Intramolecular Dehydration of Dialkylacetic Acids and Trimethylsilylacetic Acid with Dicyclohexylcarbodiimide to the Corresponding Stable Ketenes[1]

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A new, simple preparation for stable dialkyl ketenes involving intramolecular dehydration of appropriately substituted acetic acids with dicyclohexylcarbodiimide (DCC) in the presence of catalytic amounts of triethylamine gives 60–70% yield of the corresponding ketenes. Trimethylsilylacetic acid also gives trimethylsilylketene in good yield.

In 1908 Staudinger and coworkers reported the synthesis and isolation of diphenylketene,[2] the first example of a stable ketene. The traditional methods for preparation of ketenes include the dehydrohalogenation of appropriately substituted acetyl halides or the zinc dehalogenation of α-haloacetyl halides.[3] Recently, several improved methods have been reported for the generation of ketenes using *p*-toluenesulfonyl chloride[4] and Mukaiyama's reagent.[5] We now report a convenient method for the preparation of stable ketenes via intramolecular dehydration of appropriately substituted acetic acids by dicyclohexylcarbodiimide (DCC).

When a mixture of DCC and catalytic amount of trimethylamine in diethyl ether was reacted with di-*tert*-butylacetic acid, and the reaction was worked up after a stipulated time (see experimental), di-*tert*-butylketene was obtained in 70% yield as isolated product. Di(1-adamantyl)- and 1-adamantyl-*tert*-butylacetic acids gave the corresponding ketenes **2c** and **2d** in 74% and 69% yields, respectively (Table).

Table. Ketenes **2** Prepared

Product	R^1	R^2	Yield	Bp (°C)	mm	Ref.
				found	lit.	
2a	*t*-Bu	*t*-Bu	70	58°/0.5	73°/45	8
2b	Me_3Si	H	63	82°	82°	9, 10
2c	1-ada[a]	1-ada	74	102°/0.5		11
2d	1-ada	*t*-Bu	69	71°/0.5		11

[a] ada = adamantyl.

We have applied the described method primarily to the preparation of isolable stable dialkylketenes. Trimethylsilylacetic acid also gives with 63% yield the remarkable stable trimethylsilylketene. Due to the bulkiness of the Me_3Si group in this case a monosubstituted acetic acid also is well adaptable to the method.

Diphenylketene[2] and dimethylketene[6] were obtained in only low yield (20 and 30%, respectively) via the reaction of their substituted acetic acid precursors and DCC, the major reaction products being their [2 + 2] cycloaddition adducts with DCC, i.e. imino-β-lactams. It is well documented that carbodiimides are good ketenophiles, which undergo 1,2-cycloaddition with various ketenes to give the corresponding imino-β-lactams.[7] The bulky di-alkylketenes prepared in our work show significant inertness in the presence of DCC and are obtained in reasonable yields from the substituted acetic acids with DCC. Furthermore, that the corresponding substituted acetic anhydrides have not been obtained (via reaction of the ketenes with the substituted acetic acids) is also in accord with the high stability of the prepared ketenes shown in the Table.

The direct preparation of bulky, generally disubstituted ketenes via dehydration of the corresponding dialkylacetic acids should prove to be an alternative simple preparation of these stable ketenes in high purity from readily available substituted acetic acid precursors.

All products were known previously from the literature and were determined by their ^{1}H- and ^{13}C-NMR spectroscopy as well as molecular weight based on GC/MS spectroscopy.

Di(1-adamantyl)acetic acid and 1-adamantyl-*tert*-butylacetic acids were prepared[11] from the corresponding olefins synthesized according to our recent procedure.[12] Diethylether was dried over sodium under reflux.

Gas chromatographic analysis were carried out on a Varian Model 3700 gas chromatograph equipped with an ion-trap detector and interfaced with a Varian Associates Model 3500 gas chromatograph. NMR spectra were recorded on a Varian (VXR-200) superconducting NR spectrometer. Melting/boiling points were determined in a Mettler machine and are uncorrected.

Di-*tert*-butylketene (2a); Typical procedure:

To a ethereal solution of dicyclohexylcarbodiimide (DCC; 20.6 g, 0.1 mol) and dry ether (200 mL) is added a catalytic amount of freshly distilled Et_3N (ca. 0.1 g). To the reaction mixture, cooled to 0 °C in an ice bath with stirring under nitrogen, is added dropwise an ethereal solution of di-*tert*-butylacetic acid (17.2 g, 100 mmol) and dry ether (100 mL) with stirring under nitrogen during a period of 4 h at 0 °C. After the addition, the reaction mixture is stirred for 2 h at r.t. and then concentrated *in vacuo* to give crude product which is distilled at 55 Torr to afford **2a** as a bright yellow liquid; yield: 10.8 g (70%).

Preparations of other ketenes were carried out according to the same procedure as described above.

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