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BEHAVIOR OF α-METHOXYCYCLOPROPYL RADICAL IN HUNSDIECKER REACTION

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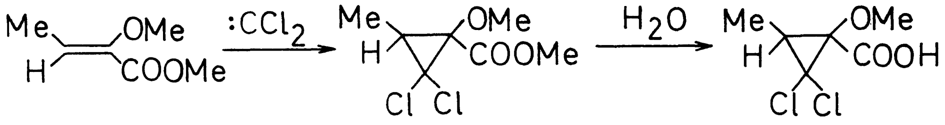
The Hunsdiecker reaction of trans-1-methoxy-2-methyl-3,3-dichlorocyclopropanecarboxylic acid with bromine in carbon tetrachloride at 0°C and 77°C has been found to occur with substantial inversion of configuration, suggesting the low configurational stability of the α-methoxycyclopropyl radical as compared with the α-methoxyvinyl radical.

Recent studies on reactions which proceed *via* α-substituted cyclopropyl radicals, *e.g.*, the Hunsdiecker reaction of α-substituted cyclopropanecarboxylic acids,$^{1)}$ the reduction of α-substituted cyclopropyl halides with organotin hydride,$^{2,3,4)}$ and the thermal or photolytic decomposition of α-substituted cyclopropanepercarboxylic acid esters,$^{1,5)}$ have revealed the profound effect of the α-substituent on the configurational stability of α-substituted cyclopropyl radicals.

The substituents hitherto examined are, however, rather limited and include only fluoro,$^{1,2a,2b,2d)}$ chloro,$^{1,2b,3b,4,5)}$ trifluoromethyl,$^{3a)}$ methoxycarbonyl,$^{2c)}$ and cyano.$^{2c)}$ The object of the present study is to generate the α-methoxycyclopropyl radical, which seems to have escaped the investigation because of its synthetic difficulty, by use of the Hunsdiecker reaction and to compare its configurational stability with those of other related radicals.

The starting material employed for the present study was methyl trans-α-methoxycrotonate (**1**).$^{6)}$ The reaction of **1** with dichlorocarbene, generated by the thermal decomposition of sodium trichloroacetate at 125-130°C,$^{7)}$ gave methyl trans-1-methoxy-2-methyl-3,3-dichlorocyclopropanecarboxylate (**2**), bp 100-106°C at 13 mm Hg, $n_D^{19.0}$ 1.4686, in a yield of 45.2%. The hydrolysis of **2** with potassium hydroxide in 50% aqueous ethanol gave the free acid (**3**), bp 114–118°C at 2.0–2.2 mm Hg, mp 75.0–75.5°C, in a yield of 82.4%.



(**1**) (**2**) (**3**)

The Hunsdiecker reaction of **3** was effected by adding an equivalent amount of bromine to a suspension of the silver salt of **3** in CCl_4[8] or to a solution of **3** in CCl_4 in the presence of HgO[9] either at 0°C or at 77°C, and keeping the reaction mixture at the same temperature for 1.5–2.5 hrs, followed by the usual work-up. The reaction conditions and the yields are summarized in Table, which also lists the isomer distributions in the products (**5a** and **5b**).

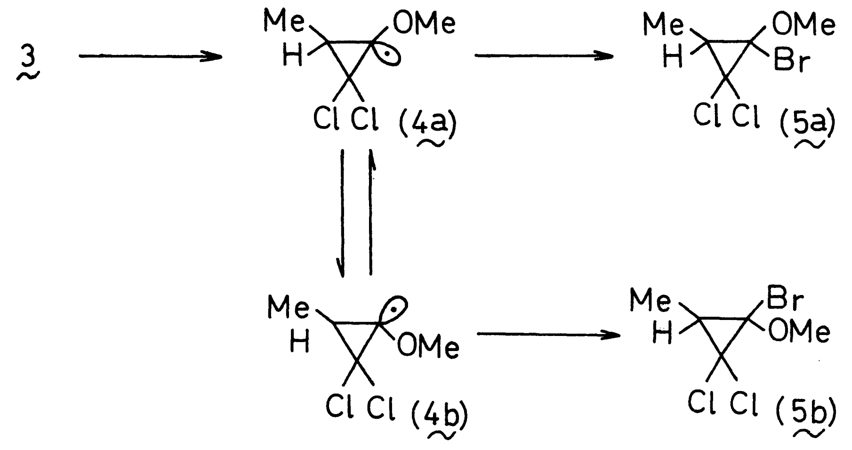
Table Hunsdiecker Reaction of **3**

Reaction Temp., °C	Method	Reaction Time, hr	Yield, %	Isomer Ratio* **5a**/**5b**
0	Ag-salt	1.5	54	58/42
		2.0	76	56/44
	HgO	1.5	56	56/44
		2.0	60	57/43
		2.5	60	53/47
77	Ag-salt	1.5	53	41/59
		2.0	59	39/61
	HgO	1.5	75	41/59
		2.0	70	37/63
		2.5	70	38/62

* Determined by vpc (7% TCP on Celite 545, 100°C, 3 mm x 3 m) before distillation. **5b** had a longer retention time than **5a**.

The configurations of **5a** and **5b** were determined based on the comparison of the rates of their ring opening in hot quinoline;[10] when a sample of the product obtained from the Hunsdiecker reaction (HgO) at 0°C was heated in quinoline at 110°C, the isomer ratio changed from 56/44 to 44/56 (after 1 hr) and to 28/72 (after 2 hrs). According to the Woodward-Hoffmann-DePuy's rule,[11] structure **5a** should be assigned to the more readily decomposing isomer. The ir, nmr, and mass spectra of **5a** and **5b** were in good agreement with the proposed structures.

Table shows that the Hunsdiecker reaction of **3** occurred with substantial inversion of configuration of the starting material even at 0°C, and that the ratio of retention to inversion



decreased as the reaction temperature increased.12) This means that radical **4a**, initially formed in the reaction, is configurationally rather unstable and inverts its configuration at a rate comparable to its bromine abstraction at 0°C, and at a rate faster than the latter at 77°C. The possibility of the equilibration between **4a** and **4b** preceding their bromine abstraction at 77°C may be ruled out because, if it is the case, **4a** should abstract bromine more rapidly than **4b** on steric grounds, and as a result **5a** should be preferentially formed contrary to the observations.

The behavior of radical **4a** reported here is in sharp contrast with those of the *cis*- and *trans*-α-methoxycrotyl radicals, both of which have been reported13) to be configurationally stable enough to retain their configurations even in the thermal decomposition of the corresponding percarboxylic acid esters in protonic solvents at 110°C.

This diffefence must be due, at least partly, to the difference in *s*-character of the odd electron orbital between the cyclopropyl and the vinyl systems, although the steric repulsion between the methyl and the methoxy groups on the same side of the ring is probably also responsible for the low configurational stability of **4a** as compared with **4b**. It seems to be noted, in this connection, that a similar difference has been observed between α-chlorocyclopropyl1) and α-chlorovinyl14) radicals.

To obtain more decisive information as to the configurational stability of both **4a** and **4b**, studies are now being made on the reduction of **5a** and **5b** with tri-*n*-butyltin hydride.15)

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15. Attempts to prepare the cis isomer of **3** by the addition of dichlorocarbene to the cis isomer of **1** were unsuccessful; the benzophenone-sensitized photoisomerization of **1**, reported[13] to give a 70/30 mixture of the trans and the cis esters, could not be duplicated in our hands for some unknown reasons.

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