

Thermogravimetric profile of decomposition of acrylate systems based on bornyl acrylate monomers

J. A. Ors and D. M. La Perriere

AT&T Engineering Research Center, PO Box 900, Princeton, NJ 08540, USA

(Received 23 January 1986; revised 22 April 1986)

This study deals with the thermal decomposition of the homopolymers of isobornyl acrylate (IBOA) and bornyl acrylate (BOA), and their relationship with polymers that contain IBOA as a reactive diluent. We have examined the profile, the mechanism and the energetics of the thermal decomposition reaction(s) and found a stereochemical dependence in the decomposition process.

(Keywords: thermal decomposition; thermogravimetric analysis; acrylates; bornyl acrylate; isobornyl acrylate; decomposition mechanism; energy of activation)

INTRODUCTION

The thermal properties of a polymer play a major role in determining its application. The materials used in the printed wiring board (PWB) industry have to withstand a variety of high-temperature operations (150°C–260°C), both during fabrication and operation. Lifetime estimates of the material at various temperatures are valuable in predicting material behaviour at operating temperatures. Similar data has been used to determine dielectric degradation leading to voltage breakdown¹.

The study of the thermal degradation of polymers via thermogravimetric analysis (t.g.a.) can provide valuable information about the polymer system², such as: (1) the relative thermal stability, (2) the degree of cure, (3) structural information (e.g., distinguishing among block, random, and segmentation polymerization in addition polymers), (4) per cent composition of individual components (based on the thermal stability of segments and/or components in a chain), (5) amount of filler materials, and (6) relative flammability index (by correlating the char residue of polymers with their limiting oxygen index (LOI)).

This work describes the thermal decomposition of IBOA and two other terpenoid derivatives, bornyl acrylate (BOA) and isobornyl methacrylate (IBOMA). The parameters examined include the pyrolysis products and mechanism, and the activation energy (E_a) of the decomposition process. The interest in these terpenoid derivatives arises from their curing behaviour, dielectric properties and relative safe handling properties when incorporated into polymer systems.

EXPERIMENTAL

Chemicals

All the components we have examined are commercially available and were used as received. IBOA was obtained from Rohm and Haas, while the BOA and IBOMA were obtained from Polysciences. The photoinitiator used is 2,2-dimethoxy-2-phenyl aceto-

phenone (DMPA), from Ciba-Geigy, at a level of 2% by weight.

Film cure

The polymerization was carried out on 0.1 mm films photocured with 3.6 Joules/cm², in a CoLight UV curing system, model UVC 24.

Equipment

The thermogravimetric measurements were done in a DuPont 1090 thermal analyser coupled to a 951 thermogravimetric analyser (t.g.a.). Volatiles and decomposition products were collected using a liquid N₂ trap attached to the purge exit of the t.g.a. oven. A Hewlett-Packard 5985B Gas Chromatography–Mass Spectrometry system was used with various sample introduction procedures.

Sealed tube pyrolysis was carried out by introducing into a tube a sample of homopolymer that had been ground to a fine powder using a freezer mill. The tube was evacuated and put through two freeze–thaw cycles with liquid N₂ before sealing. The tube was then heated to 350°C. The products were dissolved in cyclohexane for g.c./ms analysis. All products were compared with known standards.

RESULTS AND DISCUSSION

Decomposition profiles

The two step t.g.a. profile of a polymer prepared from a mixture of IBOA and an epoxy resin, shown in *Figure 1*, prompted us to investigate the decomposition mechanism involved. Since block copolymerization is not expected in this type of mixture, the dual transition must be due to monomer decomposition. Grassie and coworkers have detailed the pyrolysis of a series of poly(alkyl acrylates)^{2c-g}, and found that these materials undergo free radical decomposition leading to a variety of products whose ratios are predicated on the chemical structure of the pendant alkyl group. A direct correlation was suggested

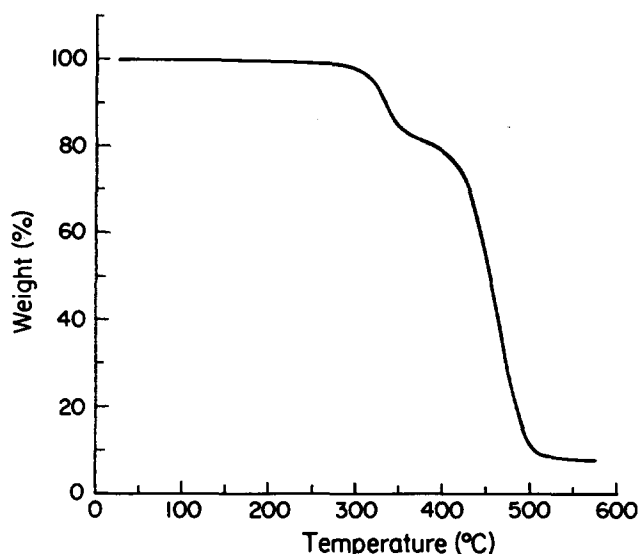


Figure 1 T.g.a. profile of IBOA containing mixture

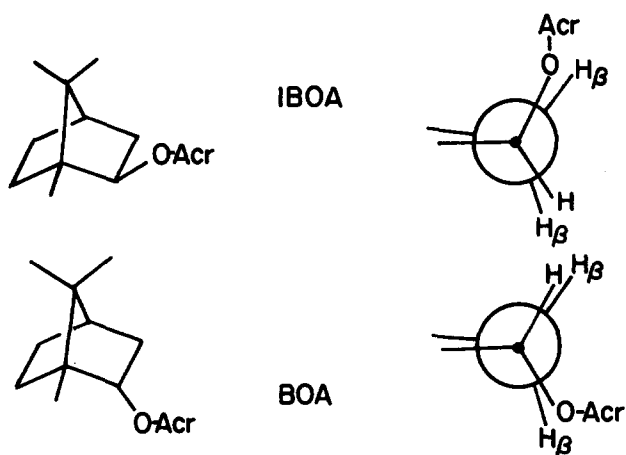


Figure 2 Chemical structure of IBOA and BOA monomers

between the per cent olefin produced and the number of β -hydrogens in the alkyl group. This is supported by a recent report dealing with the decomposition of glycidyl methacrylate-butyl acrylate copolymers³. The breakdown of the backbone is also expected to occur via a free radical mechanism but at a higher temperature.

Figure 2 shows that in both the bornyl ('endo'-substituted) and isobornyl ('exo'-substituted) ring structures there are two hydrogen atoms located ' β ' to the oxygen, with one of the hydrogens in a '*cis*' orientation to the carbonyl group. Based on the availability and orientation of these hydrogens the decomposition profile for each monomer should be similar; however, the bulk of the polyBOA decomposes at a temperature 50°C higher than its 'exo' counterpart (Figure 3). The difference in the two curves can be attributed to the stereochemistry of the monomers since the decomposition profile of the exo-methacrylate (polyIBOMA) mimics that of the polyIBOA.

Decomposition products

The g.c. trace of the volatiles trapped during thermal decomposition of polyIBOA at 350°C in the thermal analyser is shown in Figure 4. The two major volatile products are camphene (I) in about 79% yield and the nortricyclic derivative (II), 1,7,7-trimethyl

tricyclo[2.2.1.0^{2,6}]heptane, in 16% yield. The ratio of these products camphene:nortricyclic (C:N) approximates 5:1, and becomes significant later in determining the decomposition mechanism. The other minor products (<5%) were not identified. Sealed tube decomposition of this homopolymer showed identical products, with a C:N ratio of 4:1. The t.g.a./g.c. trace of polyIBOMA shows similar results.

Figure 5 shows five distinct products from the decomposition of polyBOA from the t.g.a. Two of the products, camphene (I, 44%) and the nortricyclic derivative (II, 28%) are the same as in the previous case, but at a much lower C:N ratio (1.6:1). The third major product identified is borneol (III, 14%), and its preceding peak is the 'exo' counterpart isoborneol (1%). Sealed tube pyrolysis again yielded the same products as for the t.g.a., and with similar C:N ratios.

Decomposition mechanism

The variation in C:N ratio is presumably a result of the difference in stereochemistry between the BOA (endo) and the IBOA-IBOMA (exo) monomers. The decomposition reaction can be described as a pyrolytic '*cis*'-elimination of a cyclic ester⁴. As seen in Figure 2,

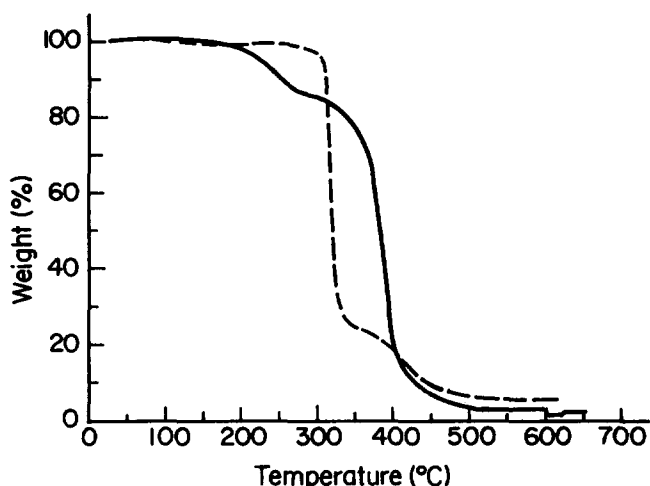


Figure 3 T.g.a. decomposition profiles of polyIBOA (---) and poly(BOA) (—) under N₂ atmosphere

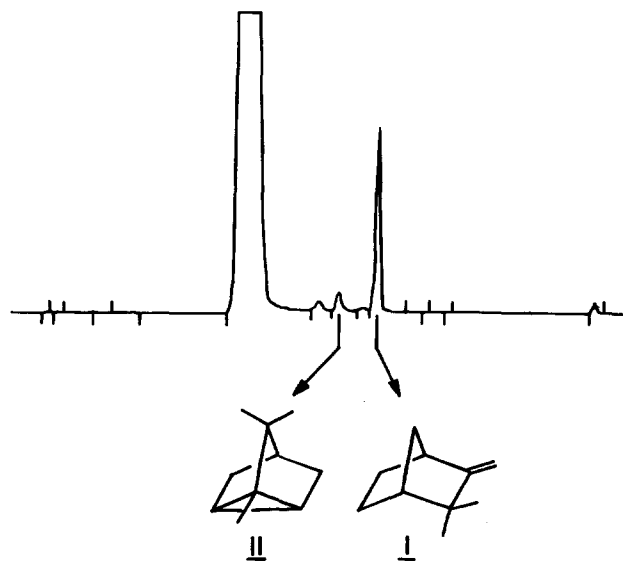


Figure 4 Gas chromatogram of volatiles from the t.g.a. of polyIBOA

both isomers contain the required hydrogens and in each case a 'cis' hydrogen is in an eclipsed conformation with the ester oxygen. The directionality of the rearrangement is restricted since the only other available α -carbon is the tetra-substituted bridgehead carbon.

The 'cis'-elimination reaction, in simple systems, generally takes place through a cyclic, concerted mechanism⁵. In acrylic polymers it has been suggested that the initial step be a scission at some unspecified point in the polymer molecule creating radicals that abstract hydrogen from the backbone and lead to stable radicals.

In the case of the polyIBOA either mechanism can be operative as shown in Figure 6. The concerted, single transition scheme should lead to the formation of bornylene (IV). Although bornylene (IV) was not detected in the product distribution (<5%) from the pyrolysis of polyIBOA, it is possible that it is present as an intermediate that thermally rearranges to camphene (I). These systems are known to undergo a variety of rearrangements⁶. The radical mechanism involves the formation of I via the free radical intermediate V through a Wagner–Meerwein rearrangement, Figure 7. Loss of hydrogen at the C-6 position of the bornyl radical V can lead to the nortricyclic product (II). This product should not be generated via the concerted mechanism unless the bornylene (IV) is so thermally unstable as to quantitatively generate V under these conditions.

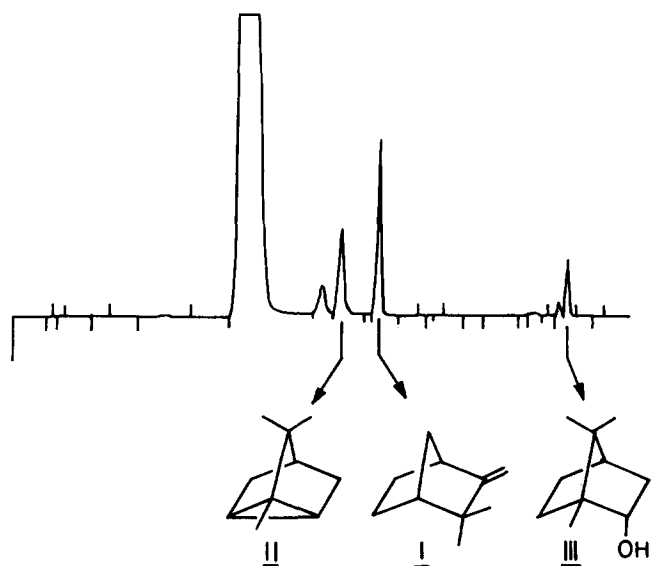


Figure 5 Gas chromatogram of volatiles from the t.g.a. of polyBOA

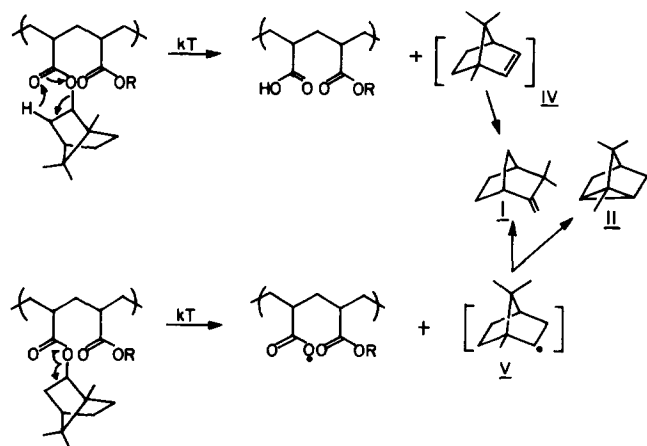


Figure 6 Schemes of the concerted (top) and free radical (bottom) mechanisms for the decomposition of polyIBOA

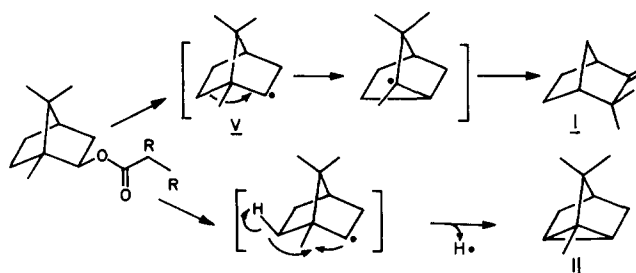


Figure 7 Wagner–Meerwein rearrangement to produce I via intermediate V (top), and the formation of II via a C-2 hydrogen loss of intermediate V (bottom)

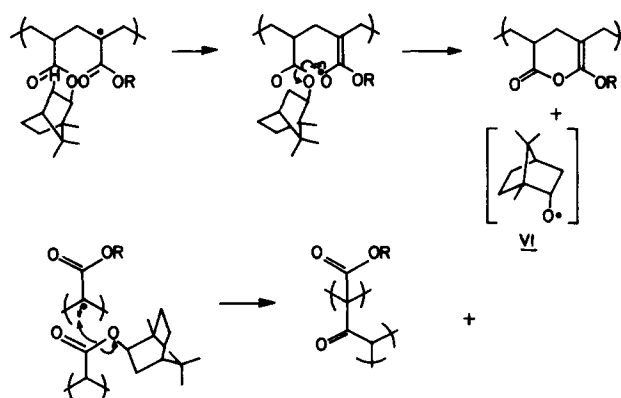


Figure 8 Schemes for the alcohol formation via borneoxy radical VI

Nevertheless, the data suggest the 'free radical' mechanism as the main operative scheme.

In the case of the polyBOA, the ratio of products I to II (1.6:1) has changed due to a threefold increase in II. This increase could be a result of the endo stereochemistry of the BOA facilitating the rearrangement to the nortricycle II through the bornyl intermediate V. In this isomer the intermediate is generated by vacating an orbital in C-2 (endo) whose orientation appears to preferentially lead to the formation of the nortricyclic ring structure by easing the loss of a C-2 hydrogen and/or hindering the formation of camphene. The vacated C-2 (endo) orbital may have a higher degree of overlap with the C-6 (exo)-hydrogen orbital than with the C-1–C-6 bonding orbital.

Cameron and Kane⁷ have suggested several mechanisms for the production of alcohols; however, based on the work by Grassie *et al.*^{2e-g} the schemes in Figure 8 seem the most likely to produce the borneoxy radical (VI) precursor to borneol III. The top mechanism involves an intramolecular reaction producing VI along with a γ,δ -unsaturated γ -lactone ring system while the bottom scheme produces a β -ketoester along with VI through an intermolecular reaction.

The presence of alcohol III and the changes in the C:N ratio, regardless of the equal availability of β -hydrogens, point toward the stereochemical dependence of the decomposition process of these two homopolymers. The orientation of the cyclic pendant groups in the polymer chain may allow a more stable conformation for the BOA homopolymer along with the stereochemical restrictions that do not facilitate the Wagner–Meerwein decomposition pathway leading to a higher E_a value, hence, a higher decomposition temperature.

Decomposition energetics

There are several thermogravimetric methods to determine the basic kinetic parameters for decomposition, and three of these are shown in Table 1. From

the relationships one can calculate the energy of activation (E_a) for the process and make estimates on the correlation between material lifetime and temperature.

Method A⁸ makes use of the loss of weight with changes in temperature, obtaining E_a from the temperature (T_i) and the weight (W_i) at the inflection point of a dw/dT trace where R is the gas constant. Method B⁹ makes use of the weight loss with time during isothermal runs to determine the activation energy. Method C¹⁰ is based on the decomposition profile at several heating rates (β') using the method of successive approximations, where b is an empirical approximation whose value depends on E_a . In the first two cases the reaction order is assumed to be unity ($n=1$).

A comparison of the $\ln k$ vs. $1/T$ plot (Method B) for polyBOA and polyIBOA, shown in Figure 9, shows $E_{aBOA} > E_{aIBOA}$ by about 7 kcal mol⁻¹. This is supported by the values obtained using Method A in Table 1. The data show good agreement despite differences in methodology. The graph also shows that a sample decomposed in air exhibited no significant deviation from the slope, thus indicating the absence of an oxygen effect in the decomposition kinetics of these pendant groups. Product ratio comparison must be carried out before

Table 1 Decomposition energetics

Method	Equation	E_a (kcal mol ⁻¹)	
		polyIBOA	polyBOA
A	$E_a = -\left(R \frac{T_i^2}{W_i}\right) \left(\frac{dw}{dT}\right)_i$	33.8	44.5
B	$\Delta \ln \left(\frac{-dw}{dt}\right) = \ln \Delta w - \frac{E_a}{R} \Delta(1/T)$	33.0	40.8
C	$E_a = -\left(\frac{R}{b}\right) \frac{d \ln \beta}{d(1/T)}$	-	43.4

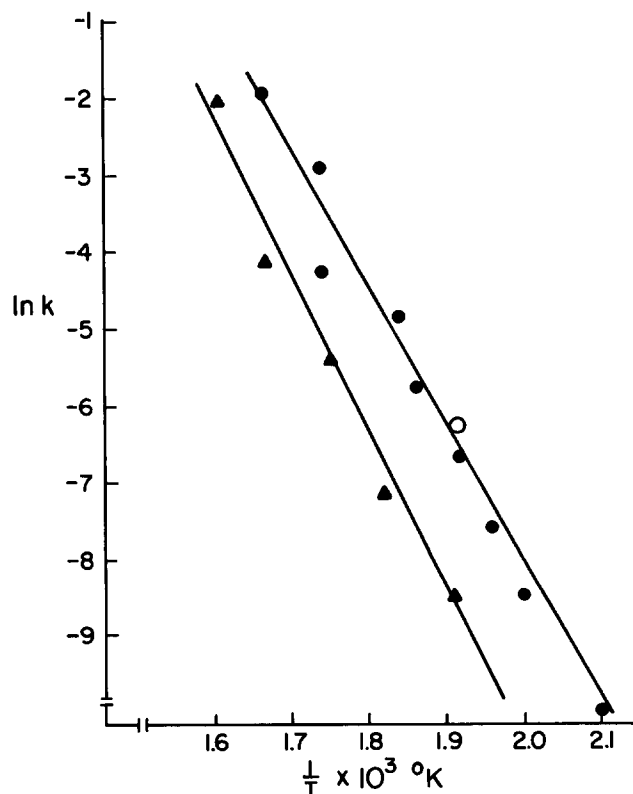


Figure 9 Method B plot for polyIBOA (●) and polyBOA (▲), sample run in an air atmosphere (○)

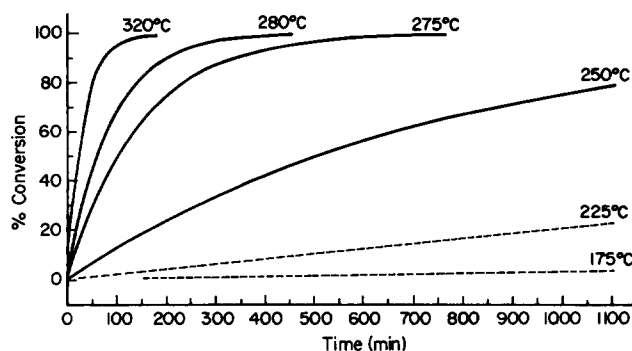


Figure 10 Estimate of the thermal lifetime of the IBOA component of a mixture, using Method C

extrapolating the above data to mechanism changes¹¹; however, no significant changes are expected due to the air atmosphere.

Using the E_a values, we can estimate the amount of decomposition that would take place at a given temperature, i.e. the thermal lifetime (Figure 10). This information dictates the formulation constraints, e.g. annealing and operating temperatures, etc., for specific applications.

In conclusion, we have shown that the thermal stability of mixtures containing IBOA, BOA and IBOMA is predicated on the use of these terpenoid derivatives. When incorporated into a polymer matrix, these monomers will polymerize in a random fashion, and decompose as esters of cyclic alcohols via a 'cis' elimination-free radical initiated mechanism showing a two-stage t.g.a. profile. The first transition (stage) serves as a measure of the concentration of the terpenoid monomer, and can be used to monitor composition changes during cure processes. The stereochemical dependence of the decomposition suggests that the orientation of the cyclic pendant group in the BOA leads to a higher E_a value than its 'exo' counterparts.

ACKNOWLEDGEMENTS

The authors would like to thank R. P. Menichelli for some of the g.c./ms data.

REFERENCES

- Toop, D. J., IEEE Trans. Elect. Insulation 1971, EI-6, 1
- Chiu, J. Appl. Polym. Symp. 1966, 3, 25 and references therein; (b) Miller, G. W. Appl. Polym. Symp. 1969, 10, 35; (c) Baer, M. J. Polym. Sci. A 1964, 10, 417; (d) Gilbert, J. B., Kipling, J. J., McEnaney, B. and Sherwood, J. N. Polymer 1962, 3, 1; (e) Grassie, N. and Speakman, J. G. J. Polym. Sci. A-1 1971, 9, 919; (f) Grassie, N., Speakman, J. G. and Davies, T. I. ibid. 1971, 9, 931; (g) Grassie, N. and Speakman, J. G. ibid. 1971, 9, 949; (h) La Perriere, D. M., Ors, J. A. and Wight, F. R. 'Thermal Analysis', (Ed. B. Miller), Vol. II, Wiley Heyden Ltd., Great Britain, 1982, p. 1373; (i) van Krevellen, D. W. Polymer 1975, 16, 615; (k) Ravey, M., Fischler, Th. and Kramer, M. Fire and Materials 1978, 2(1), 34; (l) ibid. 1978, 2(2), 80
- Dahl, P. K. and Babu, G. N. Polymer 1985, 26, 747
- DePuy, C. H. and King, R. W. Chem. Rev. 1960, 60, 431 and references therein
- Hurd, C. D. and Blunk, F. H. J. Am. Chem. Soc. 1938, 60, 2419
- Simonsen, J. L. 'The Terpenes', Vol. II, 1932, p. 221
- (a) Cameron, G. G. and Kane, D. R. Makromol. Chem. 1968, 113, 75; (b) ibid. 1967, 109, 194; (c) ibid. J. Polym. Sci. B 1964, 3, 693
- Fuoss, R. M., Salyer, I. O. and Wilson, H. S. J. Polym. Sci. A 1964, 2, 3147
- Freeman, E. S. and Carrol, B. J. Phys. Chem. 1958, 62, 394; (b) Cameron, G. G. and Rudin, A. J. Polym. Sci., Polym. Phys. Edn. 1981, 19, 1799
- Flynn, J. H. and Wall, L. A. Polym. Lett. 1966, 4, 323
- Bremmer, B. J. I&EC Prod. Res. Dev. 1964, 3, 55