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REACTION OF DIHALOCARBENE WITH SODIUM SALTS OF SOME ACTIVE METHYLENE COMPOUNDS

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TURQUIE

REACTION OF DIHALOCARBENE WITH SODIUM SALTS OF SOME ACTIVE METHYLENE COMPOUNDS

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ABSTRACT

Reaction of dichloro- or dibromocarbene with the sodium salts of ethylacetoacetate Ia, acetylacetone Ib, benzylcyanide Ic and cyclohexanone Id leads to formation of the sodium salts of 1,3-diethyl-1,3-diacetyl propene-1,3-dicarboxylate IIa, 1,1,3,3-tetraacetyl propene-1 IIb, 1,3-dicyano-1,3-diphenyl propene-1 IIc and (cyclohexylidene-2'-one)-2-methyl cyclohexanone IID, respectively. The structure of the products was established from spectra as well as analytical data.

It is noteworthy to mention here that the mode of attack by the highly electrophile dihalocarbene, that obtained from different sources, on the carbanions of some active methylene compounds Ia-d is consistent to be established.

The reaction of the sodium salt of diethyl malonate with chloroform in the presence of sodium ethoxide has been reported¹ to yield the sodium salt of tetraethyl propene-1,1,3,3-tetracarboxylate. Since Hine² has clearly demonstrated that the basic hydrolysis of chloroform proceeds via dichlorocarbene, it seemed probable that the sodium salt of tetraethyl propene-1,1,3,3-tetracarboxylate was formed from reaction with a carbene precursor.

To obtain further evidence for the possible intermediacy of dichloro- or dibromocarbene and its addition to the active methylene compounds Ia-d. The sodium salts of Ia-d were prepared in dry 1,2-dimethoxy ethane and to this solution sodium trichloroacetate was added in approximately a 2:1 molar ratio. The resulting solution was refluxed for one hour and the precipitated salt was removed from the hot solution by filtration. By concentrating and cooling the filtrate, IIa-d were obtained in 40–60 % yield (based on Ia-d).

methylene⁸. Because of the acidic nature of the hydrogen in III, an intramolecular proton transfer should readily occur, Step 2, and the carbanion IV thus formed should undergo B-elimination to yield V, Step 3. It is also possible that chloride or bromide ion is lost from III simultaneously with hydrogen migration leading directly to V, Step 2'. The Michael addition of the sodium salt Ia-d to V, Step 4, would yield the carbanion VI, which would undergo β -elimination of chloride ion to yield VII, Step 5. A proton transfer from VII to I or sodium ethoxide would result in the formation of II, Step 6.

Some support is possibly afforded Step 2 by the fact that the addition of dichlorocarbene to the sodium salt of diethyl malonate yields as the major product diethyl dichloromethylmethyl malonate⁹. However, it may also be possible that since methyl migration is much slower process compared to hydrogen migration, the anion here may have a long enough life time to combine with a proton. The Michael addition step is supported by the fact that diethyl ethoxymethylenemalonate has been reported to yield the sodium salt of tetraethyl-propene-1, 1, 3,3- tetracarboxylate in the reaction with the sodium salt of diethyl malonate¹⁰. Similar results have been reported from the reaction of ethoxymethylene malononitrile with carbanion¹¹.

EXPERIMENTAL:

Melting points are uncorrected. IR spectra in KBr were recorded on a Unicam SP 1200 spectrophotometer.

A- Reaction of Ia-d with chloroform and sodium ethoxide:

To a solution of sodium ethoxide, prepared by treating sodium (9.2 g, 0.4 g-atom) with 200 ml of absolute ethanol, there was added the active methylene compound (0.2 mole). Chloroform (12 g., 0.1 mole) was added dropwise to the stirred solution. The mixture was refluxed with stirring for 30 min., during which time a solid precipitated. The mixture was filtered while hot and the residual solid was washed with hot ethanol. After partial concentration and cooling, yellow crystals deposited from the red filtrate. The sodium salts IIa-d were filtered and crystallised from a suitable solvent to yield a pale yellow crystals (cf. Table).

B- Reaction of Ia-d with bromoform and sodium ethoxide :

To a solution of sodium ethoxide, prepared by reacting sodium (9.2 g., 0.4 g-atom) with 200 ml of absolute ethanol, there was added the active methylene compound (0.2 mole). Bromoform (27.3 g., 0.1 mole) was added dropwise to the stirred solution. A yellow colour immediately developed. The mixture was refluxed for 40 min. and was filtered while hot. The residual solid was washed with ethanol. On concentration and cooling, crystals were separated from the dark red filtrate. The sodium salts *IIa-d* were filtered and recrystallised from a suitable solvent (cf. Table). The IR spectra of the products were identical to that obtained from method (A).

C- Reaction of Ia-d with chloroform :

To a solution of active methylene compound (0.2 mole) in 100 ml. of 1,2-dimethoxyethane was added sodium (4.6 g., 0.2 g-atom). A vigorous evolution of hydrogen occurred. To the stirred solution, chloroform (12.0 g., 0.1 mole) was added dropwise. The mixture was refluxed for 20 hrs., during which time a yellow solid separated. The mixture was filtered while hot and the residual solid was washed with hot 1,2-dimethoxyethane. On concentration and cooling, crystals deposited from the filtrate. The sodium salts *IIa-d* were filtered off and recrystallised from a suitable solvent (cf. Table). The IR spectra of the products were identical to the spectra of the samples previously isolated.

D- Reaction of Ia-d with sodium trichloroacetate :

To a solution of active methylene compound (0.2 mole) in 100 ml of 1,2-dimethoxy ethane was added sodium (4.6 g., 0.2 g-atom). A vigorous evolution of hydrogen resulted. To the stirred solution was added sodium trichloroacetate (35.0 g., 0.18 mole) and the mixture was refluxed with stirring for 1 hr., during which time a tan solid separated. A vigorous evolution of carbon dioxide occurred. The mixture was filtered while hot and the residual solid was washed with hot 1,2-dimethoxyethane. On partial concentration and cooling crystals separated from the red-brown filtrate. The sodium salts *IIa-d* were filtered and recrystallised from ethanol. The IR spectra of the products were identical to the spectra of the products obtained from bromoform and chloroform reactions (cf. Table).

E- Reaction of Ia-d with ethyltrichloroacetate-sodium methoxide :

To a solution of active methylene compound (0.2 mole) in 80 ml of 1,2-dimethoxyethane was added sodium (4.5 g., 0.2 g-atom). A vigorous evolution of hydrogen occurred. The solution was cooled to 0°C and sodium methoxide (5.4 g., 0.1 mole) was added. To the stirred mixture ethyltrichloroacetate (19.2 g., 0.1 mole) was added dropwise. A muddy brown precipitate formed immediately. The reaction mixture was stirred for 10 hrs. at 0°C. The mixture was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted in a Soxhlet extractor for 24 hrs. (ethanol) to yield IIa-d. The IR spectra of the products were identical with that obtained from methods A,B,C,D.

Table Characterisation of compounds II a-d

Com. pound	M.p. °C	Method Yield%	Solvent	Formula	Analysis % (Found/ Cald.)			IR $\nu_{\max}^{\text{cm}^{-1}}$
					C	H	N	
II a	261-36	A 56%	Absolute ethanol	$\text{C}_{13}\text{H}_{17}\text{O}_6\text{Na}$	53.67	5.79		1710, 1730 1670, 1665
		B 41			53.42	5.81		
		C 10						
		D 60						
		E 13						
b	276-77	A 51%	Absolute ethanol	$\text{C}_{11}\text{H}_{13}\text{O}_4\text{Na}$	57.30	5.6		1640, 1530
		B 37			56.90	5.43		
		C 8						
		D 55						
		E 11						
c	218-20	A 40%	Absolute ethanol	$\text{C}_{17}\text{H}_{11}\text{N}_2\text{Na}$	76.71	3.88	10.45	2210, 2205
		B 33			76.69	4.10	10.55	
		C 7						
		D 10						
		E 10						
d	250-51	A 33%	Absolute ethanol	$\text{C}_{13}\text{H}_{17}\text{O}_2\text{Na}$	68.44	7.52		1710-1690, 1675-1660
		B 29			68.42	7.45		
		C 5						
		D 10						

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