Photochemistry of Non-conjugated Dienones. Part V.[1] Photolysis of (*E*)-β-Ionone and its Isomeric α-Pyran †

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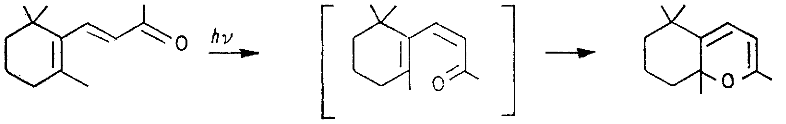
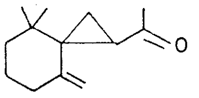
Direct photolysis of (*E*)-β-ionone at 30° leads to the formation of (*Z*)-*retro*-γ-ionone (5) and the α-pyran (2), whereas the triplet sensitized reaction only yields the latter. It is suggested that the formation of (2) proceeds through the triplet state of (*E*)-β-ionone *via* (*Z*)-β-ionone (4) as intermediate and that (*Z*)-*retro*-γ-ionone is formed from the excited singlet state. The rate of α-pyran formation and of (*E*)-β-ionone disappearance is less at −70 than at 30° due to a higher activation free energy for the formation of (*Z*)- than (*E*)-β-ionone from the (*E*)-β-ionone excited triplet state. Photoisomerization of the α-pyran (2) at 30° leads to the formation of (*E*)-β-ionone and (*Z*)-*retro*-γ-ionone. Triplet photosensitization experiments revealed that the former product results from the excited triplet and the latter from the excited singlet state of the α-pyran. (*E*)-β-Ionone is not a product at −70°, due to a substantially higher activation free energy for the conversion of excited triplet α-pyran into (*E*)-β-ionone than into ground state α-pyran. In the photoisomerization of both (*E*)-β-ionone and the α-pyran (2) eventually a tricyclic oxetan (6) is formed as a photo-product of (*Z*)-*retro*-γ-ionone. Thermal isomerization of the α-pyran (2) yields (*Z*)-*retro*-γ-ionone and (*E*)-β-ionone as primary and secondary product respectively.

THE first reports on the photolyses of ionones were given by Buchi and Yang.[2] They observed that (*E*)-β-ionone (1) upon direct photolysis leads to the formation of the α-pyran derivative (2) [2b] and a byproduct to which they tentatively assigned structure (3),[2c] and further that photoisomerization of the α-pyran (2) re-formed (*E*)-β-ionone.[2c] These investigators concluded that (*Z*)-β-ionone (4) is intermediate in the photoconversion of (1) into (2). Liu recently reported that the triplet sensitized photolysis of (*E*)-β-ionone (1) yields the α-pyran (2) as the sole product.[3] This observation substantiates the presumed initial (*E*)—(*Z*) isomerization of (*E*)-β-ionone, since this type of isomerization is a typical triplet reaction.[4]



(1) (4) (2)



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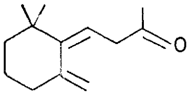

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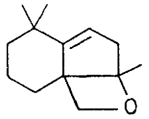

(6)

Heating of the α-pyran derivative (2) in pyridine or tetrachloroethene at 120° leads to the formation of (*Z*)-β-ionone (4).[5] Later it was shown that (2) and (4) are in fact in a strongly temperature dependent equilibrium.[5b]

This paper describes a quantitative study on the temperature dependence of the photoisomerizations of (*E*)-β-ionone and the isomeric α-pyran derivative (2). The thermal isomerizations of these two compounds were also investigated.

RESULTS

(E)-β-*Ionone*.—Photolyses of ethanolic solutions of (*E*)-β-ionone lead to the formation of 2,5,5,8a-tetramethyl-6,7,8,8a-tetrahydro-5*H*-1-benzopyran (2), further to be referred to as the α-pyran, (*Z*)-*retro*-γ-ionone, and the tricyclic oxetan derivative (6). The dependence of the amounts of the various monomeric products (as measured from the g.l.c. peak areas) on the time of photolysis is shown for −70 and 30° in Figure 1. The rate of formation of (*Z*)-*retro*-γ-ionone appears to be temperature independent. However, the initial rate of disappearance of (1) is greater at 30 than at −70°. Substrate (1) is completely converted within 7 h radiation at −70°, whereas at 30° it levels off to a constant low concentration. On the other hand, the initial rate of formation of the α-pyran (2) is greater at 30 than at −70°. Its relative amount reaches, however, a higher maximum at −70 than at 30°. After 15 h photolysis a new product appears which is identical with the tricyclic oxetan (6), formed as major product in the photoisomerization of (*Z*)-*retro*-γ-ionone.[6] The photolysis runs were discontinued after 20 h as the concurrent polymerization then prevails over the isomerization, as judged from the sum of the g.l.c.

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† Taken in part from A. van Wageningen, Thesis (in English), University of Amsterdam, 1973.

[1] Part IV, A. van Wageningen, P. C. M. van Noort, and H Cerfontain, *J.C.S. Perkin II*, 1974, 1662.

[2] G. Buchi and N. C. Yang, (*a*) *Helv. Chim. Acta*, 1955, **38**, 1338; (*b*) *Chem. and Ind.*, 1955, 357; (*c*) *J. Amer. Chem. Soc.*, 1957, **79**, 2318.

[3] R. S. H. Liu, *Pure Appl. Chem.*, 1971, Suppl. 1, 335; V. Ramamurthy, Y. Butt, C. Yang, P. Yang, and R. S. H. Liu, *J. Org. Chem.*, 1973, **38**, 1247.

[4] P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 79, 80.

[5] (*a*) E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *J. Org. Chem.*, 1966, **88**, 619; (*b*) E. N. Marvell, T. Chadwick, G. Caple, T. A. Gosink, and G. Zimmer, *J. Org. Chem.*, 1972, **37**, 2992.

[6] A. van Wageningen and H. Cerfontain, *Tetrahedron Letters*, 1972, 3679.

peak area of the monomeric products. The relative amounts of (2) and (5) then appear to be the same for −70 and 30°.

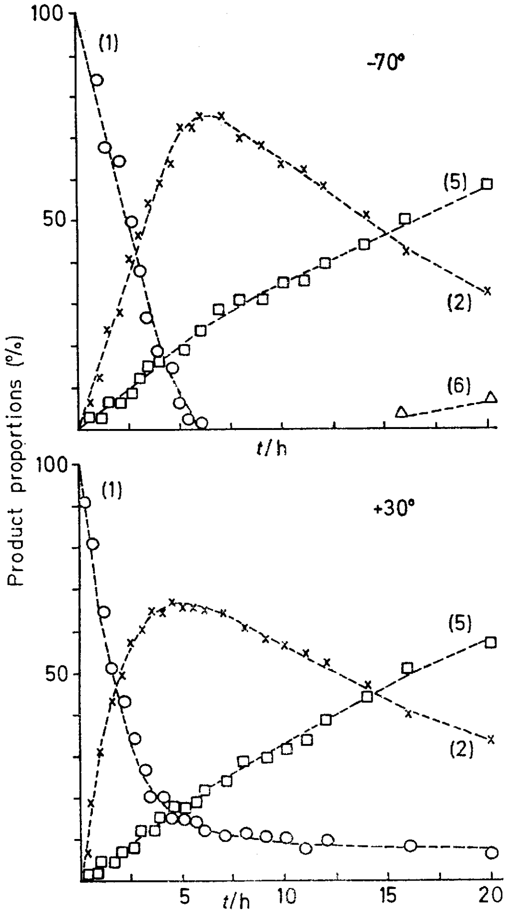

FIGURE 1 Photolysis of (*E*)-β-ionone at −70 and 30°

Irradiation of (*E*)-β-ionone in benzene in the presence of the triplet sensitizers [7] benzophenone (E_T 68.5 kcal mol^{-1}) and pyrene (E_T 48.7 kcal mol^{-1}) both with λ 350 nm, and biacetyl (E_T 54.9 kcal mol^{-1}) and 7*H*-benz[*de*]anthracen-7-one (E_T 47 kcal mol^{-1}) both with λ 403 nm led to formation of only the α-pyran (2) and no (*Z*)-*retro*-γ-ionone. Thus it may be concluded that (*Z*)-*retro*-γ-ionone arises from the excited singlet, and the α-pyran from the excited triplet state. The degree of sensitization with 7*H*-benz[*de*]anthracen-7-one is notably less than with the three other sensitizers, but still substantial. This indicates that the triplet energy of (*E*)-β-ionone is <47 kcal mol^{-1}.*

The influence of added anthracene in the photolysis of (*E*)-β-ionone at room temperature was studied at 30°. It was observed (*cf.* ref. 8*a*) that the rate of α-pyran formation is decreased by the anthracene, whereas the rate of formation of (*Z*)-*retro*-γ-ionone is unaffected. This result is in agreement with the conclusions drawn from the sensitization experiments, provided that anthracene acts only as triplet quencher in this system.

(*E*)-β-Ionone is thermally stable at 150°, as no monomeric products were formed after heating for 4 h.

2,5,5,8a-*Tetramethyl*-6,7,8,8a-*tetrahydro*-5H-1-*benzopyran* (2).—Ethanolic solutions of the α-pyran have been photoisomerized under the same conditions as for (*E*)-β-ionone. The products were (*E*)-β-ionone (1), (*Z*)-*retro*-γ-ionone (5), and the tricyclic oxetan (6). The dependence of the relative amounts of these monomeric products (as measured from the g.l.c. peak areas) on irradiation time and temperature are shown in Figure 2. The rate of formation of (*Z*)-*retro*-γ-ionone is hardly influenced by change in temperature. At −70° no (*E*)-β-ionone is formed within the limits of detection, whereas it is an important product at 30°. The tricyclic oxetan (6) is again a secondary reaction product.

Irradiation of (2) in the presence of the triplet sensitizers [7] benzophenone and pyrene both with λ 350 nm and biacetyl with λ 403 nm led in each case to the formation of only (*E*)-β-ionone and no (*Z*)-*retro*-γ-ionone. Thus it follows that the former compound arises from the excited triplet state and the latter from the excited singlet state of the α-pyran. Sensitization with 7*H*-benz[*de*]anthracen-7-one (E_T 47 kcal mol^{-1}) is very poor, whereas that with pyrene (E_T 49.8 kcal mol^{-1}) is still very efficient. This indicates that the triplet energy of the α-pyran (2) is between 47 and 50 kcal mol^{-1}.

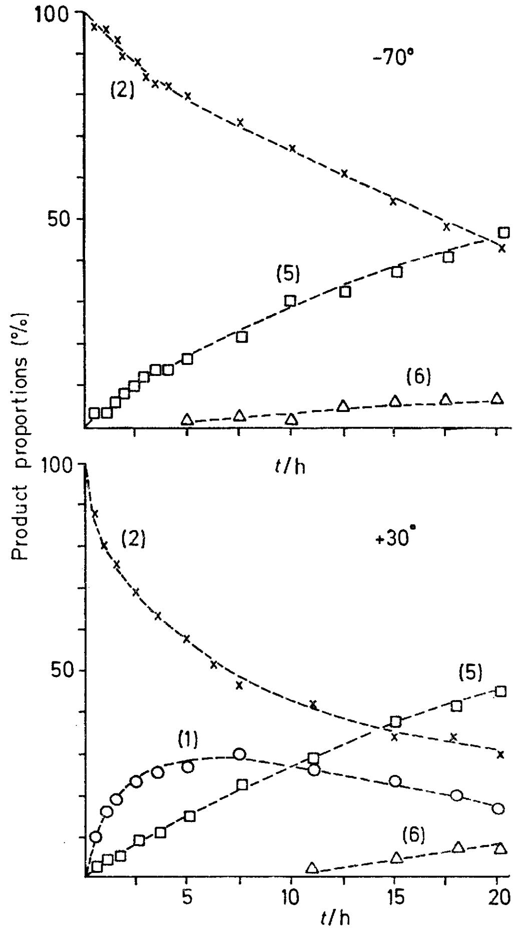

FIGURE 2 Photolysis of the α-pyran (2) at −70 and 30°

The α-pyran (2) is thermally unstable. The ^{1}H n.m.r. spectrum of a solution of (2) in dimethyl sulphoxide heated

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* Photosensitization experiments in the (*E*)-*retro*-α-ionone series indicate that the triplet energy of these compounds is in between 49 and 53 kcal mol^{-1}.[1]

[7] A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Interscience, 1969, p. 92.

at 120° exhibited δ 1.03 (*gem*-Me_2), 1.69 (8a-Me), 2.11 (2-Me), and 6.07 and 6.48 (vinylic AB, *J* 12 Hz), which absorptions are similar to those reported by Marvell for (*Z*)-β-ionone.[5a] Furthermore, the spectrum showed signals of (*Z*)-*retro*-γ-ionone [1] which were not reported by Marvell.

G.l.c. analysis of the reaction mixture of the α-pyran in dimethyl sulphoxide at 120°, or in decalin at 150°, showed the presence of two monomeric products, (*E*)-β-ionone (1) with 6.11 and 7.28 (vinylic AB, *J* 16 Hz) and (*Z*)-*retro*-γ-ionone [1] (5). The variation of the relative amounts of these monomeric products with reaction time has been reported [8b] for the thermal isomerization in decalin at 150°. The time dependence illustrates that (*Z*)-*retro*-γ-ionone is a primary and (*E*)-β-ionone a secondary product. In addition to the isomerizations, polymerization takes place. The polymeric products prevail over the monomeric ones for a reaction time >3 h.

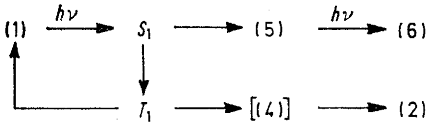
Spectral Data and Product Assignments.—Spectral data of (*E*)-β-ionone and the α-pyran (2) have been reported.[2c, 5a, 9] The structural assignments of (5) and (6) were based on the following detailed spectrometric data: (*Z*)-*retro*-γ-ionone, $\nu_{max.}$ 1 710 (C=O) and 3 080 and 905 ($C=CH_2$) cm^{-1}, Raman 1 648 and 1 636 (C=C) cm^{-1}, $\lambda_{max.}$ 208 (ε 4 000) and 275 nm (150), δ 1.04 (s, Me_2), *ca.* 1.50 (m, CH_2), 2.07 (s, MeCO), 2.10—2.30 (m, $CH_2C=$), 3.27 (d, spacing 7 Hz, CH_2CO), 4.57 (m, =CH), 4.72 (m), and 5.52 (t, spacing 7 Hz), *m/e* (70 eV) 192 (23.6%, $M^{+\cdot}$, $C_{13}H_{20}O$), 177 (100), 149 (42.5), 119 (19.7), 107 (30.7), 93 (51.2), 91 (31.5), 81 (22.8), 79 (28.3), 77 (20.5), 69 (26.8), 43 (55.9), 41 (20.5), and 18 (32.3), oxetan (6), $\nu_{max.}$ 3 040 and 850 (C=CH) and (oxetan ring) 990 cm^{-1}, Raman 1 637 (C=C) cm^{-1}, $\lambda_{max.}$ <205 nm, δ 1.03 (s) and 1.14 (s) (Me_2), 1.31 (s, MeCO), 1.40—1.70 (m, CH_2CH_2), 1.90—2.10 (m, CH_2CCO), 2.21 and 2.52 (both dd, spacings 2 and 17 Hz, $C=CCH_2CO$), 4.38 (s, CH_2O), and 5.40 (t, spacing 2 Hz, C=CH), *m/e* (70 eV) 192 (8.5%, $M^{+\cdot}$, $C_{13}H_{20}O$), 177 (28.6), 162 (36.0), 149 (28.2), 147 (100), 119 (22.0), 93 (28.0), 91 (23.4), 43 (38.5), 41 (22.2), and 28 (22.4). The mass spectrum of (6) is highly informative because of the process *m/e* 192 ⟶ 162 (*m** 136.7) which is followed by elimination of a methyl radical. The first process is compatible with loss of formaldehyde from the oxetan radical cation, the second with subsequent loss of a methyl radical from *gem*-Me_2.

DISCUSSION

(*E*)-β-Ionone (1) upon photolysis at −70° is eventually completely converted, whereas at 30° it levels off to a constant low concentration. (*E*)-β-Ionone is a product in the photoisomerization of the α-pyran (2) at 30°, but not at −70°. The eventual constant low concentration of (*E*)-β-ionone observed in its photoisomerization at 30° may thus be explained in terms of photoreconversion of the α-pyran.

The rate of photoformation of (*Z*)-*retro*-γ-ionone (5) from (*E*)-β-ionone (1) is temperature independent. (*Z*)-*retro*-γ-Ionone is further not formed upon heating (*E*)-β-ionone at 150—200°. Mousseron-Canet *et al.*[10] have suggested that the photoformation of (5) from (1) proceeds *via* (*Z*)-β-ionone (4) and subsequent intramolecular hydrogen abstraction by its photo-excited carbonyl group (*i.e.* by a [1,7] hydrogen shift) followed by enol-keto isomerization of the resulting enol. An alternative route for the formation of (5) is a direct sigmatropic [1,5] hydrogen shift from (*E*)- or (*Z*)-β-ionone. Such a shift occurs in the photoconversion of (*E*)-β-ionol into (*Z*)-*retro*-γ-ionol,[10] where no alternative [1,7] hydrogen shift is feasible.

The triplet photosensitization experiments of (*E*)-β-ionone showed that (*Z*)-*retro*-γ-ionone results from the excited singlet state of (*E*)-β-ionone, and the α-pyran from the excited triplet state. Considering that (*Z*)-(*E*) isomerizations are usually triplet reactions,[4,11] the triplet sensitization experiments render the possibility that (*Z*)-*retro*-γ-ionone is formed *via* (*Z*)-β-ionone unlikely. They further make it very likely that the α-pyran is formed *via* (*Z*)-β-ionone which itself results from the excited triplet state of (*E*)-β-ionone (Scheme 1).



SCHEME 1

Moreover, the simultaneous increase in the rates of (*E*)-β-ionone disappearance and α-pyran formation with increasing temperature of the photolysis, and the temperature independence of the rate of (*Z*)-*retro*-γ-ionone formation (Figure 1) also seem to exclude the possibility that (*Z*)-β-ionone is intermediate in the formation of (*Z*)-*retro*-γ-ionone. For an increase in rate of reconversion of (*Z*)- into (*E*)-β-ionone with increasing temperature would involve a lower rate of formation of (*Z*)-*retro*-γ-ionone, whereas this rate is in fact temperature independent.

The higher rate of photoconversion of (*E*)-β-ionone at 30 than at −70° may be explained in terms of a higher activation free energy for the formatian of (*Z*)- than (*E*)-β-ionone from the excited triplet state of (*E*)-β-ionone. This infers that the degree of reconversion of the excited triplet to the ground state (by *e.g.* phosphorescence, or intersystem crossing and subsequent internal conversion) increases with decreasing temperature. This problem will be the object of further study.

The photoisomerization of the α-pyran (2) at −70° initially leads only to the formation of (*Z*)-*retro*-γ-ionone (5), whereas at 30° initially both this product and (*E*)-β-ionone (1) are produced. The rate of formation of (*Z*)-*retro*-γ-ionone is the same at −70 and 30°. The initial rate of substrate conversion is much greater at 30 than at −70°. The photosensitization experiments showed that (*Z*)-*retro*-γ-ionone results from the excited singlet and (*E*)-β-ionone from the excited triplet state of the α-pyran. The photolysis of the α-pyran may therefore be explained by the reaction steps shown in Scheme 2. Excited

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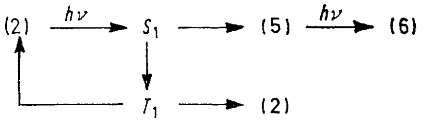
[8] A. van Wageningen, Thesis (in English), University of Amsterdam, 1973, (*a*) p. 70; (*b*) p. 72.

[9] Varian High Resolution N.m.r. Spectra Catalog, vol. 2, no. 617.

[10] M. Mousseron-Canet, M. Mousseron, and P. Legendre, *Bull. Soc. chim. France*, 1964, 50.

[11] R. B. Cundall and A. Gilbert, 'Photochemistry,' Nelson, London, 1970, p. 168.

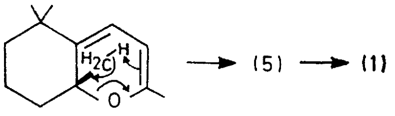
singlet α-pyran, formed on photo-excitation of (2), either isomerizes to (*Z*)-*retro*-γ-ionone or gives intersystem crossing with formation of excited triplet α-pyran. This excited triplet state yields (*Z*)-β-ionone (4), which at low temperatures (−70°) reconverts exclusively to α-pyran, but at high temperature (30°) yields (*E*)-β-ionone. Apparently the activation free energy is substantially higher for the latter than the former step. In the later stages of the photolysis the tricyclic oxetan (6) is again formed as a photoproduct of (*Z*)-*retro*-γ-ionone.



SCHEME 2

A comparison of the Schemes 1 and 2 shows that the fate of excited triplet (*E*)-β-ionone differs from that of excited triplet α-pyran. Accordingly, the excited singlet states of (*E*)-β-ionone and α-pyran also have to be different.

In the thermal isomerization of the α-pyran (2) (*Z*)-*retro*-γ-ionone is the primary product, whereas (*E*)-β-ionone is the secondary product. This infers that (*Z*)-*retro*-γ-ionone is formed directly from the α-pyran. A careful examination of framework molecular models (Dreiding and Prentice Hall) of the α-pyran showed that one of the methyl hydrogens is located in a favourable position to migrate to C-3 of the α-pyran (Scheme 3).



SCHEME 3

The (*E*)-β-ionone is formed consecutively from the (*Z*)-*retro*-γ-ionone *via* a sigmatropic [1,5] hydrogen shift.

EXPERIMENTAL

β-Ionone was obtained from Naarden International, Holland. The α-pyran (2) was obtained by irradiation of (*E*)-β-ionone [2c] and purified by preparative g.l.c. on a semi-analytical column.

Photolyses.—Ethanolic solutions of (*E*)-β-ionone and the α-pyran (2) (2.5% v/v) contained in a quartz double wall vessel were photolysed using a Hanau TQ 81 medium pressure mercury lamp. Both the radiation source and the reaction vessel were placed in a silver coated Dewar vessel. By circulating ethanol from a Kryomat (Lauda) constant temperature bath through the Dewar vessel, the cooling jackets of the mercury lamp and the reaction vessel, any desired reaction temperature between −75 and 40° could be obtained. For the quenching experiments the solutions to be irradiated were made up by addition of 2.5% (v/v) of (*E*)-β-ionone to a saturated solution of anthracene in ethanol.

Photosensitization.—Benzene solutions of either (*E*)-β-ionone or the α-pyran (0.1M) and a suitable photosensitizer (1.0M or saturated solution) were photolysed in Pyrex vessels with λ 350 nm at 35° (Rayonet photoreactor) or 403 nm at 15° (Philips SP-500 mercury arc).

Thermolyses.—Solutions of the α-pyran (2) in decalin and dimethyl sulphoxide (*ca*. 30% v/v) were heated at 150 and 120° respectively. Thermolyses of (*E*)-β-ionone were carried out by heating a sample (250 mg) as such, or in decalin (0.5 ml), at 150°.

Product Analysis.—The progress of the photolyses, the photosensitized experiments, and the pyrolyses was monitored by sampling at appropriate times, and subsequent g.l.c. analysis on a semi-analytical (3.5 m, diam. 6 mm, 15% Reoplex-400–Chromosorb-W 45—60 mesh, 150 ml He min^{-1}, 175°) and an analytical column (5 m, diam. 6 mm, 3% SE-30–Chromosorb W 45—60 mesh, 55 ml He min^{-1}, 150°). The identification of the components was based on spectrometric analysis and/or g.l.c. retention times.

Spectral Data.—The i.r. spectra were recorded from the pure components on a Unicam SP 200 or a Beckman IR 18A spectrometer. The Raman spectra were obtained with a Coderg PH 1 spectrometer using a CRL 52 Mg laser. The u.v. spectra were recorded from ethanolic solutions on a Shimadzu UV 200 or a Beckman DB-GT spectrometer. The ^1H n.m.r. spectra were recorded from dilute CCl_4 solutions (5—10%) with tetramethylsilane as internal standard on a Varian HA100 or A60 spectrometer. The mass spectra were obtained with a Varian-Mat 711 double focusing mass spectrometer coupled to a Spectrosystem 100.

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