

This small wave was not observed in the case of other diazo compounds studied in this Laboratory.

This work was made possible by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

#### Experimental

*o*-Carboxybenzenediazonium chloride was prepared from anthranilic acid by a method similar to that used for benzenediazonium chloride.<sup>2</sup> Other materials and apparatus were the same as those used earlier.<sup>2</sup> Our coulometric cell had a capacity about twice that of the original model and this required very careful deaeration to avoid interference from hydrogen peroxide waves which were encountered at *pH* 4.1 and *pH* 1.1. At these *pH* values (in contrast to *pH* 7 where it was negligible) the non-electrolytic decomposition of diazotized aniline in the presence of the large stirred mercury cathode became noticeable. The extent of decomposition during the 40–90 min. required for a typical coulometric analysis was measured by noting the decrease in the diffusion currents of either wave. It was observed that, for example, the actual electron consumption at  $-0.6$  v. (0.90 electron/mole  $RN_2X$ ) was raised to the integral value by correction for the non-electrolytic decomposition. In cases where the electrolysis was interrupted at an intermediate stage it was necessary to remove the solution from contact with the cathode since the non-electrolytic decomposition of the diazo compound was still more rapid in the presence of the mercury dust which accumulated on the cathode during electrolysis. It was only our good fortune in removing a partially electrolyzed solution from the cell which permitted us to observe the increase in polarographic activity which occurred on standing. The increase in diffusion currents was observed by recording polarograms of fresh portions of the solution at 15-minute intervals. It was observed that the return of polarographic activity continued for about one hour.

No difficulty from non-electrolytic decomposition was experienced with diazotized anthranilic acid.

Coulometric analyses performed during the present work showed a precision of 2%.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF NEW HAMPSHIRE  
DURHAM, N. H.

### Acrylates of Difficultly Esterified Alcohols

By ARTHUR H. AHLBRECHT AND DONALD W. CODDING

RECEIVED OCTOBER 6, 1952

The use of trifluoroacetic acid anhydride as an esterification agent has been extended to the preparation of acrylate esters of alcohols which normally need to be treated with acrylyl chloride or acrylic anhydride.

The procedure is essentially that of Bourne, Stacey, Tatlow and Tedder<sup>1</sup> who used trifluoroacetic acid anhydride in the esterification of alcohols and phenols. In this process, the alcohol is added to a mixture of acrylic acid and trifluoroacetic acid anhydride. The resulting acrylate ester is easily recovered in very good yield by washing and distilling.

This procedure was developed primarily for the production of acrylate and methacrylate esters of 1,1-dihydroperfluoroalkyl alcohols, but it also worked very well when applied to the preparation of phenyl acrylate. As noted by previous workers<sup>1,2</sup> the only ester formed is the one resulting from esterification with the non-fluorinated carboxylic acid.

(1) E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

(2) P. W. Morgan, *This Journal*, **73**, 860 (1951).

#### Experimental

**Preparation of Phenyl Acrylate.**—To a 2-liter 3-necked flask immersed in an ice-bath and equipped with reflux condenser, stirrer, dropping funnel and thermometer is added 288 g. (4 moles) of hydroquinone inhibited glacial acrylic acid. Trifluoroacetic acid anhydride (840 g., 4 moles) is then added through the dropping funnel at such a rate that the temperature of the stirred solution does not exceed 15°. Stirring is continued 15 minutes after the addition of the anhydride and during the addition of the phenol (376 g., 4 moles), which is added at such a rate that the temperature of the cooled mixture does not exceed 25°. After 90 minutes additional stirring, the reaction mixture is transferred to a separatory funnel and water is added until two layers separate. The top ester layer is washed with water, 5% NaOH and again with water. Using hydroquinone and copper flake as inhibitors, two distillations through an efficient column packed with glass helices produced 332 g. (56%) of pure phenyl acrylate,<sup>3</sup> b.p. 65° (1 mm.),  $n_D^{20}$  1.5210. The bottom layer consists of trifluoroacetic acid and water from which the  $CF_3COOH$  can be recovered as the sodium salt by neutralization with sodium hydroxide and evaporation to dryness on the steam-bath.

**Preparation of 1,1-Dihydroperfluorobutyl Acrylate.**—Using almost the same procedure, 1,1-dihydroperfluorobutyl alcohol was esterified with glacial acrylic acid in yields of 85–90%. The 1,1-dihydroperfluorobutyl acrylate had the following physical properties, b.p. 51° (50 mm.),  $n_D^{20}$  1.3317,  $d_4^{20}$  1.409. *Anal.* Calcd. for  $C_7H_5O_2F_7$ : C, 33.1; F, 52.4. Found: C, 33.1; F, 52.4.

(3) E. M. Filachione, J. H. Lengel and C. H. Fisher, *ibid.*, **66**, 494 (1944).

CONTRIBUTION No. 62 FROM THE  
CENTRAL RESEARCH DEPARTMENT  
MINNESOTA MINING AND MANUFACTURING Co.  
ST. PAUL, MINNESOTA

### The Preparation of Tris-acetylaceton-Rhodium(III) and -Iridium(III)

By F. P. DWYER AND A. M. SARGESON

RECEIVED SEPTEMBER 17, 1952

No acetylaceton complexes of rhodium or iridium in any valency state appear to have been described. The trivalent complexes have been prepared in connection with the study of the optical properties of non-electrolytic complexes. Rhodium(III) hydroxide or sodium rhodate(III) failed to react with acetylaceton. Small amounts of the compound were obtained by refluxing sodium hexachlorrhodate(III) with sodium acetylacetonate but the best results by heating a mixture of rhodium(III) nitrate with acetylaceton at *pH* 4. The iridium compound was obtained in small yield from iridium(III) hydroxide. An unstable reddish water-soluble substance of unknown composition also resulted. This was possibly the acid  $H[Ir(OH)_2(Aca)_2]$ .

**Tris-acetylaceton-rhodium(III).**—Rhodium(III) nitrate solution (0.1 g. Rh) in 0.2 *N* nitric acid (10 ml.) was neutralized with sodium bicarbonate solution (10%) to *pH* 4. At this acidity the light yellow hydroxide (or basic nitrate) just commenced to separate. Acetylaceton (5 ml.) was added and the mixture refluxed. After a few minutes orange-yellow crystals started to separate, the *pH* of the mixture falling. After 30 minutes the *pH* was readjusted and the refluxing continued for a further 15 minutes. The substance after crystallization from aqueous methanol gave orange-yellow monoclinic plates, m.p. 260°, yield 0.3 g., 75% sublimed at 240° at 1.0 mm. pressure, and decomposed at 280° forming a rhodium mirror. The substance was insoluble in water, slightly soluble in alcohol and petroleum ether, but easily soluble in benzene and chloroform. It was stable to boiling dilute acids and 10% aqueous caustic soda.