

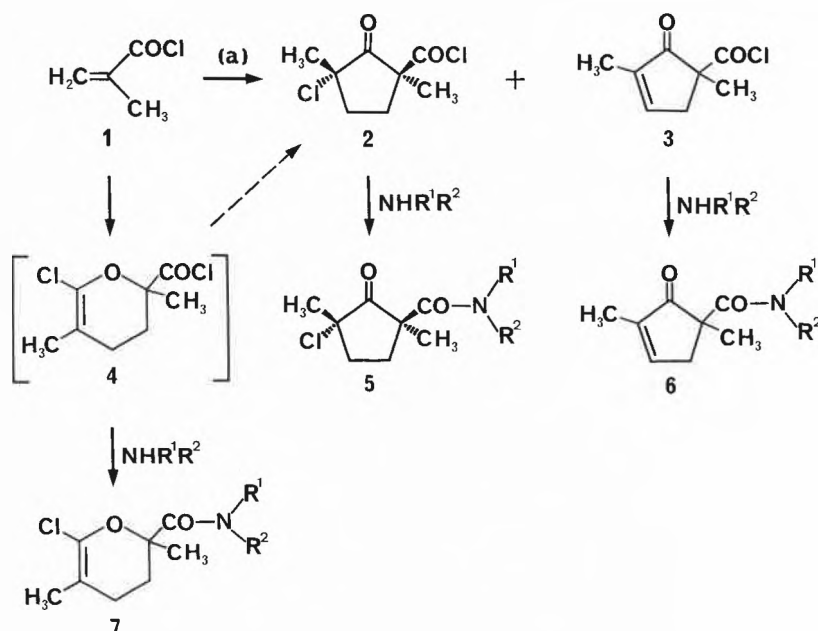
New Cyclic Dimers of Methacryloyl Chloride

Walter Fischer*, Daniel Belluš, Alex Alder, Eric Francotte, and Achim Roloff

Abstract: Methacryloyl chloride (1) forms cyclic dimers 2, 3, and 4 on storage over several years. Attempts to find a quicker high-yield preparation of 2, 3, and 4 were until now unsuccessful (maximum yield 17%). The stereochemistry of 2 was established by X-ray analysis of its amide derivative 5 ($R^1 = H$; $R^2 = C_6H_3-3,5-Cl_2$).

Derivatives of methacrylic acid are known to cyclodimerise thermally to either 1,1,2,2-tetrasubstituted (head-to-head dimers)^[1] or to 1,1,3,3-tetrasubstituted (head-to-tail dimers)^[2] cyclobutanes. Ene-reaction products have also been described^[1c,2]. No cyclodimers with five- or six-membered rings have been described yet although six-membered cyclodimers have been postulated in oligomerisation reactions^[3].

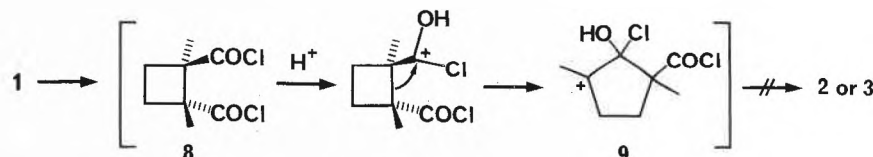
Typically, a sample of 1 that had been stored in a glass bottle in the dark at room temperature for more than 4 years contained, besides some 1 and tarry material, 50% of a mixture of 2 and 3 that distilled at 111–117°C/17 Torr^[5]. 2 and 3 were further characterised by conversion to the anilides 5 (29%) and 6 (26%) ($R^1 = H$; $R^2 = C_6H_3-3,5-Cl_2$) by reacting a mixture of 2 and 3 with 3,5-dichloroaniline in dioxane/pyridine at 80°C and



Scheme 1. (a) > 4 years, room temperature, or 40 hours, reflux, neutral Al_2O_3 (cat.).

We found that the unprecedented five-membered cyclic dimers 2 and 3 as well as six-membered cyclodimer 4 are frequently present in commercial samples of 1^[4] which have been stored in the dark in glass bottles for several years. Despite the widespread use of 1 as a reagent in organic and polymer chemistry none of the cyclodimers 2, 3, and 4 have been mentioned in the literature so far.

separating the products^[6]. Since 1H -NMR-spectra did not give conclusive results on the relative stereochemistry of the substituents in 5 an X-ray structure analysis was performed^[7,8].



The two methyl groups in 5 turned out to be *trans*. This result indicates that the

methyl groups in 2 must also be *trans* since no other isomer could be detected by NMR. Another sample of 1 of uncertain age^[4] that contained 2 almost exclusively was reacted with an excess of indoline in methylene chloride to give 59% of the indoline derivative^[9].

In an attempt to prepare 2 and/or 3 in a reasonable period of time a commercial sample of 1 (54.1 g, 517 mmol)^[10] was refluxed with neutral aluminium oxide (20 g; activity I, Woelm) for 40 hours. Direct distillation gave a fraction of *b.p.* 112–118°C/19 Torr (8.96 g) containing 5.32 g (10% yield) of 2 and 3.08 g (7% yield) of 3 besides minor impurities as estimated by 1H -NMR^[9].

In another set of experiments, flash-distilled methacryloyl chloride (1)^[11] was reacted with amines to obtain the corresponding methacrylamides. In addition, amides 7 of the oxa-Diels-Alder dimer 4^[12] were formed as by-products in modest yields (see Table 1). This indicates that 4 was already present in the original sample of 1^[11] since pure 1 (obtained by distillation under normal pressure through a Vigreux-column) did not give any 7, neither with the corresponding amines nor with preformed methacrylamides under the same conditions.

Table 1. Preparation of 7 by reaction of flash-distilled 1 (containing some 4) [11] with amines.

R^1	R^2	Reaction conditions	Yield of 7
H	Cholesteryl-	CH_2Cl_2 , NEt_3 , 0°C	16% [a]
H	$C_6H_4-4-NO_2$	CH_2Cl_2 , NEt_3 , 25°C	19% [b]
2-Methyl-2-propenyl	$C_6H_3-3,5-Cl_2$	hexane, NEt_3 , 25°C	9% [c]

[a] Besides 60% of the corresponding methacrylamide; [b] besides 46% of the corresponding methacrylamide and 4% of 5 ($R^1 = H$; $R^2 = C_6H_4-4-NO_2$) [13]; c) besides 40% of the corresponding methacrylamide.

The question of how 2 and 3 are formed has still to be answered. To test the hypothesis that 2 and 3 could arise via the acid catalysed ring expansion of an intermediately formed *trans* dimer 8^[5] we prepared 8 by an independent route^[16] and heated it in the presence of gaseous HCl and neutral Al_2O_3 at temperatures up to 130°C.

However, no trace of 2 or 3 could be detected by NMR. Thus, although the present work rules out the intermediacy of 8 and 9, the real pathway leading to 2 and 3 remains to be elucidated. Perhaps 4

is the elusive precursor of 2 and 3: In one case 4 was detected in a sample of flash-

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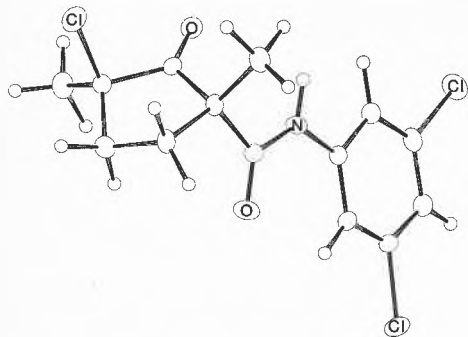


Fig. 1. ORTEP drawing of the molecular structure of **5** ($R^1 = H$; $R^2 = C_6H_3-3,5-Cl_2$)^[7, 8].

distilled **1** by 1H -NMR^[11] as well as by its reactions with amines to give **7**, but attempts to isolate **4** by distillation resulted in its rearrangement to **2**^[5].

Received: November 23, 1984 [FC 1]

- [1] a) D. Seebach: *Houben-Weyl, Methoden der Organischen Chemie*, Thieme Verlag, Stuttgart 1971, Vol. IV/4, p. 267 (review); b) W. von E. Doering, C. A. Guyton, *J. Am. Chem. Soc.* 100 (1978) 3229; c) J. Lingnau, M. Stickler, G. Meyerhoff, *Eur. Polym. J.* 16 (1980) 785.
- [2] A. Alder, D. Belluš, *J. Am. Chem. Soc.* 105 (1983) 6712.
- [3] a) K. D. Gundermann, R. Thomas, *Chem. Ber.* 92 (1959) 1503; b) M. Stickler, G. Meyerhoff, *Makromol. Chem.* 181 (1980) 131.
- [4] Samples of **1** were purchased from Fluka AG (Buchs).
- [5] **2** and **3** occurred in different fractions in somewhat varying amounts. Thus the following 1H -NMR assignments could be made (CCl_4 , $\delta_{TMS} = 0$): **2**: 1.67 (3H, s) and 1.73 (3H, s, $2 \times CH_3$), 2.2–2.7 (4H, m, $-CH_2CH_2-$). **3**: 1.39 (3H, s, CH_3), 1.80 (3H, m, $CH_3-C=C$), 3.10 (1H, m) and 3.41 (1H, m, CH_2), 7.20 (1H, m, $-CH=$).
- [6] Column chromatography (silica gel, CH_2Cl_2): **5** ($R^1 = H$; $R^2 = C_6H_3-3,5-Cl_2$), *m.p.* (hexane) 114–116°C [14]; 1H -NMR ($CDCl_3$): 1.64 and 1.66 (6H, $2 \times s$, $2 \times CH_3$), 1.8–2.6 (tot. 3H, m) and 2.8–3.15 (1H, m, $-CH_2CH_2-$), 7.05 (1H, m) and 7.44 (2H, m, Ar-H), 8.27 (1H, br. m, NH). **6** ($R^1 = H$; $R^2 = C_6H_3-3,5-Cl_2$), *m.p.* (hexane) 75–77°C [14]; 1H -NMR ($CDCl_3$): 1.52 (3H, s, CH_3); 1.81 (3H, m, $CH_3-C=C$), 2.45 (1H, $2 \times m$, $J = 18$ Hz) and 3.48 (1H, $2 \times m$, $J = 18$ Hz, CH_2), 7.03 (1H, m) and 7.49 (2H, m, Ar-H), 7.40 (1H, m, $-CH=$), 9.17 (1H, br. m, NH).
- [7] We thank Mrs. G. Rihs for the X-ray structure analysis and Dr. G. Rist and Dr. T. Winkler for 1H -NMR investigations.
- [8] The atomic coordinates for this work are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (CSD 51127), or from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.
- [9] **5** ($R^1, R^2 = -CH_2CH_2-o-C_6H_4-$) was isolated by chromatography with ethyl acetate/toluene 1:10 on silica gel, *m.p.* 133°C. 1H -NMR ($CDCl_3$): 1.67 (3H, s) and 1.74 (3H, s, $2 \times CH_3$), 2.1–2.4 (3H, m) and 2.65–2.8 (1H, m, $-CH_2CH_2-$), 3.05–3.3 (2H, m) and 4.1–4.35 (2H, m, $-CH_2CH_2-$ of indoline), 7.06 (1H, m), 7.20 (2H, m) and 8.09 (1H, d, Ar-H).
- [10] This sample was not distilled before use and contained ca. 80% of **1**, no **3** and only trace amounts of **2**, but some other unknown impurities.

- [11] This sample was distilled in a rotary evaporator at reduced pressure at room temperature (conditions under which dimers might have codistilled). A reexamination of the distillate by 1H -NMR showed mainly **1**, almost none of **2** and **3**, but ca. 20% of **4**, 1H -NMR (CCl_4): 1.60 (s) and 1.70 (s, $2 \times CH_3$), (other peaks not clearly identified).
- [12] Some very electrophilic acrylates are known to give products of oxa-Diels-Alder reactions: a) D. Belluš, H.-P. Fischer, H. Greuter, P. Martin, *Helv. Chim. Acta* 61 (1978) 1784, footnote 15; b) B. B. Snider, D. M. Roush, T. A. Killinger, *J. Am. Chem. Soc.* 101 (1979) 6023; c) H. K. Hall, H. A. A. Rasoul, M. Gillard, M. Abdelkader, P. Noguees, R. C. Sentman, *Tetrahedron Lett.* 23 (1982) 603.
- [13] In this case both cyclodimers, **2** and **4**, gave derivatives in the same reaction which were separated by column chromatography [14]: **5** ($R^1 = H$; $R^2 = C_6H_4-4-NO_2$): *m.p.* 165.5–166°C; 1H -NMR ($CDCl_3$): 1.68 (3H, s) and 1.73 (3H, s, $2 \times CH_3$), 1.9–2.2 (2H, m), 2.35 (1H, m) and 2.95–3.1 (1H, m, $-CH_2CH_2-$), 7.71 (2H, d, $J = 8.5$ Hz) and 8.23 (2H, d, $J = 8.5$ Hz, Ar-H), 8.64 (1H, br. m, NH). — **7** ($R^1 = H$; $R^2 = C_6H_4-4-NO_2$): *m.p.* 141–142°C; 1H -NMR ($CDCl_3$): 1.58 (3H, s, CH_3), 1.70 (3H, s, CH_3), 1.8–2.0 (1H, m), 2.05–2.2 (2H, m) and 2.3–2.45 (1H, m, $-CH_2CH_2-$), 7.75 (2H, d, $J = 8.5$ Hz) and 8.25 (2H, d, $J = 8.5$ Hz, Ar-H), 8.50 (1H, br. m, NH).
- [14] All new compounds gave satisfactory elemental analyses (C, H, N, Cl; $\pm 0.3\%$).
- [15] For ring expansion reactions of cyclobutyl-substituted cations see [1a], p. 430 ff.
- [16] **8** was prepared in quantitative yield by treatment of *trans*-1,2-dimethyl-1,2-cyclobutanedicarboxylic acid [17] with $SOCl_2$ (reflux, 1 h) [18a]; 1H -NMR (CCl_4): 1.67 (s) and 1.5–1.9 (m, tot. 8H, $2 \times CH_3$ and $2 \times CH$), 2.2–2.65 (2H, m, $2 \times CH$).
- [17] D. J. Trecker, J. P. Henry, R. L. Brandon (Union Carbide Corp.), *US Patent 3453197* (1969). We prepared this compound by acid catalysed hydrolysis of *trans*-1,2-dimethyl-1,2-dicyanocyclobutane [18].
- [18] a) M. Baumann, D. Belluš, unpublished results; b) J. Barltrop, H. A. J. Carless, *J. Am. Chem. Soc.* 94 (1972) 1951.