Nonstereospecificity in the Simmons–Smith Reaction of αβ-Unsaturated Ketones

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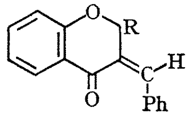
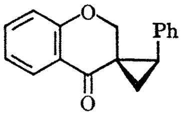
Summary *cis*-Chromindogenide reacted nonstereospecifically with methylene iodide/zinc–copper couple to form *trans*-2-phenylcyclopropyl-1-spiro-3-chromanone—the cyclopropyl ketone also formed in the Simmons–Smith reaction of *trans*-chromindogenide.

BASED on the stereospecific reaction of the more stable isomer of benzylideneacetone with methylene iodide/zinc–copper couple, Conia and Limasset[1] found that the Simmons–Smith reaction is stereospecific for αβ-unsaturated ketones. However, the production[2] of identical cyclopropanes from the *cis*- (I; R = Ph) and *trans*-isomers of flavindogenide, under the usual conditions[3] of the Simmons–Smith reaction, showed that this is not always so and led us to examine the products of this reaction with the *cis*- (I; R = H) and *trans*-isomers of the simpler parent compound, chromindogenide.



(I)



(II)

Before doing so, the effect of the individual components of the reaction on *cis* ⟷ *trans* isomerisation of the substrate was examined. The results are given in Table 1.

TABLE 1

Component and conditions	% Isomerisation *cis*-to-*trans*	% Isomerisation *trans*-to-*cis*
T[a] + CH_2I_2	0	14
T + glyme	0	20
T	4	4
T + ZnI_2	80	6
T + I_2	100	0
T + Zn/Cu	100	

[a] At temperature of refluxing ether for 5·25 hr. in daylight.

The *trans*-to-*cis* isomerisation must be due to a photochemical process; most probably methylene iodide and glyme act as sensitisers.

TABLE 2

Chromindogenide isomer	Time (hr.)	Light	Glyme	Product composition: Chromindogenide residue Wt. (mg.)	% *cis*	% *trans*	*trans*-Cyclopropane (II); wt. (mg.)
cis	24	yes	yes	515	11	89	18
cis	6	yes	no	747	24	76	13
cis	21	yes	no	740	14	86	60
trans	67	no	yes	672	19	81	42
trans	20	no	no	550	19	81	36
trans	119	yes	yes	536	69	31	64
trans	5·25	yes	no	658	50	50	37

The optimum conditions for the Simmons–Smith reaction on *cis*-chromindogenide (I; R = H) therefore appeared to include the filtering off of excess of zinc–copper couple,[4] the complexing of zinc iodide by-product with glyme, and the use of a minimum of iodine. The result of this experiment and of several others on both the *cis*- and the *trans*-isomers are given below (Table 2). All reactions were carried out in refluxing ether on 1 g. of chromindogenide in the absence of an excess of the couple and under deoxygenated nitrogen.† The results quoted in each case are those for the experiment giving the greatest yield of cyclopropane.

In no case was *cis*-2-phenylcyclopropyl-1-spiro-3-chromanone‡ detected (n.m.r. and t.l.c.); the cyclopropane obtained was the *trans*-isomer (II).

The substantial isomerisation of *trans*-chromindogenide during the Simmons–Smith reaction must be due to a combination of daylight and the photosensitising action of the reaction components. This is supported by the fact that, in the absence of light, *trans*-to-*cis* isomerisation was greatly reduced (what occurred probably took place during the work-up in daylight).

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† An essential condition for cyclopropane formation from chromindogenides in the absence of an excess of zinc–copper couple.

‡ Prepared (m.p. 83°) for establishment of its physical properties by photochemical or thermal (310°) rearrangement of its *trans*-somer (II), m.p. 61°.

[1] J. Conia and J. Limasset, *Tetrahedron Letters*, 1965, 3151.
[2] J. A. Donnelly, unpublished work.
[3] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256.
[4] E. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048.