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

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Experimental

o-Carboxybenzenediazonium chloride was prepared from anthranilic acid by a method similar to that used for benzenediazonium chloride.[2] Other materials and apparatus were the same as those used earlier.[2] 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 *p*H 4.1 and *p*H 1.1. At these *p*H values (in contrast to *p*H 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

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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[1] 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[1,2] the only ester formed is the one resulting from esterification with the non-fluorinated carboxylic acid.

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,[3] b.p. 65° (1 mm.), $n^{20}{}_D$ 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.), $n^{20}{}_D$ 1.3317, $d^{20}{}_4$ 1.409. *Anal.* Calcd. for $C_7H_5O_2F_7$: C, 33.1; F, 52.4. Found: C, 33.1; F, 52.4.

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[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).

[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-acetylacetone–Rhodium(III) and -Iridium(III)

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

RECEIVED SEPTEMBER 17, 1952

No acetylacetone complexes of rhodium or iridium in any valency state appear to have been described. The tervalent 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 acetylacetone. Small amounts of the compound were obtained by refluxing sodium hexachlorhodate(III) with sodium acetylacetonate but the best results by heating a mixture of rhodium(III) nitrate with acetylacetone at *p*H 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-acetylacetone–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 *p*H 4. At this acidity the light yellow hydroxide (or basic nitrate) just commenced to separate. Acetylacetone (5 ml.) was added and the mixture refluxed. After a few minutes orange-yellow crystals started to separate, the *p*H of the mixture falling. After 30 minutes the *p*H 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.

Anal. Calcd. for $C_{15}H_{21}O_6Rh$: Rh, 25.75; C, 45.01; H, 5.29; mol. wt., 400. Found: Rh, 25.5; C, 45.2; H, 5.35; mol. wt. (Rast in camphor), 390.

Tris-acetylacetone–iridium(III).—Freshly precipitated iridium dioxide, from potassium hexachloriridate(IV) (1.0 g.) was dissolved by heating with sulfuric acid (1 *N*, 25 ml.) and a few crystals of sodium sulfate, and evaporated until the acid started to fume. The cooled solution was diluted to the original volume, and the undissolved iridium dioxide removed by centrifuging. The light green solution was treated with 10% caustic soda solution until the green iridium(III) hydroxide precipitate was just redissolved. The substance was reprecipitated quickly in order to avoid oxidation, the solution adjusted to *p*H 6, and the mixture heated at 60° with acetylacetone (2 ml.) for an hour. The solution became red, depositing a yellow crystalline precipitate, which crystallized from aqueous methanol in orthorhombic plates, m.p. 269° (yield 0.1 g., 10%). The substance sublimed at 260° under 1 mm. pressure and decomposed at 290° depositing an iridium mirror. The solubility in solvents was similar to the rhodium compound.

Anal. Calcd. for $C_{15}H_{21}O_6Ir$: Ir, 39.37; C, 36.73; H, 4.32; mol. wt., 490. Found: Ir, 39.3; C, 36.9; H, 4.4; mol. wt. (Rast in camphor), 400.

DEPT. OF CHEMISTRY
UNIVERSITY OF SYDNEY, AUSTRALIA

Extension of the Leuckart Synthesis of Tertiary Amines, Including its Application to α,β-Unsaturated Carbonyl Compounds[1]

BY J. F. BUNNETT,[2] JEAN LOVENDAHL MARKS AND HENRY MOE

RECEIVED JULY 16, 1952

In 1949, we reported[3] the preparation of a number of tertiary amines by the reaction of ketones with dialkylformamides in the presence of formic acid and magnesium chloride; conversions[4] in the range 20 to 55% and adjusted yields[4] in the range 40 to 60% were obtained. We now report the application of an improved variation of this technique to a number of additional carbonyl compounds; our results are summarized in Table I.

TABLE I

TERTIARY AMINES SYNTHESIZED BY THE LEUCKART REACTION

Tertiary amine product[a]	Conversion,[4] %	Adjusted yield,[4] %	B.p. °C.	Mm.	Picrate m.p., °C.	Hydrochloride m.p., °C.	Refractive index n_D^t	t, °C.
N,N-Dimethyl-α-ethylbenzylamine (I)	30	79	105–106	25	165.5–166.6		1.5002	25
α-Ethylbenzylpiperidine (II)	65	77	155–157	25		187–188	1.5210	25
N,N,1-Trimethyl-3-phenylpropylamine (III)	43	60	118–121	14	113.5–114		1.4985	23
1-Methyl-3-phenylpropylpiperidine (IV)	57	57	176–177	25		164.5–165.5	1.5140	25
N,N,1-Trimethyl-3-(*p*-methoxyphenyl)-propylamine (V)	30	55	152–154	14	129.5–130.5	169–170	1.5060	24
N,N-Dimethyl-3-phenylallylamine (VI)	55	55	125–132	25	123.5–124.5	187.5–188.5		
N,N,1-Trimethyl-3-phenylallylamine (VII)	23	44	139–140	25	138–139		1.5350	25
1-Methyl-3-phenylallylpiperidine (VIII)	15	15	180–187	25	142.5–143.5			

[a] Experimental details and data supporting structures are given in the Experimental section.

It will be noted that in general the yields reported here range higher than those reported previously. This improvement is due in part to the use of a longer reaction time (eight hours instead of three or four hours) and in part to a modified technique for removing the low-boiling constituents (principally water and formic acid) of the original reaction mixture. This technique involves distilling the reaction mixture rapidly until the pot temperature approximates the boiling point of the formamide being used, and then allowing the system to reflux. Efforts to improve the yield by the use of excess formic acid or by the use of nickel catalyst[5] (from pyrolysis of nickel formate) were not fruitful. It is of parenthetical interest that when the magnesium chloride and formic acid of a typical reaction mixture were replaced by phosphoric acid (making the molar ratio phosphoric acid:propiophenone:formpiperidide = 1:1:4), the conversion[4] to α-ethylbenzylpiperidine was 30% compared to 65% by our best procedure.

Shortly after the appearance of our earlier paper,[3] Staple and Wagner[6] published a careful study of factors influencing the rate of formation of tertiary amines from piperidine formate or formpiperidide and benzaldehyde or cyclohexanone. Using these particularly reactive carbonyl compounds, they found that a faster reaction and better yields were obtained when the amine formate was used rather than formpiperidide. On the basis of this experience, they suggested that the amine formate would in general prove to be the better reagent for tertiary amine synthesis. We attempted to prepare amines from 4-(*p*-methoxyphenyl)-butanone-2 and dimethylamine formate, and from propiophenone and piperidine formate by their recommended procedure, but in neither case were we able to obtain any measurable amount of the expected tertiary amine. Since the successful preparation of both these tertiary amines is recorded in Table I, we believe that our procedure is more suitable for the preparation of tertiary amines from carbonyl compounds in general.

Our success in obtaining unsaturated tertiary amines (the last three amines in Table I) from α,β-unsaturated carbonyl compounds contrasts with the

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(1) Based in part on the B.A. Thesis of Henry Moe, June, 1952. Presented at The Northwest Regional Meeting of The American Chemical Society, Corvallis, Oregon, June 20, 1952.

(2) Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, N. C.

(3) J. F. Bunnett and J. L. Marks, THIS JOURNAL, **71**, 1587 (1949).

(4) In this paper, "conversion" means yield based on the amount of ketone introduced, and "adjusted yield" means yield based on the amount of ketone consumed, that is, on the amount introduced less the amount recovered.

(5) A. N. Kost, A. P. Terent'ev and G. A. Shvekhgeimer, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 150 (1951) [*C. A.*, **45**, 10194 (1951)], reported catalysis of the Leuckart synthesis of primary and secondary amines by nickel metal and other hydrogenation catalysts.

(6) E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949).