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Preliminary communication

ALKYLCOBALT CARBONYLS

VI*. REACTION OF [(ETHOXYCARBONYL)METHYL] COBALT TETRACARBONYL WITH I_2 DISSOLVED IN MeOH

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Summary

Reaction of $EtOOCCH_2Co(CO)_4$ with I_2 dissolved in MeOH yields XCH_2COOEt (X = H, I, COOMe): the product with X = COOMe was formed even in the reaction in Ar.

The reaction of iodine dissolved in lower aliphatic alcohols with alkyl- and/or acyl-cobalt carbonyls is routinely used in the elucidation of the structure of these sensitive compounds [2—6]. Important conclusions about the mechanism of the stoichiometric (and perhaps even the catalytic) hydroformylation were made on the basis of results obtained with this reagent [5], though it should be noted that these were questioned by an Italian group [7] on the basis of their earlier observations [8,9].

We used this reagent to decompose the remaining cobalt carbonyls in a study on thermal decomposition of $RCH(COOMe)Co(CO)_4$ (R = Me, t-Bu, Ph) compounds [1]. Unexpectedly we always found carbonylation products among the organic compounds, although we were unable to detect acylcobalt carbonyls in the starting solutions even immediately before adding the reagent. When the cobalt carbonyls were removed by treatment with $HCo(CO)_4$ and precipitation of the $Co_2(CO)_8$ formed by PPh_3, the same organic products were found except for malonic ester derivatives.

These inconsistencies prompted us to initiate a systematic study of the reaction of the I_2/MeOH reagent with an alkylcobalt tetracarbonyl which can

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*For Part V, see ref. 1.

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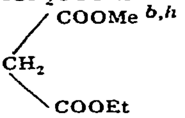
TABLE 1

REACTION PRODUCTS OF $EtOOCCH_2Co(CO)_4$ IN Et_2O WITH I_2/MeOH OR I_2 AT 21°C (I_2/Co RATIO 3, MeOH/Co RATIO 150)

Reaction products	Addition time of I_2/MeOH reagent						Addition time of I_2 10 sec	
	40 min		10—20 sec					
	Ar atm.	CO atm.	Ar atm.	CO atm.	Ar atm. [c]	CO atm. [c]	Ar atm.	CO atm.
CO [a,g]	3.7	3.8	3.7 [d]	3.9 [d]	3.9 [d]	4.1 [d]	— [e]	— [e]
$H_3CCOOEt$ [b,h]	81	65	55	11	27	10	92	60
ICH_2COOEt [b,h]	1	13	12	24	18	19	8	38
 $CH_2(COOMe)(COOEt)$ [b,h]	18	22	33	65	55	71	—	2 [f]

[a] By gas volumetry, corrected for Et_2O tension. [b] GC/MS, MAT-111 and (GC) HP-5830/A 10 m glass capillary column, SE-30, 50—200°C progr. 10°min, Ar 2 cm^3/min. [c] In these experiments MeOH was first added and then at once 3 eq. of crystalline I_2. [d] Exothermic reaction, correction for Et_2O tension difficult. [e] Exothermic reaction, gas volume could not be determined because of high Et_2O tension. [f] $CH_2(COOEt)_2$. [g] mole/atom Co. [h] mole %/atom Co.

be isolated in pure form. The obvious choice was a compound of the type $ROOCCH_2Co(CO)_4$ [6].

We treated $EtOOCCH_2Co(CO)_4$ with I_2/MeOH under various conditions and measured the CO evolved carrying out GC/MS analysis of the organic products. The results (Table 1) were rather poorly reproducible, and the data shown in the Table are reliable only to ±20—30%, but some important conclusions can be drawn: (i) The stable, isolated alkylcobalt tetracarbonyl, $EtOOCCH_2Co(CO)_4$, yields significant amounts of the carbonylation product $CH_2(COOEt)(COOMe)$ when treated with I_2/MeOH even under Ar at. This can be explained in terms of the Lewis-base (L) character of the alcohol taking into account the well-known eq. 1 and 2 [10].

$$RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 \qquad (1)$$

$$RCOCo(CO)_3 + L \rightleftharpoons RCOCo(CO)_3(L) \qquad (2)$$

It should be noted that very recently a multicomponent reagent also containing an aliphatic alcohol, was suggested [11] for the carbonylation of aryl halides. This component seems to be responsible for the carbonylation activity in that case also.

(ii) The formation of large amounts of ethyl acetate (the hydrogenation or hydrogenolysis product) when I_2 was used without the alcohol suggests a contribution from radical processes*.

We suggest that results obtained by the use of the I_2/ROH reagent in the isomerization of alkyl- (or acyl) cobalt carbonyls [5] should be carefully reinvestigated. Our observation must also be taken into account in mechanistic speculations about the cobalt catalysed, I_2-promoted homologation of lower aliphatic alcohols [13,14] especially in the light of the observations of Rathke and Feder [15].

It should be noted that we observed in all experiments the formation of a cobalt complex characterized by a strong absorption band at 2069 cm^{-1} (Et_2O). This complex probably contains Et_2O and I^- (or I_2) ligands. Attempts to isolate it have so far failed.

The experimental technique used was essentially the same as that given in ref. 1, and other relevant conditions are specified in Table 1.

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*The Lewis base character of the alcohol and the availability its mobile proton could be responsible for the formation of $HCo(CO)_4$ from the cobalt carbonyls present [12].