

phthalic anhydride remain intact, it is postulated no phthalonitrile is formed and the immediate precursors of copper phthalocyanine are either or both monoiminophthalimide or 1-amino-3-imino-isoindolenine.

It is shown, using urea tagged with carbon-14, that under the set of reaction conditions described below, urea does not contribute carbon atoms in the formation of copper phthalocyanine from phthalic anhydride and urea.

Experimental

The reaction was carried out in a 250-ml. flask with nitrogen carrier gas flow through the reactor and downstream gas train at 1–2 ml./sec. The flask was heated in an oil bath held at 200°. The gas train system consisted of an air condenser, to trap sublimed organic by-products, Drierite tube to trap water, Ascarite tower (50:50 mixture of Ascarite and Drierite to prevent clogging of tower from traces of moisture) to trap carbon dioxide, Ascarite tube to test efficiency of Ascarite tower, back-up flask, and concd. sulfuric acid bubbler to collect ammonia gas, followed by exhaustion to atmosphere of the nitrogen purge.

The urea mix for the reaction was prepared as follows: 0.4 mg. of carbon-14 urea (Source: Tracer Laboratories, Inc.; specific activity: 3.69 mc./mM.) and 10 g. of urea were dissolved in 20 ml. of distilled water; the solution was evaporated. The residue was ground in a mortar preparatory to introduction into the crude reaction mix. For each of the three test reactions that were made, 15.93 g. of mix was prepared from which three samples, each weighing 3.54 g., were drawn: 1.25 g. of phthalic anhydride, 2.00 g. of urea mix, 212 mg. of cuprous chloride, 26 mg. of copper, and 52 mg. of molybdic trioxide.³ The constituents were weighed in a Nettler Balance with stated sensitivity of about ± 0.02 mg. The reaction mixture was ground and blended with mortar and pestle. The reaction mass was heated to temperature 1 hr. and held at 200° for 4 hr. The reaction product in the 250-ml. flask was weighed and purified in sulfuric acid solution. The acid suspension was filtered and the filter cake was washed acid free to Congo Red paper, dried, and weighed to determine the yield. In the second test run there was no filter cake, presumably due to solution or sulfonation of the copper phthalocyanine in sulfuric acid solution. Infrared absorption characteristics of the purified residues of the first and third test runs, made with a Perkin-Elmer Model 21 spectrophotometer, over 2.5 μ to 15.5 μ , gave no evidence of compounds other than copper phthalocyanine. One hundred-milligram samples of reaction mix, crude reaction product, purified reaction product, and contents of Drierite and Ascarite tubes were tested for radioactivity with a Nuclear Corp. Model 2612-P portable radiation survey meter. The only samples that gave radioactive counts were from the reaction mixture, crude reaction product, and Ascarite tower. Copper phthalocyanine gave no count. Drierite and Ascarite tubes gave no count. Although not necessary to the purpose at hand, the amount of ammonia absorbed in the concd. sulfuric acid tower was determined by the formaldehyde method.

Yield data, radioactive counts, and weight of reaction mixture, reaction crude, copper phthalocyanine, Drierite and Ascarite tubes, Ascarite tower, and ammonia are given in Table I.

Compounds Containing the Trifluoromethyl Group¹

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Details of the preparation and polymerization of monomers containing the trifluoromethyl group have appeared elsewhere.³ We would like to report here related work, for the most part concerned with the attempted preparation of compounds bearing a trifluoromethyl group on a tertiary carbon atom. Compounds of this type are not reported in the literature except for the special example of 1,1-bis(trifluoromethyl)cyclobutane. This compound was prepared by Hasek⁴ from the reaction of cyclobutane dicarboxylic acid with sulfur tetrafluoride. We were unable to convert α,α -dimethyl substituted carboxylic acids, specifically 2,2-dimethylpent-4-eneoic and 2,2-dimethyl-3-acetoxybutyric acid to the corresponding trifluoromethyl derivatives using sulfur tetrafluoride. Severe reaction conditions caused carbonization and milder conditions gave no reaction. The lack of reactivity in the latter two instances is attributable to steric hindrance of the carboxyl group. The steric requirements are somewhat lessened in the case of cyclobutanedicarboxylic acid because of the presence of fewer interfering hydrogen atoms and the removal of the hydrogen atoms from the site of reaction due to the ring structure.

Sulfur tetrafluoride easily converted isobutyric acid to 2-trifluoromethylpropane. This compound was obtained also from hydrogenation of 2-trifluoromethylpropene. The former reaction is preferable for the preparation of large quantities of this material. It was felt that 2-trifluoromethylpropane might be alkylated in a manner similar to that for isobutyronitrile. Alkylation was attempted with phenyllithium and allyl bromide in ether and sodium amide and allyl bromide in ammonia. The reactions were not successful. Ethyl 2-cyano-3-trifluoromethylbutenoate was prepared by condensation of trifluoroacetone with ethyl cyanoacetate in pyridine solvent with piperidine as catalyst. It is interesting to note that the intermediate ethyl 2-cyano-3-hydroxy-3-trifluoromethylbutyrate was not isolated; it dehydrated at room temperature to give the desired product. This can be contrasted to the dehydration of 2-trifluoromethyl-2-propanol which required prolonged heating at

(1) The financial support of the Wright Air Development Division, Dayton, Ohio, is acknowledged (Contract No. AF33(616)-6866).

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(4) W. Hasek, W. Smith, and V. Englehardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

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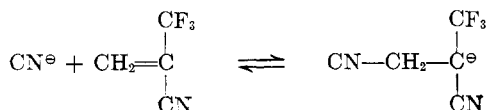
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(3) A. Riley, U. S. Patent 2,214,477, September 10, 1940,

135° over phosphorus pentoxide.⁵ Similarly, ethyl 3-hydroxy-3-trifluoromethylbutyrate was prepared by a Reformatsky reaction of trifluoroacetone with zinc and ethyl bromoacetate and did not appreciably dehydrate upon distillation at 176°. Walborsky⁶ heated 3-hydroxy-3-trifluoromethylbutyric acid, prepared from the condensation of trifluoroacetone with malonic acid, over phosphorus pentoxide in order to effect dehydration.

The monomer, trifluoromethylacrylonitrile, is known and was prepared according to Buxton.⁷ The literature does not reveal much concerning the polymerization of this monomer. Dickey⁸ polymerized trifluoromethylacrylonitrile with triallyl arsines, stibines, and phosphines at -20° in solvents; di- and trialkylphosphites were reported to polymerize trifluoromethylacrylonitrile in bulk at -50°. In the present work, trifluoromethylacrylonitrile was polymerized in bulk and solution with a variety of bases to give solid polymers; *e.g.*, bases such as ammonia, *n*-butylamine, and piperidine gave colored polymers from yellow to orange; *n*-butyllithium gave a black polymer; potassium hydroxide gave a white polymer; and sodium cyanide gave a pink polymer. Acetonitrile and pyridine were found to be suitable solvents for homogeneous polymerizations.

Solution polymerizations were characterized by development of a yellow coloration and absorption at 494 m μ . The color appeared instantaneously upon addition of the catalyst and it was felt that the rate of change of absorption at 494 m μ could be used to follow the rate of polymerization. The system, sodium cyanide in dimethylformamide was used for this purpose. It became apparent that the absorption was not related to the rate of propagation when a 1:1 = monomer: catalyst reaction showed the same effect. Evidently the spectrophotometric method is following the rate of production of the ionic propagating species



Several unsuccessful attempts were made to isolate this species as the sodium salt.

Experimental

Ethyl 3-Hydroxy-3-trifluoromethylbutyrate.—Half of a solution composed of trifluoroacetone 51 g. (0.46 mole), and dry benzene, 250 ml., was added to activated zinc powder, 32 g. (0.5 g.-atom). The materials were heated until reaction commenced, after which the remaining solution was added at a rate such that gentle refluxing was

maintained. After an additional 2 hr. of refluxing, the material was poured into a cold solution of sulfuric acid, 49 g. (0.5 mole), in 500 ml. of water. The organic phase was separated and combined with the benzene extracts of the aqueous phase; this solution was water washed until the washes were neutral to litmus. The solution was dried, and after the solvent removed by distillation, ethyl 3-hydroxy-3-trifluoromethylbutyrate was obtained, 50 g. (55% yield), b.p. 176° (atm.), n_D^{25} 1.3769, d_4^{25} 1.2207.

Anal. Calcd. for C₇H₁₁F₃O₂: C, 42.00; H, 5.59; F, 28.48. Found: C, 41.28; H, 5.69; F, 28.98.

Ethyl 2-Cyano-3-trifluoromethylbutenoate.—Trifluoroacetone, 33 g. (0.28 mole), ethyl cyanoacetate, 33 g. (0.28 mole), piperidine 2 ml., and dry pyridine 150 ml. were mixed and allowed to stand at 0° for 12 hr. After 24 hr. at room temperature the volatile materials were removed under reduced pressure and a solid residue was obtained. The solid was crystallized from 95% ethanol and then from carbon tetrachloride to give ethyl trifluoromethylisopropylidene cyanoacetate, 29 g. (87% yield), m.p. 124–125°.

Anal. Calcd. for C₈H₈NF₃O₂: C, 46.38; H, 3.89; N, 6.76; F, 27.52. Found: C, 46.43; H, 4.08; N, 6.54; F, 27.71.

2-Trifluoromethylpropane.—2-Trifluoromethylpropene, prepared according to Henne⁵, 25.3 g. (0.23 mole), was condensed into a pressure bottle containing platinum oxide, 0.46 g., and ethanol, 30 ml. The contents were cooled, and the bottle flushed with nitrogen prior to the introduction of hydrogen. After 4 days at room temperature, the hydrogen uptake ceased, the material having absorbed 46% of the theoretical quantity. Low-boiling compounds were removed by flash distillation and passed through bromine which was illuminated with ultraviolet light. 2-Trifluoromethylpropane, 4.4 g. (18% yield), b.p. 11.8–12.7° (atm.) was obtained still contaminated with 2-trifluoromethylpropene as evidenced from the infrared spectrum. An elemental analysis could not be performed on this material because of experimental difficulties. 1,2-Dibromo-2-trifluoromethylpropane, 2 g. (3% yield), b.p. 130° (atm.) was recovered after removal of excess bromine. (b.p. 130–130.8°).

A stainless steel bomb was charged with isobutyric acid, 13.2 g. (0.15 mole), and sulfur tetrafluoride, 54 g. (0.50 mole), after which it was heated to 160° for 9 hr. The contents were vented at room temperature through a trap containing 10% sodium hydroxide solution, a trap cooled to 0° and one cooled to -78°. The material in the last trap was distilled to give 2-trifluoromethylpropane, 11 g. (65% yield), b.p. 130° (atm.). This material gave an infrared spectrum identical to that obtained from the catalytic hydrogenation except for the absence of bonds due to unsaturation.

Attempted Preparation of 2-Methyl-2-trifluoromethyl-3-acetoxybutane and 4-Methyl-4-trifluoromethylpentene-1.—Methyl 2-bromo-isobutyrate was prepared according to Smith and Norton¹¹ in 65% yield. This was converted to 2,2-dimethyl-3-hydroxybutanoic acid and then to 2,2-dimethyl-3-acetoxybutanoic acid according to Courtot.¹²

4-Methyl-4-cyanopentene-1 was prepared according to Wittig,¹³ and was converted to 2,2-dimethylpent-4-enoic acid according to Brown and van Gulick.¹⁴

The first of the above compounds reacted by a procedure similar to that described in the preceding section, except that 1,2-dimethoxyethane was used as solvent. The starting material was recovered from this reaction along with a small amount of a yellow crystalline solid which was not identified.

The reaction of 2,2-dimethylpent-4-enoic acid with sulfur tetrafluoride was characterized by carbonization. The use of diethyl ether or dimethoxyethane as solvent eliminated the

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carbonization; however, the desired product was not obtained.

Polymerization of Trifluoromethacrylonitrile.—Trifluoromethacrylonitrile was prepared from trifluoroacetone according to Buxton.⁷ The polymerizations were carried out in a vacuum system. The catalyst, sodium cyanide, was crystallized from water and dried at room temperature at 7×10^{-3} mm. for 1 week. A weighed quantity, 0.018 g. (3.7×10^{-4} mole) was placed in a reaction vessel and degassed for 0.5 hr. at 0.05 mm. Trifluoromethacrylonitrile, 3.47 g. (0.029 mole), was distilled from the reservoir on the vacuum line to a side arm on the reaction flask which, by rotation, could be inverted to discharge its contents into the flask. The monomer was kept frozen in the side arm with liquid nitrogen until needed. Dimethylformamide was refluxed over phosphorus pentoxide and distilled at reduced pressure prior to storage on the vacuum line over methylenebis(*p,p*-diphenyl diisocyanate). Dimethylformamide, 25 ml., was transferred from its reservoir into the reaction flask and the sodium cyanide dissolved to give a clear solution by stirring for 1 hr. at room temperature under an atmosphere of argon. The solution was cooled to -40° ; the monomer was thawed and the side arm emptied into the reaction flask causing an immediate production of orange-brown solution. The polymerization was terminated by addition of 3 ml. of a 2% solution of sulfuric acid in dimethylformamide, and the polymer isolated by precipitation into water containing potassium hydroxide. The polymer was obtained as a pink powder. Polymerizations carried out for 30, 9, and 4 min. gave essentially quantitative yields, m.p. 190° dec. Intrinsic viscosities were determined in dimethylformamide and in cyclohexanone. The curves showed an electrolyte effect; $[\eta]$ was of the order $0.1 \frac{dl}{g}$.

Anal. Calcd. for $(C_4H_2NF_3)_n$: C, 39.68; H, 1.67; N, 11.57; F, 47.08. Found: C, 40.19; H, 2.03; N, 10.75; F, 45.48.

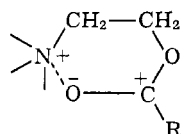
Hydrolysis of an Ester with a Neighboring Carboxyl and a Quaternary Ammonium Group¹

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The enhanced reactivity of esters of the choline type² has been explained by assuming that the positively charged nitrogen stabilizes a negative charge on the carbonyl oxygen, making the carbonyl carbon more susceptible to attack by a nucleophilic reagent as indicated by:



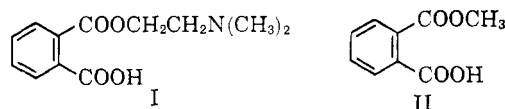
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This type of catalysis has been classified by Bender³ as intramolecular general acid catalysis. The difference in reactivity of esters of cyclohexanol derivatives with a *cis* or a *trans* quaternary nitrogen has been offered as evidence for the above mechanism.⁴ By analogy, a neighboring positively charged nitrogen should make the carbonyl carbon more susceptible to neighboring carboxylate attack. It has been shown previously that an ester containing both an ionized and an unionized neighboring carboxyl group is highly reactive, and this effect has been attributed to a stabilization of the transition state by hydrogen bonding between the carbonyl oxygen of the ester and the unionized carboxyl.⁵ It was suggested that a similar stabilization might be achieved by ion-pair formation involving the partial negative charge of the carbonyl oxygen and a neighboring cationic group.⁵

To demonstrate this effect, we carried out a study of the pH dependence of the rate of hydrolysis of β -*N,N*-dimethylaminoethyl hydrogen phthalate (I). An analogous ester lacking the cationic group, *i.e.*, methyl hydrogen phthalate II has been investigated previously.⁶



The pseudo-first-order rate constants for the hydrolysis of ester I in various buffers and at different temperatures are given in Table I.

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF β ,*N,N*-DIMETHYLAMINO ETHYL HYDROGEN PHTHALATE

pH	10^3 Sec.^{-1} (at 75°)	pH	10^3 Sec.^{-1}	Temp.
1.11	3.3	7.92	41	75.5
2.82	2.8	6.06	3.0	75.5
3.26	2.7	6.06	0.033	34.5
4.92	3.0	6.06	1.13	65.5
6.39	3.8	6.06	6.65	85.4
6.99	8.1			

In Fig. 1 the logarithms of the rate constants obtained at 75.5° are plotted against pH along with a similar plot for the hydrolysis of methyl hydrogen phthalate taken from ref. 6.

An Arrhenius plot of rates obtained at pH 6.06 gave an activation enthalpy of 23.4 kcal./mole as against 33.7 kcal./mole reported for ester II⁶.

The results of this study show that the amphoteric ester I is much more reactive than the acid ester II, but that the hydrolysis rate of I unlike that of II, is pH independent in the region of

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