

system are similar and there is only one termination reaction; *e.g.*, it is found that

$$-d[\text{CO}]/dt \propto I^{1/2}[\text{CO}][\text{M}] \quad (5)$$

It should be added that the inhomogeneity of the polyketone product¹ is not necessarily due to a multiplicity of mechanisms, but very probably arises from (i) the change in p_{CO} and $p_{\text{C}_2\text{H}_4}$ during reaction, if the polymer composition is not the same as the feed composition, and (ii) the increase in molecular weight caused by a decrease in catalyst concentration during the reaction.

Since this Note was originally submitted, some further data and a proposed interpretation assuming CO and C₂H₄ to be reacting entities have been published by Coffman, *et al.*⁸ Of these new data, the temperature-dependence which the authors report would follow either from their mechanism or that suggested here. Again, the expected composition of the azeotropic mixture under conditions where Coffman, *et al.*, calculate 46% would be very similar, *viz.*, 44.5%, on the scheme in this Note; the mean experimental value, 45.2%, does not decide between these alternatives. On the other hand, the writer's assumption of a CO/C₂H₄ complex does seem to have the advantage of explaining, at least qualitatively, the reported dependence of the azeotropic composition on the total pressure⁸; this would merely be a special case of the variation of polymer composition with total pressure, discussed above in connection with the data of Brubaker, *et al.*¹ Finally, it is to be pointed out that much of the work of Coffman, *et al.*, has been carried out under heterogeneous conditions, in the absence of a solvent, and that this may constitute a kinetically more complicated system than obtains in solution.

I should like to thank Dr. C. H. Bamford for a discussion of this paper.

(8) D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood and H. S. Young, *THIS JOURNAL*, **74**, 3391 (1952).

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The Carboethoxylation Products of *p*-Aminoacetophenone and *p*-Dimethylaminoacetophenone¹

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RECEIVED AUGUST 29, 1952

During the course of a program of synthesis of β -keto esters, the method of carboethoxylating the α -carbon atom of ketones by replacement of active hydrogen using sodium amide and ethyl carbonate² was applied to *p*-aminoacetophenone (I) in the hope that the α -carbon might be carboethoxylated as well as the nitrogen atom. In spite of the use of very large excesses of reactants and elevated temperatures, however, the only obtainable product was ethyl *p*-acetylphenylurethan (II) resulting from attack on the nitrogen alone, nor was it possible to effect further carboethoxylation of II by the same procedure subsequent to its isolation.

(1) Abstracted from a thesis presented by Chao-Yuan Chu in partial fulfillment of the requirements for a degree of Master of Science at Brigham Young University.

(2) R. Levine and C. R. Hauser, *THIS JOURNAL*, **66**, 1768 (1944).

The structure of II was established by elementary analysis, cryoscopic molecular weight determination, alkaline hydrolysis to I, comparison with an authentic sample obtained from I and ethyl chloro-carbonate,³ and nitration to ethyl 2-nitro-4-acetylphenylurethan³ previously synthesized. It was further characterized by the preparation of its 2,4-dinitrophenylhydrazone, hitherto unknown.

p-Dimethylaminoacetophenone (III) was successfully carboethoxylated by the same procedure to yield the new ethyl *p*-dimethylaminobenzoylacetate (IV) in low yields. The structure of IV was established by elementary analysis, molecular weight determination, hydrolysis to III and by conversion to 1-(2,4-dinitrophenyl)-3-(*p*-dimethylaminophenyl)-5-pyrazolone and 3-(*p*-dimethylaminophenyl)-5-isoxazolone, both new compounds.

It is interesting to note that both II and IV are very resistant to acid hydrolysis, but they are easily cleaved by 5% alcoholic potassium hydroxide.

Experimental

Ethyl *p*-Acetylphenylurethan (II).—Four hundred ml. of liquid ammonia was placed in a 1-l. three-neck flask fitted with a reflux condenser and Hershberg stirrer followed by 1 g. of anhydrous ferric chloride and 13.8 g. (0.6 atom) of clean sodium. As soon as the reaction forming sodamide was complete, a slurry of 27 g. (0.2 mole) of I in 600 ml. dry ether was added all at once. During two hours stirring, the evaporating ammonia was replaced by an equal volume of dry ether. Then 71 g. (0.6 mole) of diethyl carbonate was added and the whole suspension was refluxed for two hours with vigorous stirring. Finally the reaction mixture was slowly poured with stirring into 50 ml. of acetic acid and 500 g. of ice. The product was filtered dry and recrystallized from ethanol yielding 28 g. (68%) of pale yellow crystals melting at 157–158°. Even when the molar ratio of sodamide and ethyl carbonate to II was raised to six, no other product was obtained—only slight increase in yield.

II is insoluble in hot and cold water and ligroin, sparingly soluble in cold benzene and alcohol, quite soluble in acetone, dioxane, hot alcohol and hot benzene. It is soluble in concentrated sulfuric acid producing an orange-red color, but it is recovered unchanged upon dilution.

Anal. Calcd. for C₁₁H₁₃O₃N: N, 6.76; mol. wt., 207.2. Found: N, 6.97, 6.82; mol. wt. (Rast method), 206, 202, 201; (cryoscopic, in dioxane solution), 207.3, 205.8, 208.1.

Ethyl-*p*-acetylphenylurethan-2,4-dinitrophenylhydrazone was prepared in the usual manner. It occurs as orange-red crystals melting at 232–234°.

Anal. Calcd. for C₁₇H₁₇O₆N: N, 18.08. Found: N, 18.30, 18.19.

Ethyl *p*-Dimethylaminobenzoylacetate (IV).—A suspension of 0.26 mole of sodamide in 300 ml. of liquid ammonia was prepared in the same manner described above. After the ammonia had evaporated while being simultaneously replaced with dry ether, 16 g. (0.1 mole) of *p*-dimethylaminoacetophenone⁴ dissolved in 300 ml. of ether was added. The mixture was then refluxed two hours. Finally 30 g. (0.254 mole) of diethyl carbonate was added, and stirring and refluxing were continued for four hours. After cooling, 500 ml. of water was cautiously added. The ether phase was washed, dried with anhydrous sodium sulfate and evaporated to dryness. After recrystallization from ethanol-water 2.5 g. (11%) of pale yellow needles melting at 64° was obtained.

IV is very slightly soluble in cold water and ligroin. It is quite soluble in 5% aqueous hydrochloric acid, warm 5% aqueous sodium hydroxide, ether, dioxane, acetone, hot alcohol and hot benzene.

Anal. Calcd. for C₁₂H₁₇O₃N: N, 5.95; mol. wt., 235.3. Found: N, 6.08, 6.17; mol. wt. (cryoscopic, in dioxane), 234.0, 233.6.

(3) Chr. W. Raadsvelde, *Rec. trav. chim.*, **64**, 813 (1935).

(4) Prepared by treatment of *p*-aminoacetophenone with dimethyl sulfate: Weil, *Monatsh.*, **29**, 905 (1908).

1-(2,4-Dinitrophenyl)-3-(*p*-dimethylaminophenyl)-5-pyrazolone was prepared by treating 0.5 g. of IV with 1 g. of 2,4-dinitrophenylhydrazine and 2 ml. of concentrated hydrochloric acid in 15 ml. of ethanol. An orange-red precipitate immediately formed changing quickly to a dark purple-red. It was recrystallized from methanol yielding 0.4 g. (52%), m.p. 243–244°.

Anal. Calcd. for $C_{17}H_{15}O_5N_5$: N, 18.96. Found: N, 18.62.

3-(*p*-Dimethylaminophenyl)-5-isoxazolone was prepared by refluxing 0.7 g. of IV and 0.5 g. of hydroxylamine hydrochloride in 10 ml. of ethanol for one hour. On cooling and scratching the inner wall of the flask with a glass rod, 0.3 g. (50%) of white needles was obtained, m.p. 164°.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: N, 13.72. Found: N, 13.52.

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trans-Dichlorobis-(N- or C-alkylethylenediamine)-cobalt(III) Chlorides¹

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RECEIVED AUGUST 4, 1952

During the course of some investigations on the mechanism of substitution reactions in complex ions^{2,3} it became of interest to compare the rates of reaction for an analogous series of compounds. Since *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride⁴ is one of the more readily available complexes suitable for this purpose, it was decided to attempt the synthesis of similar substituted ethylenediamine compounds. The preparation of some C-substituted ethylenediamine complexes^{5,6} of this type have been described but no report was found for the synthesis of N-alkylethylenediamine derivatives. However, Keller and Edwards⁷ have recently described the preparation of tris-(N-alkylethylenediamine)cobalt(III) salts.

An account is given in this paper of the method of synthesis and some properties of *trans*-dichlorobis-(substituted-ethylenediamine)-cobalt(III) chlorides. The diamines employed and the symbolization used here are indicated below.

Diamine	Symbol
$CH_3NHCH_2CH_2NH_2$	N-Meen
$CH_3CH_2NHCH_2CH_2NH_2$	N-Eten
$CH_3CH_2CH_2NHCH_2CH_2NH_2$	N- <i>n</i> -Pren
$NH_2C(CH_3)_2CH_2NH_2$	Iso-bn
$NH_2C(CH_3)_2C(CH_3)_2NH_2$	Tetra-Meen

Attempts to prepare corresponding compounds with N-isopropylethylenediamine and N-*n*-butylethylenediamine were not successful. Addition of N-isopropylethylenediamine to an aqueous solution of cobalt(II) chloride resulted in the separation of a gelatinous precipitate of cobalt(II) hydroxide. Although the reaction with N-*n*-butylethylene-

(1) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

(2) F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

(3) R. G. Pearson, C. R. Boston and F. Basolo, *THIS JOURNAL*, **74**, 2943 (1952).

(4) S. M. Jorgensen, *J. prakt. Chem.*, **39**, 16 (1889); **41**, 448 (1890).

(5) A. Werner and A. Fröhlich, *Ber.*, **40**, 2225 (1907).

(6) I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

(7) R. N. Keller and L. J. Edwards, *THIS JOURNAL*, **74**, 215 (1952).

diamine appears to proceed as with the lower alkylethylenediamines, it was not possible to isolate a crystalline product from the final green concentrate.

These green substituted ethylenediamine salts resemble the corresponding *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in color as shown by their similar absorption spectra (Fig. 1). The salts are all soluble in methanol and extremely soluble in water. Aqueous solutions of the N-alkylethylenediamine complexes turn red or aquate at about the same rate as does *trans*-[Coen₂Cl₂]Cl while the isobutylethylenediamine and tetramethylethylenediamine derivatives aquate much more rapidly.⁸

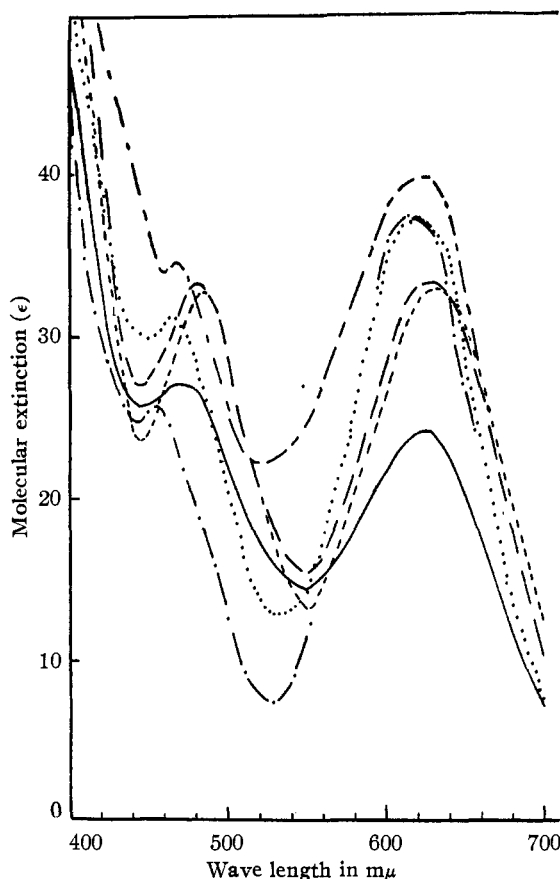


Fig. 1.—Absorption spectra of *trans*-[Co(AA)₂Cl₂]Cl complexes in methanol solution: en (0.0071M) ---; N-Meen (0.0068M), —; N-Eten (0.0053M), — —; N-*n*-Pren (0.0050M), - - - -; iso-bn (0.0057M),; tetra-Meen (0.0058M), — — —.

These green salts crystallize from acid solution as hydrogen chloride addition compounds but lose this adduct less readily than does the corresponding *trans*-[Coen₂Cl₂]Cl·HCl. In fact even after heating the solid at 110° overnight, the complexes still contain as much as a half a mole of hydrogen chloride. No attempt was made to liberate all of the hydrogen chloride by either prolonged heating or use of a higher temperature. Finally, in no case was the *trans* isomer converted to the *cis* complex. The usual procedure⁴ of

(8) Quantitative studies on these rates of aquation will soon be reported in *THIS JOURNAL*.