[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DELHI UNIVERSITY]

Coupling[1] of Aconitic Acid and Itaconic Acid with Certain Diazonium Chlorides

BY K. B. L. MATHUR, M. KRISHNAMURTI AND UPENDRA KUMAR PANDIT

RECEIVED DECEMBER 7, 1951

Meerwein's diazo reaction[2] with unsaturated acids of the type of maleic[3] (R = H, CH_3, Br) and acrylic[4] (R = H, CH_2) gives cinnamic acids

$$ArN_2Cl + HOOC{-}CH{=}C(R)COOH = ArCH{=}C(R)COOH + CO_2 + N_2 + HCl$$

$$ArN_2Cl + CH_2{=}C(R)COOH = ArCH{=}C(R)COOH + N_2 + HCl$$

The reaction of diazotized bases with unsaturated acids has now been extended to include aconitic and itaconic acids (R = CH_2COOH).

Irradiation of the product obtained by the reaction of *p*-chlorobenzenediazonium chloride with aconitic acid gives *p*-chlorophenylitaconic acid, a substance identical with that synthesized from *p*-chlorobenzaldehyde and diethyl succinate in the presence of sodium ethoxide.[5] Before irradiation, the product appears to be a mixture of *p*-chlorophenylitaconic acid and the *p*-chlorophenylaticonic acid. Analogous products have been obtained from three other diazotized bases.

$$ArN_2Cl + HOOC{-}CH{=}C(COOH)CH_2COOH = Ar{-}CH{=}C(COOH)CH_2COOH + CO_2 + N_2 + HCl$$

TABLE I

ARYLITACONIC ACIDS, $ArCH{=}C(COOH)CH_2COOH$

Ar[c]	M.p., °C.	Empirical formula	Analyses, % Calcd.	Analyses, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
p-Chlorophenyl	193–194[a]	$C_{11}H_9O_4Cl$	Cl 14.76	14.25	120.25	120
p-Nitrophenyl	193[b]	$C_{11}H_9O_6N$	N 5.58	5.62	125.5	128.4
m-Bromophenyl	174–175[b]	$C_{11}H_9O_4Br$	Br ...	...	142.5	142
p-Bromophenyl	200[b,d]	$C_{11}H_9O_4Br_2$	Br 28.00	27.5	142.5	144

[a] The product (1.5 g.) deposited crystals from $Et_2O–C_6H_6$, m.p. 161–163°, having % Cl and neut. equiv. as for $C_{11}H_9O_4Cl$; after irradiation gave m.p. above. *p*-Chlorophenylitaconic acid was also synthesized from p-ClC_6H_4CHO, $(CH_2COOEt)_2$ and NaOEt as indicated. The initial sample (m.p. 170°) after irradiation gave a product (Calcd. for $C_{11}H_9O_4Cl$; Cl, 14.75; neut. equiv., 120.25. Found: Cl, 14.4; neut. equiv., 120) having m.p. and mixed m.p. with above sample 192–193°. [b] Working the oily products (1.5–2 g.) gave crystals (0.5–1 g.) of crude acids, the solvents retaining the oily mass. (%Br and neut. equiv. as for $C_{11}H_9O_4Br$). [c] Products from diazotized aniline, *m*-nitro-, *m*-chloro-, *o*-bromoanilines were uncrystallizable oils. The oils and the acids in ammoniacal solutions gave precipitates with aqueous calcium or barium chloride. [d] Crude m.p. 183–185°.

TABLE II

α-BENZYLACRYLIC ACIDS, $ArCH_2C(COOH){=}CH_2$

Ar	Product G.	M.p., °C.	Empirical formula	Analyses, % Calcd.	Analyses, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
p-Chlorophenyl[a]	0.5	102	$C_{10}H_9O_2Cl$	C 61.0	61.0	196.5	196
				H 4.6	4.7		
				Cl 18.05	17.76		
Phenyl[b]	Few drops crude	68	$C_{10}H_{10}O_2$	...	...	162	158
o-Chlorophenyl	0.8	90	$C_{10}H_9O_2Cl$	Cl 18.05	17.90	196.5	190
p-Bromophenyl[c]	1.2	119	$C_{10}H_9O_2Br$	Br 33.2	32.7	241	243
p-Nitrophenyl[d]	0.92	142	$C_{10}H_9O_4N$	N 6.76	6.49	207	213

[a] The acid (0.2 g.) in $CHCl_3$ (10 ml.) and Br (0.5 ml.) yielded the dibromide, crystallized from $AcOH{\cdot}H_2O$ (1:1) in cubes, m.p. 150° (Found: 0.2468 g. gave AgCl + AgBr, 0.3516 g.; calcd. for $C_{10}H_9O_2ClBr_2$, AgCl + AgBr, 0.3596 g.). [b] Polymerized when impure or in presence of HCl; dibromide, m.p. 143°, identical with that of α-benzylacrylic acid (*vide* J. L. Simonsen, *J. Chem. Soc.*, 117, 568 (1920)). [c] Polymerized with cold concd. H_2SO_4. [d] Polymerized on prolonged treatment with hot concd. HCl or upon heating its sodium salt at 250° for 2 hours.

TABLE III

Acids	M.p., °C.	Empirical formula	Analyses, % Calcd.	Analyses, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
p-Chlorobenzalmalonic	199	$C_{10}H_7O_4Cl$	Cl 15.67	15.2	113.25	111
p-Chlorobenzylmalonic[a]	157	$C_{10}H_9O_4Cl$	Cl 15.53	15.3	114.25	112.5
Piperidinomethyl-*p*-chlorobenzylmalonic[b]	162	$C_{16}H_{20}NO_4Cl$	Cl 10.9	11.2	162.7	162
α-*p*-Chlorobenzylacrylic[d]	102	$C_{10}H_9O_2Cl$	Cl 18.05	18.28	195.5	195
α-*p*-Chlorobenzylacrylic dibromide[c,d]	151	$C_{10}H_9O_2ClBr_2$	Br 44.88	45.26	....	...

[a] The piperidine acid salt (2 g.), formalin (7 ml.) upon refrigeration yielded a solid. Its (solid) alkaline extract upon acidification gave piperidinomethyl-*p*-chlorobenzylmalonic acid, purified by washing with water and then alcohol. [b] Piperidinomethyl-*p*-chlorobenzylmalonic acid (1.5 g.), hydroquinone (few crystals) were heated (150–170°) under slight vacuum for 1/2 hour. The aq. $NaHCO_3$ extract contained α-*p*-chlorobenzylacrylic acid. [c] 0.2644 g. gave AgCl + AgBr, 0.3798 g. (calcd. 0.3854 g.). [d] M.p.'s remained undepressed with materials prepared as above, respectively.

---

[1] Based on Paper No. 31 (Organic Section), XIIth International Congress of Pure and Applied Chemistry, New York (1951). Publication delayed by manuscript loss and transit mishap.

[2] (a) V. H. Meerwein, E. Buchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1939); (b) *cf.* also C. F. Koelsch and V. Boekelheide, THIS JOURNAL, **66**, 412 (1944).

[3] (a) D. R. Dhingra and K. B. L. Mathur, *J. Indian Chem. Soc.*, **24**, 123 (1947); (b) *cf.* J. Rai and K. B. L. Mathur, *ibid.*, **24**, 383 (1947); (c) Sain Dass and K. B. L. Mathur, *ibid.*, **28**, 540 (1951).

[4] (a) J. Rai and K. B. L. Mathur, *ibid.*, **24**, 413 (1947); (b) M. Krishnamurti and K. B. L. Mathur, *ibid.*, **28**, 507 (1951).

[5] *Cf.* Hans Stobbe, *Ber.*, **41**, 4353 (1908), for the parent acid.

The reaction of *p*-chlorobenzenediazonium chloride with itaconic acid gives an unsaturated monobasic acid, identified as α-*p*-chlorobenzylacrylic acid by the following synthesis: *p*-Chlorobenzalmalonic acid was reduced to *p*-chlorobenzylmalonic acid,[6a] which was converted by the Mannich reaction (with piperidine and formaldehyde) into piperidinomethyl - *p* - chlorobenzylmalonic acid, which was in turn pyrolyzed[6b] to give α-*p*-chlorobenzylacrylic acid.

$$C_5H_{10}NCH_2{-}C(COOH)_2CH_2C_6H_4Cl = CH_2{=}C(COOH)CH_2C_6H_4Cl + C_5H_{10}NH + CO_2$$

Itaconic acid reacts with other diazotized bases in the same way.

$$ArN_2Cl + CH_2{=}C(COOH)CH_2COOH = ArCH_2{-}C(COOH){=}CH_2 + CO_2 + N_2 + HCl$$

In the above reactions, presumably initiated by a chain mechanism,[2b,3a] the transient formation of the ion $(R'CHAr\text{-}\underset{+}{C}(COOH)CH_2COOH)$ is postulated, followed by the loss of carbon dioxide and hydrogen ion. When R′ is COOH, the final product is an itaconic acid; when R′ is hydrogen, the final product is an acrylic acid. Thus, the diazo reaction with both aconitic and itaconic acids involves decarboxylation.

Experimental

Coupling Reactions.—The amine (0.025 mole) dissolved in 6 ml. of warm concd. hydrochloric acid, diluted with 10 ml. of water, then cooled with 5 g. of crushed ice, was diazotized by addition of sodium nitrite (0.025 mole) in 7 ml. of water. The diazo solution was added with stirring to the acid, aconitic or itaconic (0.025 mole), 1 g. of cupric chloride and 5.75 g. of sodium acetate in 20 ml. of water. The temperature was kept at 30–35°. Brisk effervescence usually followed. After standing overnight, the products were isolated from the solid or semi-solid matter that had separated by extraction with 10% aqueous sodium bicarbonate and acidification with dilute hydrochloric acid. The precipitated acids from aconitic acid were oils. However, in several cases concentration of their solutions in ether–benzene (1:1) yielded crystals. Upon irradiation (about two hours) with traces of bromine in ether–chloroform, removal of the solvent, and recrystallization from hot water, the melting point rose to that of the aryl itaconic acid (Table I). The products from itaconic acid were α-benzylacrylic acids (Table II), crystallized from water.

α-*p*-Chlorobenzylacrylic acid and its dibromide were synthesized by another route as described. The relevant details, including those for the intermediates, are shown in Table III.

The authors desire to thank Prof. T. R. Seshadri for his interest in this work.

DELHI, INDIA

(6) For the parent acids: *cf.* (a) L. Claisen and L. Crismer, *Ann.*, **218**, 139 (1883); (b) C. Mannich and E. Ganz, *Ber.*, **55**, 3495 (1922).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

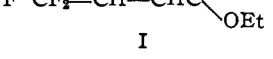
Addition Reactions to Ethyl γ,γ,γ-Trifluorocrotonate

BY HARRY M. WALBORSKY AND MEYER SCHWARZ

RECEIVED FEBRUARY 23, 1953

The preparation of ethyl γ,γ,γ-trifluorocrotonate is reported. The addition of unsymmetrical reagents to the double bond is investigated and it is demonstrated that the CF_3 group does not reverse the normal mode of addition. The dissociation constant of γ,γ,γ-trifluorocrotonic acid is 7.1 ± 0.1 × 10^{-4}.

The direction of addition of unsymmetrical reagents to ethyl γ,γ,γ-trifluorocrotonate was of interest in order to determine whether the trifluoromethyl group or the carbethoxy group would be the controlling factor. In the former case, the trifluoromethyl group might be expected to direct the entering anion to the α-carbon atom through an inductive or hyperconjugative effect[1] as illustrated in I. If the carbethoxy group were more important, the nucleophilic reagent would react at the β-position. The determining factor would thus be the resonance stabilization produced by interaction of the carbethoxy group with the double bond (II),


$F^{-}CF_2{=}CH{-}\overset{+}{C}HC(=O)OEt$

I


$CF_3{-}\overset{+}{C}H\text{---}CH\text{---}C(O^{-})OEt$

II

Henne and co-workers[2] have shown that ionic addition (both acid- and base-catalyzed) as well as radical addition of unsymmetrical reagents to 3,3,3-trifluoropropene yields exclusively "anti-Markovnikow" products. Thus the addition of hydrogen bromide produced 1,1,1-trifluoro-3-bromopropane. In this case the CF_3 group polarized the double bond so that the terminal carbon atom possessed the lowest electron density. The strong polarizing effect of the CF_3 group was clearly demonstrated.

On the other hand, it is well known that when one adds hydrogen iodide,[3] hydrogen bromide,[3] alcohol[4] and ammonia[5] to ethyl crotonate, the nucleophilic attack of these unsymmetrical reagents is directed at the β-carbon atom to yield β-substituted derivatives of ethyl butyrate.

The system under investigation, ethyl γ,γ,γ-trifluorocrotonate, was prepared by the dehydration of ethyl β-hydroxy-γ,γ,γ-trifluorobutyrate. The dehydration of alcohols which have a trifluoromethyl group adjacent to the carbon atom containing the hydroxyl group, has been described as difficult.[6] Conventional methods of dehydration (potassium acid sulfate or concd. sulfuric acid) gave no unsaturated products. The yield using phosphorus pentoxide was too low for preparative use. The carbinol was finally converted to the

---

(1) N. Haszeldine, *J. Chem. Soc.*, 3483 (1952).

(2) A. Henne, *et al.*, THIS JOURNAL, **72**, 3369, 4756 (1950); **73**, 5527 (1951).

(3) W. Hemilian, *Ann.*, **174**, 324 (1874).

(4) Purdie and Marshall, *J. Chem. Soc.*, **59**, 478 (1891).

(5) K. Morsch, *Monatsh.*, **60**, 50 (1932).

(6) K. Campbell, J. Knobloch and B. Campbell, THIS JOURNAL, **72**, 4380 (1950).