Michael-type Additions of Oxime and Hydrazone Anions with Methyl α-Bromoacrylate. *X*-Ray Structure Determination of a Bromocyclopropane Derivative

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Oxime and hydrazone anions undergo a Michael-type addition with methyl α-bromoacrylate leading to bromocyclopropane derivatives, the structure of which has been established by *X*-ray analysis.

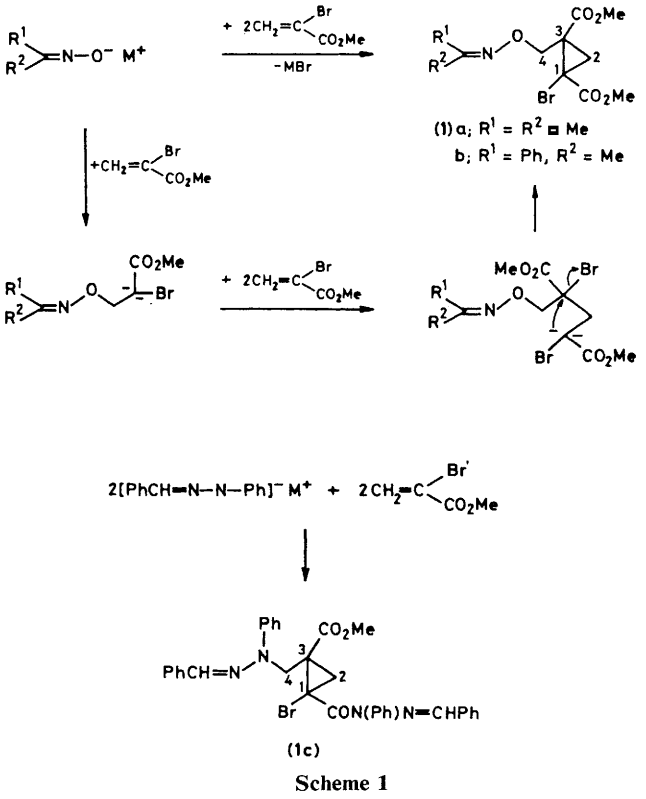
In a previous paper the formation of 1-azabicyclo[2.1.0]pentanes from the reaction between imine anions and methyl α-bromoacrylate was described.[1] We now report the reactions of the same olefin derivative with anions of oximes and hydrazones.

In each case, the only product of the reaction may be identified as a possible bromo-cyclopropane derivative (**1**) which would be formed *via* two Michael-type additions and a further intramolecular elimination of the bromine anion as shown in Scheme 1.

Several attempts were made to study the course of the reaction using Bu^{n}Li, lithium di-isopropylamide, and NaH as bases and tetrahydrofuran (THF), THF–hexamethylphosphoric triamide, dimethoxyethane, and diethyl ether at low and room temperatures. In all cases only compound (**1**) was identified in the crude material (yield 40—60%). The ^{1}H and ^{13}C n.m.r. spectra were in good agreement with the structure shown for (**1**).†

To confirm the structure of compound (**1c**) and to determine which of the ester groups was substituted by the hydrazino-group an *X*-ray analysis was necessary.

Crystal data: $C_{33}H_{29}BrN_4O_3$, $M = 609.52$, triclinic, space group $P\bar{1}$, $a = 10.643(4)$, $b = 11.373(2)$, $c = 13.030(3)$ Å, $\alpha = 85.39(3)$, $\beta = 79.43(4)$, $\gamma = 70.70(4)°$, $Z = 2$. The intensities



Scheme 1

of 3920 independent reflections with $I > 2\sigma(I)$ were measured (Mo-K_α radiation) with an automatic Enraf–Nonius CAD-4 diffractometer of the 'Centre de Diffractométrie' of the University of Rennes. The structure was solved by direct

† *Selected spectral data:* (**1a**), ^{1}H n.m.r. δ ($CDCl_3$–$SiMe_4$) 1.68 and 2.38 (*J* 6.5 Hz, 2-H), 4.24, and 4.77 (*J* 11.4 Hz, 4-H); ^{13}C n.m.r. δ 26.02 p.p.m. [*J* (^{13}C–H) 168 Hz, C-2]. (**1b**) ^{1}H n.m.r. δ 1.68 and 2.41 (*J* 6.6 Hz, 2-H), 4.41 and 4.93 (*J* 11.1 Hz, 4-H). (**1c**) ^{1}H n.m.r. δ 1.78 and 2.68 (*J* 7.5 Hz, 2-H), 4.45 and 5.25 (*J* 14.0 Hz, 4-H); ^{13}C n.m.r. δ 25.92 p.p.m. [*J* (^{13}C–H) 168 Hz, C-2]. As was noticed by a Referee, the C-4 protons for (**1c**) are at lower field than those for (**1a**) and (**1b**). This could result either from the three-dimensional structure of these compounds or from the effect of the phenyl group attached to the nitrogen atom next to C-4.

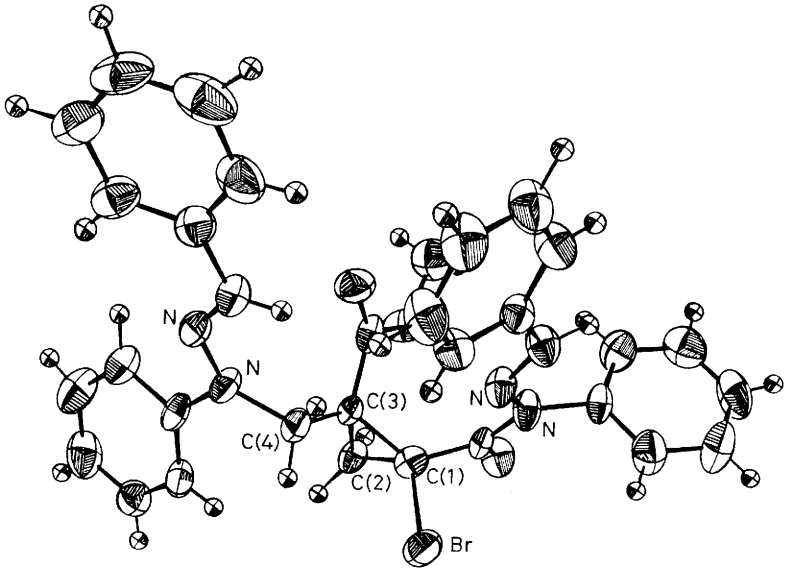


Figure 1. Crystal structure of compound (**1c**); C(1)–C(2) 1.488(6), C(2)–C(3) 1.523(6), C(1)–C(3) 1.547(6), C(3)–C(4) 1.532(6) Å, C(2)–C(1)–C(3) 60.2(3), C(1)–C(2)–C(3) 61.8(3), and C(1)–C(3)–C(2) 58.0(3)°.

methods with the SDP-Enraf–Nonius package and was refined by least-squares to a final *R*-value of 0.032.‡

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23369 (12 pp) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.

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2 B. A. Frenz, in 'Enraf–Nonius CAD-42DP, Real Time System for Current *X*-Ray Data Collection and Crystal Structure Determination in Crystallography,' eds. M. Schenk and R. Olthof-Hazekamp, 1978.