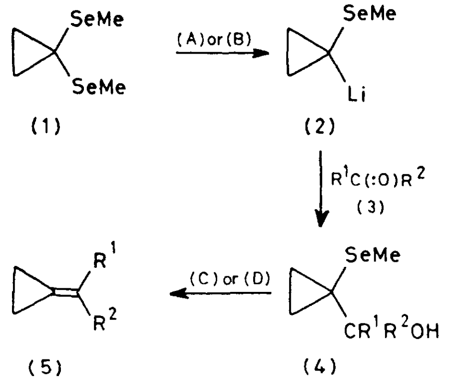
Regiospecific Synthesis of Alkylidene Cyclopropanes†

By SERGE HALAZY and ALAIN KRIEF*

(*Department of Chemistry, Facultés Universitaires N.D. de la Paix* 61, *rue de Bruxelles, Namur, Belgium*)

Summary Alkylidene cyclopropanes are prepared from carbonyl compounds and α-selenolithiocyclopropane with formation of new C–C bonds.

FEW reports[1] deal with the synthesis of alkylidenes cyclopropanes from carbonyl compounds. We have found that 1-methylseleno-1-lithiocyclopropane[3] is a valuable reagent in the synthesis of alkylidene cyclopropanes from aldehydes and ketones, even those which are readily enolisable such as deoxybenzoin and 2,2,6-trimethylcyclohexanone.



SCHEME 1.

The transformation shown in Scheme 1 takes advantage of the improved nucleophilicity of the carbanion towards carbonyl compounds when ether‡ is used as solvent (method A) instead of tetrahydrofuran (THF) (method B), and the discovery that the β-hydroxycyclopropyl selenides (**4**) give alkylidene cyclopropanes (**5**) on reaction with carbonyldi-imidazole (2 mol. equiv.; toluene 110 °C; method C) for those derived from aldehydes and on reaction with phosphorus tri-iodide (2 mol equiv., NEt_3; CH_2Cl_2; 20 °C; method D) for those derived from ketones (Table). Methods

TABLE

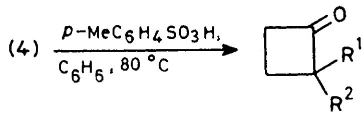
		% Yield of (4)		% Yield of (5) (time/h)	
R^1	R^2	(A)[a]	(B)[a]	(C)[a]	(D)[a]
$C_{10}H_{21}$	H	—	75	65 (15)	—
C_9H_{19}	Me	70	54	33[b] (40)	58 (0·5)
Ph	CH_2Ph	70	—	—	75 (2)
$-CMe_2-[CH_2]_3-CHMe-$		64	—	—	75 (2·5)

[a] Method (A): Bu^tLi in Et_2O; (B) Bu^nLi in THF; (C) carbonyl di-imidazole; (D) PI_3. [b] A mixture of allylcyclopropylselenides was also isolated in 35% yield.

---

† Part of this work was presented at the 3rd International Symposium on Selenium and Tellurium chemistry held in Metz (July 1979).

‡ Bis(methylseleno)cyclopropane is not cleaved by Bu^nLi in ether and requires the use of Bu^tLi (*cf.* ref. 2).



(6)

Scheme 2

$R^1 = C_{10}H_{21}$, $R^2 = H$; 73% yield of (**6**); 6 h reaction.
$R^1 = C_9H_{19}$, $R^2 = Me$; 73% yield of (**6**); 0·2 h reaction.

C and D also allow the very efficient synthesis of straight-chain olefins from the corresponding *β*-hydroxyselenides. However, other reagents already described[3] for this purpose were found to be ineffective for the synthesis of alkylidene cyclopropanes; toluene-*p*-sulphonic acid in benzene produces cyclobutanones instead of olefins.[3b] The latter transformation, similar to that described by Trost,[4] is better achieved in wet benzene[4] (Scheme 2).

We thank I.R.S.I.A. (Belgium) for a fellowship (to S. H.).

(*Received*, 29*th August* 1979; *Com.* 930.)

---

[1] (a) H. J. Bestman and T. Denzel, *Tetrahedron Letters*, 1966, 3591; (b) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, 1968, **33**, 336.

[2] S. Halazy, J. Lucchetti, and A. Krief, *Tetrahedron Letters*, 1978, 3971.

[3] (a) H. J. Reich and F. Chow, *J.C.S. Chem. Comm.*, 1975, 790; (b) J. Remion, W. Dumont, and A. Krief, *Tetrahedron Letters*, 1976, 1385; (c) J. Remion and A. Krief, *ibid.*, 1976, 3743.

[4] B. M. Trost, D. E. Keeley, H. C. Arndt, and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 1977, **99**, 3088.