2{=}CH$), 6.45 (dd, 1 H, ^2J 1.5 Hz, ^3J 17.3 Hz, $CH_2{=}CH$), 7.09 (m, 2 H, 4-H, 7-H), and 7.23 (m, 2 H, 5-H, 6-H) (Found: C, 70.6; H, 8.8; N, 3.9. $C_{22}H_{33}NO_4$ requires C, 70.4; H, 8.9; N, 3.7%).

2-t-Butoxy-3-(1,1,3,3-tetramethyl-1,3-dihydroisoindol-2-yloxy)propyl Acrylate (**7**).—$\delta_C(CDCl_3)$ ring Me (not seen), 28.4 (Me_3CO), 65.9 (CO_2CH_2CH), 67.4 (C-1, C-3), 67.9 (CH_2ON), 74.5 (Me_3CO), 78.2 (Me_3COCH), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 128.6 ($CH_2{=}CH$), 130.7 ($CH_2{=}CH$), 145.1 (C-3a, C-7a), and 166.2 (C=O); $\delta_H(CDCl_3)$ 1.25 (s, 9 H, Me_3C), 1.43 (v br s, 12 H, 4 Me), 3.9—4.0 (m, 3 H, $Me_3COCHCH_2ON$), 4.22 (dd, 1 H, ^2J 11.5 Hz, ^3J 6.0 Hz, CO_2CH_2), 4.34 (dd, 1 H, ^2J 11.5 Hz, ^3J 4.3 Hz, CO_2CH_2), 5.85 (dd, 1 H, ^2J 1.5 Hz, ^3J 10.4 Hz, $CH_2{=}CH$), 6.17 (dd, 1 H, ^3J 10.4 and 17.3 Hz, $CH_2{=}CH$), 6.45 (dd, 1 H, ^2J 1.5 Hz, ^3J 17.3 Hz, $CH_2{=}CH$), 7.09 (m, 2 H, 4-H, 7-H), and 7.22 (m, 2 H, 5-H, 6-H) (Found: C, 70.5; H, 8.8; N, 3.6. $C_{22}H_{33}NO_4$ requires C, 70.4; H, 8.9; N, 3.7%).

(E)-3-(1,1,3,3-Tetramethyl-1,3-dihydroisoindol-2-yloxy)prop-1-enyl Acrylate (**8**).—$\delta_C(CDCl_3)$ 25.0—29.0 (broad hump, ring Me), 67.3 (C-1, C-3), 73.7 (CH_2ON), 111.3 ($CH{=}CHCH_2ON$), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 127.4 ($CH_2{=}CHCO_2$), 132.5 ($CH_2{=}CHCO_2$), 138.5 ($CH{=}CHCH_2$), 145.1 (C-3a, C-7a), and 163.1 (C=O); $\delta_H(CDCl_3)$ 1.43 (v br s, 12 H, 4 Me), 4.44 (dd, 2 H, ^3J 7.3 Hz, ^4J 1.3 Hz, CH_2ON), 5.75 (dt, 1 H, ^3J 7.3 and 12.5 Hz, $CH{=}CHCH_2ON$), 5.96 (dd, 1 H, ^2J 1.3 Hz, ^3J 10.5 Hz, $CH_2{=}CHCO_2$), 6.17 (dd, 1 H, ^3J 10.5 and 17.3 Hz, $CH_2{=}CHCO_2$), 6.54 (dd, 1 H, ^2J 1.3 Hz, ^3J 17.3 Hz, $CH_2{=}CHCO_2$), 7.10 (m, 2 H, 4-H, 7-H), 7.23 (m, 2 H, 5-H, 6-H), and 7.46 (dt, 1 H, ^3J 12.5 Hz, ^4J 1.3 Hz, $CH{=}CHCH_2ON$) (Found: C, 71.5; H, 7.9; N, 4.9. $C_{18}H_{23}NO_3$ requires C, 71.7; H, 7.7; N, 4.7%).

1-(1,1,3,3-Tetramethyl-1,3-dihydroisoindol-2-yloxy)allyl Acrylate (**9**).—M.p. 71—83 °C; $\delta_C(CDCl_3)$ 25.3, 25.5, 29.4 and 29.8 (ring Me), 67.5, and 68.2, (C-1, C-3), 101.6 (OCHO), 119.2 ($NOCHCH{=}CH_2$), 121.5, and 121.6 (C-4, C-7), 127.4 (C-5, C-6), 128.8 ($CH_2{=}CHCO_2$), 131.1 ($NOCHCH{=}CH_2$), 132.4 ($CH_2{=}CHCO_2$), 144.4 and 144.6 (C-3a, C-7a), and 164.8 (C=O); $\delta_H(CDCl_3)$ 1.39 (br s, 6 H), 1.45 (br s, 3 H), 1.55 (br s, 3 H, 4 Me), 5.37 (ddd, 1 H, $^2J = {}^4J$ = 1.2 Hz, ^3J 10.4 Hz, $CH_2{=}CHCHON$), 5.57 (ddd, 1 H, $^2J = {}^4J$ = 1.2 Hz, ^3J 17.3 Hz, $CH_2{=}CHCHON$), 5.87 (ddd, 1 H, ^2J 1.5 Hz, ^3J 10.4 Hz, $CH_2{=}CHCO_2$), 5.98 (ddd, 1 H, ^3J 5.4, 10.4 and 17.3 Hz,

CH_2=CHCHON), 6.18 (dd, 1 H, ^3J 10.4 and 17.3 Hz, CH_2=C*H*CO_2), 6.47 (dd, 1 H, ^2J 1.5 Hz, ^3J 17.3 Hz, *C*H_2=CHCO_2), 6.62 (dt, 1 H, ^3J 5.4 Hz, ^4J 1.2 Hz, C*H*ON), 7.09 (m, 2 H, 4-H 7-H), and 7.23 (m, 2 H, 5-H, 6-H) (Found: C, 71.6; H, 8.0; N, 4.9. $C_{18}H_{23}NO_3$ requires C, 71.7; H, 7.7; N, 4.7%).

(Z)-3-(1,1,3,3-*Tetramethyl*-1,3,-*dihydroisoindol*-2-*yloxy*)*prop*-1-*enyl Acrylate* (**10**).—Low melting solid, δ_C($CDCl_3$) 25.0—29.0 (broad hump, ring Me), 67.2 (C-1, C-3), 70.2 (CH_2ON), 110.8 (CH=*C*HCH_2ON), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 127.5 (*C*H_2=CHCO_2), 132.6 (CH_2=*C*HCO_2), 135.6 (*C*H=CHCH_2ON), 145.1 (C-3a, C-7a), and 162.7 (C=O); δ_H($CDCl_3$) 1.37 (v br s, 12 H, 4 Me), 4.56 (dd, 2 H, ^3J 7.0 Hz, ^4J 1.4 Hz, CH_2ON), 5.22 (dt, 1 H, ^3J 6.6 Hz, ^3J 7.0 Hz, CH=C*H*CH_2ON), 5.89 (dd, 1 H, ^2J 1.3 Hz, ^3J 10.4 Hz, *C*H_2=CHCO_2), 6.12 (dd, 1 H, ^3J 10.4, 17.3 Hz, CH_2=C*H*CO_2), 6.47 (dd, 1 H, ^2J 1.3 Hz, ^3J 17.3 Hz, *C*H_2=CHCO_2), 7.03 (m, 2 H, 4-H, 7-H), 7.16 (m, 2 H, 5-H, 6-H), and 7.20 (dt, 1 H, ^3J 6.6 Hz, ^4J 1.4 Hz, *C*H=CHCH_2ON) (Found: C, 71.5; H, 7.8; N, 4.8. $C_{18}H_{23}NO_3$ requires C, 71.7; H, 7.7; N, 4.7%).

Allyl (E)-3-(1,1,3,3-*Tetramethyl*-1,3-*dihydroisoindol*-2-*yloxy*)*prop*-1-*enyl Ether* (**12**).—δ_C($CDCl_3$) 25.0—29.7 (broad hump, ring Me), 67.0 (C-1, C-3), 70.1 (CH_2=C*H*CH_2O), 75.1 (CH_2ON), 100.6 (CH=*C*HCH_2ON), 117.7 (*C*H_2=CHCH_2O), 121.5 (C-4, C-7), 127.1 (C-5, C-6), 133.2 (CH_2=*C*HCH_2O), 145.2 (C-3a, C-7a), and 150.3 (*C*H=CHCH_2ON); δ_H($CDCl_3$) 1.42 (v br s, 12 H, 4 Me), 4.26 (dt, 2 H, ^3J 5.4 Hz, ^4J 1.4 Hz, CH_2=CH*C*H_2O), 4.30 (dd, 2 H, ^3J 7.6 Hz, ^4J 1.0 Hz, CH_2ON), 5.06 (dt, 1 H, ^3J 7.6, and 12.6 Hz, CH=C*H*CH_2ON), 5.21 (ddt, 1 H, ^3J 10.4 Hz, ^2J = ^4J = 1.4 Hz, *C*H_2=CHCH_2O), 5.31 (ddt, 1 H, ^3J 17.2 Hz, ^2J = ^4J = 1.4 Hz, C*H*$_2$=CHCH_2O), 5.92 (ddt, 1 H, ^3J 5.4, 10.4, and 17.2 Hz, CH_2=C*H*CH_2), 6.50 (br d, 1 H ^3J 12.6 Hz, C*H*=CHCH_2ON), 7.05 (m, 2 H, 4-H, 7-H), and 7.15 (m, 2 H, 5-H, 6-H) (Found: C, 75.1; H, 8.7; N, 5.0. $C_{18}H_{25}NO_2$ requires C, 75.2; H, 8.8; N, 4.9%).

Allyl 1-(1,1,3,3-*Tetramethyl*-1,3-*dihydroisoindol*-2-*yloxy*)*allyl Ether* (**13**).—δ_C($CDCl_3$) 25.4 (q, 29.3, q, 29.9, q, ring Me), 67.5, 68.0, (2 s, C-1, C-3), 68.5 (t, CH_2=CH*C*H_2O), 107.1 (d, CHON), 116.5* (t, *C*H_2=CHCHON) 117.9* (t, *C*H_2=CHCH_2O), 121.4, and 121.7 (2 × d, C-4, C-7), 127.3 (d, C-5, C-6), 134.9 (d, CH_2=*C*HCH_2O and CH_2=*C*HCHON), and 144.7 and 145.3 (2 s, C-3a, C-7a); δ_H($CDCl_3$) 1.36, 1.37, 1.48, and 1.57 (4 × br s, 12 H, 4 Me), 4.18 (ddt, 1 H, ^2J 12.8 Hz, ^3J 5.7 Hz, ^4J 1.5 Hz, CH_2=C*H*CH_2O), 5.13 (ddt, ^3J 10.3 Hz, ^2J = ^4J = 1.5 Hz, *C*H_2 = CHCH_2O), 5.23 (dt, 1 H, ^3J 5.4 Hz, ^4J 1.4 Hz, OC*H*ON), 5.27 (ddt, 1 H, ^3J 17.3 Hz, ^2J = ^4J = 1.5 Hz, C*H*$_2$=CHCH_2O), 5.28 (ddd, 1 H, ^3J 10.5 Hz, ^2J = ^4J = 1.4 Hz, NOCHCH=C*H*$_2$), 5.43 (ddd, 1 H, ^3J 17.3 Hz, ^2J = ^4J = 1.4 Hz, NOCHC*H*=CH$_2$), 5.917 (ddd, 1 H, ^3J 5.4, 10.5, and 17.3 Hz, NOCHC*H*=CH$_2$), 5.920 (ddt, 1 H, ^3J 5.7, 10.3, and 17.3 Hz, CH_2=C*H*CH_2O), 7.05 (m, 2 H, 4-H, 7-H), and 7.19 (m, 2 H, 5-H, 6-H) (Found: C, 75.0; H, 8.7; N, 4.9. $C_{18}H_{25}NO_2$ requires C, 75.2; H, 8.8; N, 4.9%).

Allyl (Z)-3-(1,1,3,3-*Tetramethyl*-1,3-*dihydroisoindol*-2-*yloxy*)*prop*-1-*enyl Ether* (**14**).—δ_C($CDCl_3$) 25.4, and 29.7 (broad hump, ring Me), 67.0 (C-1, C-3), 70.6 (CH_2=C*H*CH_2O), 72.9 (CH_2ON), 103.1 (CH=*C*HCH_2ON), 117.4 (*C*H_2=CHCH_2O), 121.5 (C-4, C-7), 127.1 (C-5, C-6), 133.8 (CH_2=*C*HCH_2O), 145.4 (C-3a, C-7a), and 147.2 (*C*H=CHCH_2ON); δ_H($CDCl_3$) 1.44 (v br s, 12 H, 4 Me), 4.30 (dt, 2 H, ^3J 5.3 Hz, ^4J 1.5 Hz, CH_2=CH*C*H_2O), 4.54 (dd, 2 H, ^3J 6.6 Hz, ^4J 1.0 Hz, CH_2ON), 4.74 (dt, 1 H, ^3J 6.3, 6.6 Hz, CH=C*H*CH_2ON), 5.23 (ddt, 1 H, ^3J 9.0 Hz, ^2J = ^4J = 1.5 Hz, *C*H_2=CHCH_2O), 5.33 (ddt, 1 H, ^3J 17.2 Hz, ^2J = ^4J = 1.5 Hz, *C*H_2 = CHCH_2O), 5.92 (ddt, 1 H, ^3J 5.3, 9.0, and 17.2 Hz, CH_2=C*H*CH_2O), 6.11 (dt, 1 H, ^3J 6.3 Hz, ^4J 1.0 Hz, C*H*=CHCH_2ON), 7.09 (m, 2 H, 4-H, 7-H), and 7.22 (m, 2 H, 5-H, 6-H) (Found: C, 74.9; H, 9.0; N, 5.0. $C_{18}H_{25}NO_2$ requires C, 75.2; H, 8.8; N, 4.9%).

2-*Allyloxy*-1,1,3,3-*tetramethyl*-1,3-*dihydroisoindole* (**15**).—M.p. 57—59 °C, δ_C($CDCl_3$) 25.2, 28.9 (ring Me), 68.3, (C-1, C-3), 68.8 (O*C*H_2CH=CH_2), 119.0 (OCH_2CH=*C*H_2), 121.5 (C-4, C-7), 127.7 (C-5, C-6), 131.6 (OCH_2*C*H=CH_2), and 143.8 (C-3a, C-7a); δ_H($CDCl_3$) 1.42, 1.52 (2 br s, 12 H, 4 Me), 4.72 (dt, 2 H, ^3J 5.8 Hz, ^4J 1.4 Hz, CH_2ON), 5.31 (ddt, 1 H, ^3J 10.4 Hz, ^2J = ^4J = 1.4 Hz, *C*H_2=CH), 5.41 (ddt, 1 H, ^3J 17.2 Hz, ^2J = ^4J = 1.4 Hz, *C*H_2=CH), 6.00 (ddt, 1 H, ^3J 5.8, 10.4, and 17.2 Hz, CH_2=C*H*), 7.12 (m, 2 H, 4-H, 7-H), and 7.26 (m, 2 H, 5-H, 6-H) (Found: C, 78.1; H, 9.0; N, 6.0. $C_{15}H_{21}NO$ requires C, 77.9; H, 9.2; N, 6.1%).

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* Interchangeable.

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