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CATHODIC ADDITION OF TETRACHLOROMETHANE AND ETHYL TRICHLOROACETATE TO CARBONYL COMPOUNDS

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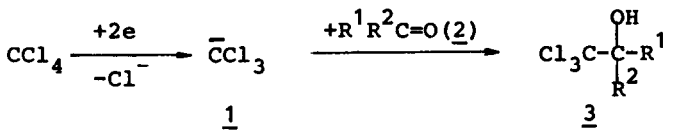
Deprotonation of trichloromethane yields the trichloromethyl anion (1), that can be added to carbonyl compounds.[1] We wish to report that this addition can also be achieved cathodically. 1 can be generated at -0.75 V vs. s.c.e.[2] from tetrachloromethane and reacted with aldehydes and ketones to form trichloromethyl carbinols (3) (Table I).



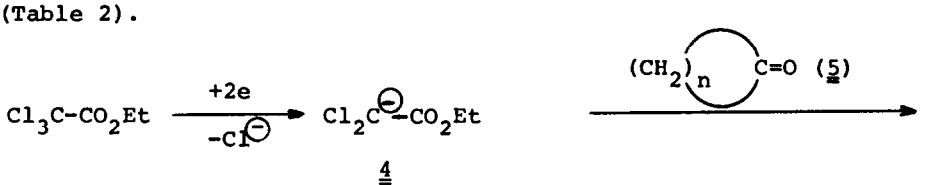
1 3

Table I. Cathodic addition of tetrachloromethane to carbonyl compounds

2 R^1	R^2	3-yield %	a)
Phenyl	H	70	(80)
$-(CH_2)_5-$		25	(23)
Methyl	Ethyl	10	(13)
^{i}Prop	H	30	(34)
Prop	H	32	(—)

a) current yields; numbers in parentheses are yields achieved by phase-transfer catalyzed addition of trichloromethane.[1a]

The ethyl dichloroacetate anion (4), cathodically generated from ethyl trichloroacetate,[3] adds to cyclic ketones 5 to yield the keto esters 6 and 7 (Table 2).



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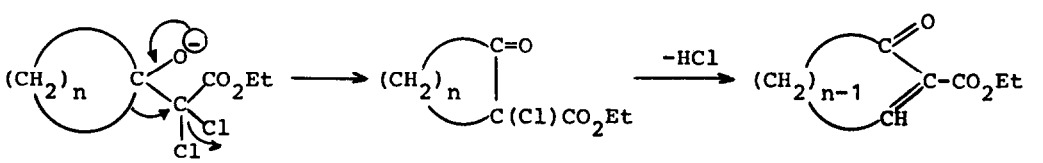

8 6 7

The formation of 6 can be conceived by a ring-expansion reaction of the adduct 8.[4,5]

Table II. Cathodic addition of ethyl trichloroacetate to cyclic ketones.

5 n	6 yield	7 % a)
3	43	-
4	27	-
5	7	20

a) current yields.

Ethyl 1-chloro-2-oxo-1-cyclohexanecarboxylate 6 (n=4): 50 mmol ethyl trichloroacetate and 50 mmol cyclopentanone are electrolyzed in a divided cell in 80 ml DMF (4.2 g $LiClO_4$) at a mercury cathode at 0°C and a potential of -0.9 to -1.0 V vs. s.c.e. until 0.07 F were consumed. The catholyte was poured into 250 ml water and extracted with ether. Bulb to bulb distillation afforded 1.98 g 6 (n=4); ^{1}H-NMR (CCl_4, ppm): 4.33 (2H, q, J=7 Hz), 2.38 (4 H,m), 1.98 (4 H,m), 1.40 (3 H,t, J=7 Hz); IR (film): 1730/cm; MS m/e (%): 168 (2), 140 (6), 95 (72), 67 (base).

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