

SIMPLE NEW SYNTHESIS OF GEM-CHLOROBROMO COMPOUNDS BY HOMOLYTIC
PHOTOSUBSTITUTION OF GEM-CHLORONITROSO COMPOUNDS

J Pfab

Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland

(Received in UK 29 January 1976; accepted for publication 16 February 1976)

In contrast to gem.-dichlorides and gem.-dibromides the mixed geminal dihalides with the exception of the corresponding cyclopropanes are not readily available.

In a previous investigation of the mechanism of the (n^*,π^*) photochemistry of gem.-chloronitroso compounds¹ it was shown that the use of bromine as radical scavenger in the photolysis of 1-chloro-1-nitrosocyclohexane leads to quantitative formation of 1-chloro-1-bromocyclohexane. The preparative potential of this method, which is evident from the earlier work^{1,2} has now been verified and its scope explored. The method is of synthetic interest for two reasons the starting materials are readily available, since gem.-chloronitroso compounds can be made easily by chlorination of oximes; and the use of specialised photochemical equipment is not essential, external irradiation with unfiltered light of ordinary tungsten filament lamps being adequate

Typically, the reaction is carried out with a $5-15 \times 10^{-2}$ M solution of the chloro-nitroso compound in CCl_4 or CFCl_3 in the presence of a five-fold molar excess of Br_2 . A 400 W high pressure sodium lamp used in the arrangement described previously³, although not essential, is optimally suited. The photolysis is completed within 10 to 30 minutes. Standard work-up procedures afford good yields of the gem.-chlorobromo compounds, as indicated by the examples summarised in the table. If tungsten lamps are used as light sources the conversion rate is lower due to the lower light intensity, the yields being unaffected

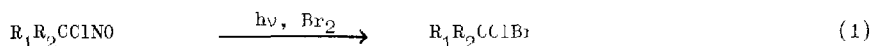
Table: gem -chlorobromo compounds $\text{R}_1\text{R}_2\text{CClBr}$ prepared

Compound	R_1	R_2	yields*	Literature
1	CH_3	CH_3	75	4,5
2	CH_3	C_2H_5	85	4,5
3	C_2H_5	C_2H_5	90	5
4	CH_3	$t\text{-C}_4\text{H}_9$	70	6
5	cyclo- C_6H_{10}		89	1,7
6	2,2-adamantyl		92	-

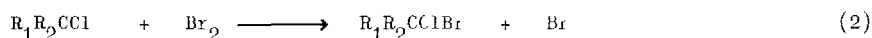
* isolated yields, purity (by g l.c.) > 98%.

All of the compounds have been described previously in the literature with the exception of 2-chloro-2-bromoadamantane, which had m.p. 185^o, ν (KBr). 2930, 2860, 1560, 1455, 1353, 1270, 1100, 960, 902, 772 and 640 cm^{-1} and was identified by its correct microanalysis

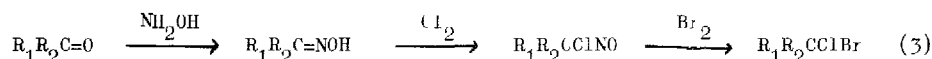
The reaction described here is new apart from the original brief mention^{1,2} and can be summarised as in (1)



The absorption of light of wavelengths 500–700 nm results in photodissociation of the C–N bond of the nitroso compound. The reaction of the photolytically generated α -chloroalkyl radical with Br_2 will lead to the observed product and can be classified as an $\text{S}_{\text{H}}2$ reaction, in which a bromine atom is displaced (2)



The results summarised in the table indicate clearly that route (3) provides an attractive method for converting carbonyl compounds into the gem-chlorobromo compounds via the oximes and chloronitroso compounds



The use of iodine instead of bromine as radical scavenger permits the synthesis of gem.-chloroiodo compounds according to equation 4



As the weak n^*, π^* absorption band of the nitroso compound is submerged in the strong iodine absorption, the irradiation times are longer and the yields smaller due to side reactions. Optimal experimental conditions for (4) have yet to be found, however

Acknowledgement. The author thanks Professor Gowenlock for his interest in this work

References

- 1 B. G. Gowenlock, J. Pfab and G. Kresze, *J. Chem. Soc. Perkin II*, 1974, 511
- 2 J. Pfab, Ph.D. thesis, Technical University Munich, 1972, page 57 and 130
- 3 B. G. Gowenlock, G. Kresze and J. Pfab, *Tetrahedron Letters*, 29, 5587 (1973)
- 4 M. S. Kharasch, W. S. Zimmt and W. Nudenberg, *J. Org. Chem.* 20, 1430 (1955)
- 5 C. I. Stevens, T. K. Mukherjee and V. J. Traynelis, *J. Am. Chem. Soc.* 78, 2264 (1956)
- 6 B. I. Hawkins, W. Bremser, S. Brodic and J. D. Roberts, *J. Am. Chem. Soc.* 93, 4472 (1971)
- 7 H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.* 79, 6270 (1957)