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CARBOXYLATION OF ACTIVE METHYLENE COMPOUNDS USING THE REAGENT OF 1,8-DIAZABICYCLO(5.4.0)-7-UNDECENE AND CARBON DIOXIDE

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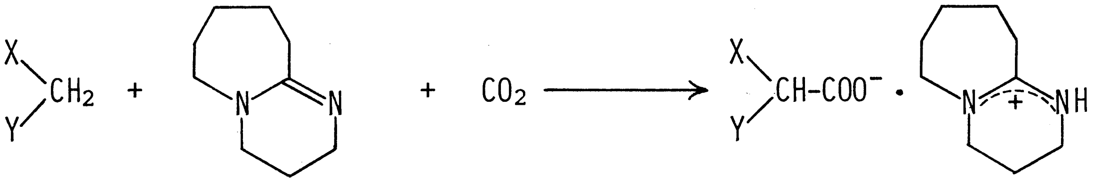
Various active methylene compounds were carboxylated by employing the reagent system, 1,8-diazabicyclo(5.4.0)-7-undecene and carbon dioxide, in organic solvents or without solvent at room temperature.

In a previous paper[1] dealing with a model reaction for the biotin-promoted carboxylation, we have reported that a number of active methylene compounds are carboxylated by employing the reagent system, Triton B—dicyclohexylcarbodiimide and carbon dioxide or a lithium salt of urea derivatives and carbon dioxide. Recently, Corey and Chen[2] have reported that the carboxylation of a variety of organic compounds can be performed by using lithium 4-methyl-2,6-di-tert-butylphenoxide and carbon dioxide.

We now wish to report that the reagent system, 1,8-diazabicyclo(5.4.0)-7-undecene (DBU) and carbon dioxide, is also useful for the carboxylation of various active methylene compounds.



A typical procedure employed is shown in an example of the carboxylation of indanone. A 0.83 g (6.3 mmol) of indanone was dissolved in a mixture of 10 ml of DMSO and 3.8 g (25 mmol) of DBU. Dry carbon dioxide was passed into the above solution for 3 hr at room temperature. The resulting mixture was diluted with 200 ml of water and then extracted with ether. Cooling with addition of ice, the aqueous layer was acidified with aqueous hydrochloric acid and extracted with three 50 ml portions of ether. The ethereal extract was dried over magnesium sulfate, concentrated to 20 ml below 40°C, finally evaporated to dryness with a rotary evaporator in vacuo at room temperature to give 0.92 g of white solid. The solid thus obtained was identical in every respect with the authentic indanone-2-carboxylic acid which was prepared by the reaction of the Stiles reagent[3] with indanone.

By a similar procedure the substrates listed in Table I were carboxylated. These data suggest that the reagent system reported in this communication can be

Table I. The carboxylation of active methylene compounds with DBU-CO_2 system.

Substrate[a]		Solvent,ml	DBU used,g	Reaction time,hr	Product[b]	Yield[c],%
Cyclohexanone	A	DMF 10	3.8	3	Cyclohexanone-2-carboxylic acid	43
	A	DMF 10	3.8	6		47
	A	DMSO 10	3.8	3		52
	A	DMSO 10	3.8	6		61
	A	none	10.0	3		63
Acetophenone	A	DMF 10	3.8	6	Benzoylacetic acid	30
	A	DMSO 10	3.8	3		41
	A	none	15.0	3		43
1-Indanone	A	DMF 10	3.8	3	1-Indanone-2-carboxylic acid	68
	B	DMSO 10	3.8	3		83
Indene	C	DMSO 10	5.7	3	Indenemonocarboxylic[d] acid	90
Fluorene	D	DMSO 5	10.0	18	Fluorene-9-carboxylic acid	30

a) The amounts of the substrates used were: A, 12.5 mmol; B, 6.3 mmol; C, 8.6 mmol; D, 5 mmol.

b) The products were identified by comparisons of IR spectrum and melting point with those of the respective authentic samples.

c) The yields were calculated on the basis of amounts of the substrates used.

d) The IR spectrum of the crude product implied that the product initially produced was indenedicarboxylic acid. However, indenedicarboxylic acid could not be purified because of its ready decarboxylation to indenemonocarboxylic acid upon heating. Therefore, the product was confirmed as indenemonocarboxylic acid.

used to promote the carboxylation of relatively stronger acidic substrates, but that it is ineffective toward less acidic substrates. The extensive study on this carboxylation reaction under pressure at elevated temperatures and also the carboxylation using other bases are now in progress in our laboratory.

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