175 ml. of absolute ethanol, an additional 20 ml. of absolute ethanol being used for rinsing. The salt precipitated instantly with incipient boiling of the solution. The hot mixture was stirred thoroughly to ensure homogeneity and was stored at 6° for 2 days. The microcrystalline salt was collected by suction filtration, washed with 20 ml. of absolute ethanol and dried under reduced pressure at 60–80° for several days to remove alcohol, which was held very tenaciously.

Somewhat less ethanol was employed for formation of the adipic acid salts of the other two isomers. The *cis-trans* salt precipitated as tiny, oily spheres that crystallized rapidly on scratching. The diamine samples were weighed in a nitrogen-filled dry-box to prevent absorption of carbon dioxide and water during handling. Polonium-plated gold foil was employed to dissipate the static charges acquired by the diamines during handling. The inflection points for the three salts were in the *p*H range of 7.53–7.58, as determined by electrometric titration of 0.5% aqueous solutions.

Preparation of Polyamides.—Polymer preparations were carried out in Pyrex brand glass tubes 28 × 180 mm. o.d. with a wall thickness of 2 mm. to which were sealed necks 11 × 220 mm. o.d. About 10 g. of salts was polymerized in each run. Mixtures of salts of the different isomers were stirred to assure that the resulting polyamide would be homogeneous. The tube containing the salt was evacuated and filled with oxygen-free nitrogen three times at atmospheric pressure, and then evacuated to a pressure of 5 mm. and sealed. The sealed tube was heated for one hour at 210° in a lead-bath. The tube was then cooled and opened and the contents heated under oxygen-free nitrogen at 1 atm. pressure for one-half hour at 306° (benzophenone vapor bath). Heating was continued for 1.5 hours at 285° (diphenylene oxide vapor bath) without allowing the molten polymer to cool appreciably while changing the bath.

Characterization of Polyamides.—Inherent viscosities[3] were predominantly in the range 0.72–1.05 which indicated that high molecular weight was attained. Polymer melting points were determined in air on a copper block.

---

(3) Determined with 0.5 g. of polymer in 100 ml. of *m*-cresol at 25°; *cf.* L. H. Cragg, *J. Colloid Sci.*, **1**, 261 (1946).

CONTRIBUTION NO. 297, CHEMICAL DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE

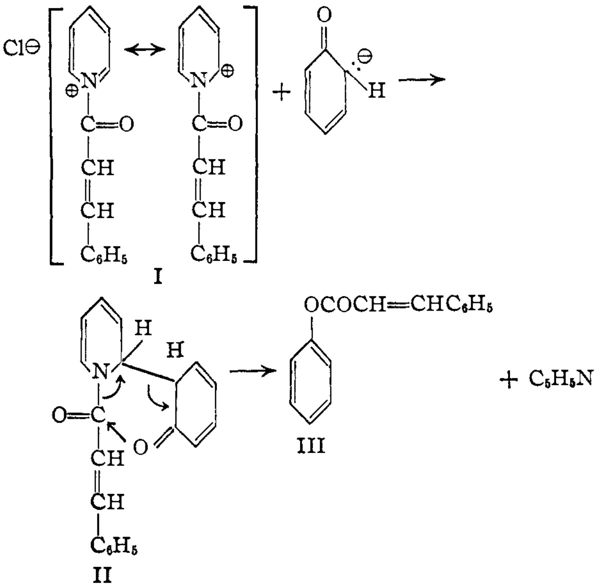
Some Reactions of Cinnamoylpyridinium Chloride

BY HENRY E. BAUMGARTEN

RECEIVED OCTOBER 13, 1952

In the course of another investigation we had cause to examine the chemical behavior of cinnamoylpyridinium chloride (I) and, in view of the recent interest[1,2,3,4] in compounds of the same general type as I, we are reporting our results at this time. The reaction of cinnamoyl chloride and pyridine in dry ethereal solution at or slightly below room temperature gave I in essentially quantitative yield as a white solid of rather indefinite melting point. The compound was a powerful acylating agent, reacting with water[1] or dilute solutions of bases[5] to give cinnamic anhydride in 13–71% yield depending on the conditions of the experiment. Acylation of ethyl benzoylacetate with I gave ethyl β-cinnamoyloxycrotonate in 59% yield. The reaction of pyridine, benzoyl chloride and dimethylaniline at room temperature for seven weeks or at 100° for six days has been reported to give 4-(*p*-dimethylaminophenyl)-pyridine in 22–27% yield.[4,6] The latter was obtained in 35% yield (along with traces of cinnamaldehyde) from the reaction of I and dimethylaniline in pyridine at steam-bath temperatures for eight hours.

The most interesting cinnamoylation was that of phenol, for this reaction appeared to take place in two distinct steps. When I was mixed with phenol (in the presence or absence of pyridine) a bright yellow substance formed which slowly and completely disappeared as crystals of colorless phenyl cinnamate deposited (73–83% yield). 2,6-Dimethylphenol behaved in the same fashion, giving 76% of 2,6-dimethylphenyl cinnamate. If the colored substance may be assumed to be a true intermediate, its formation may be rationalized by assuming a mechanism for the reaction similar to that proposed by Doering and McEwen[2] for several reactions of benzoylpyridinium chloride.[7] Thus, I which has an electron deficiency at the α- and γ-positions, reacts with the electron-donating keto form of the phenoxide ion to give the colored complex II,[8] which is converted *via* the quasi six-membered ring to the ester III.



Experimental[9]

Cinnamoylpyridinium Chloride (I).—To a solution of 83.5 g. (0.5 mole) of cinnamoyl chloride (prepared in 95% yield from cinnamic acid and 1.5 moles of thionyl chloride, b.p. 133–134° (15 mm.)) in 200 ml. of dry ether was added slowly with cooling 60 g. (0.76 mole) of pyridine dissolved in 100 ml. of dry ether. The mixture was allowed to stand 30 minutes (protected from moisture) and was filtered, washed with cold ether and dried over potassium hydroxide *in vacuo*. The yield of cinnamoylpyridinium chloride was 113–122 g. (92–98%), m.p. about 122–124°. The compound decomposed when distilled under reduced pressure. The com-

---

(1) H. Adkins and Q. E. Thompson, THIS JOURNAL, **71**, 2242 (1949).

(2) W. von E. Doering and W. E. McEwen, *ibid.*, **73**, 2104 (1951).

(3) Q. E. Thompson, *ibid.*, **73**, 5841 (1951).

(4) W. E. McEwen, E. H. Terss and I. W. Elliott, *ibid.*, **74**, 3605 (1952).

(5) E. Wedekind, *Ber.*, **34**, 2070 (1901).

(6) For the original report of this reaction see: E. Koenigs and E. Ruppelt, *Ann.*, **509**, 142 (1934).

(7) See footnote 4 of ref. 2. Apparently Adkins and Thompson[1] have succeeded in isolating benzoylpyridinium chloride (although not in analytically pure form) as well as numerous other aroylpyridinium chlorides.

(8) Intermediate II may be in equilibrium with a similar substance in which the cyclohexadienone unit is in the γ-position (see ref. 2).

(9) Melting points are corrected, boiling points are not. Analyses were by Clark Microanalytical Laboratory, Urbana, Illinois, unless otherwise noted.

pound was also prepared using dry petroleum ether or dry benzene as the reaction medium.

Anal. Calcd. for $C_{14}H_{12}NOCl$: Cl, 15.17. Found: (analysis by author) Cl, 14.85.

Some preparations gave products (usually pale yellow or off-white in color) that were obviously not pure, but these were found to be satisfactory for synthetic use. All of the reactions cited below were run with the solid cinnamoylpyridinium chloride and most of them were run also by adding the calculated amount of cinnamoyl chloride and pyridine to the other reactants. The yields were comparable by both procedures.

Cinnamic Anhydride.—To a solution of 2 ml. of water in 70 ml. of acetone was added 15 g. (0.06 mole) of cinnamoylpyridinium chloride. The mixture was stirred vigorously for five minutes and poured into 500 ml. of water containing 5 ml. of hydrochloric acid. The solid was filtered off, washed with 5% sodium bicarbonate and with water. The air-dried product was recrystallized from absolute ethanol, giving 6.0 g. (71%) of cinnamic anhydride, m.p. 135–136°. When the procedure of Wedekind[5] was followed, the yield of cinnamic anhydride was 13% (after recrystallization). The principal product whenever a large excess of water was used (as in the Wedekind procedure) was cinnamic acid.

Ethyl β-Cinnamoyloxycrotonate.—A mixture of 24.6 g. (0.1 mole) of cinamoylpyridinium chloride and 19.2 g. (0.1 mole) of ethyl benzoylacetate was warmed on the steam-bath for two hours and allowed to stand overnight. The crude mixture was washed with 5% hydrochloric acid, water, 5% sodium bicarbonate and water in that order. The solid remaining was recrystallized from absolute ethanol, giving 19 g. (59%) of ethyl β-cinnamoyloxycrotonate, m.p. 125.4–126.1°. The product gave no enolic tests.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.30; H, 5.39.

4-(*p*-Dimethylaminophenyl)-pyridine.—A mixture of 12.3 g. (0.05 mole) of cinnamoylpyridinium chloride, 4.0 g. (0.05 mole) of pyridine and 6.0 g. (0.05 mole) of dimethylaniline was heated on the steam-bath for eight hours. The mushy mixture was made acid with concentrated hydrochloric acid and steam distilled. The 150-ml. of steam distillate was extracted with ether, the ether evaporated and the residue treated with phenylhydrazine in ethanol,[10] giving *ca.* 0.1 g. of cinnamaldehyde phenylhydrazone, m.p. 167–168°. The residue from the distillation was filtered from a large mass of black tarry material and the filtrate was made alkaline. Steam distillation of the alkaline mixture yielded 3.0 g. (50%) of dimethylaniline. The residue in the distillation flask was filtered off and recrystallized three times from 9:1 ethanol:chloroform to give 3.5 g. (35%) of 4-(*p*-dimethylaminophenyl)-pyridine, m.p. 234–235°, as colorless, flat plates which colored quickly in air to a light yellow solid. This interesting substance had, as one might expect, indicator properties, being yellow in acidic (organic or inorganic) and colorless in neutral or alkaline solutions. It reacted (in chloroform solution) with acid halides to give brilliantly colored complexes, *e.g.*, a bright red with benzoyl chloride and a deeper red with cinnamoyl chloride, even in high dilutions.

Phenyl Cinnamate.—To 24.5 g. (0.1 mole) of cinnamoylpyridinium chloride was added 9.4 g. (0.1 mole) of phenol. A bright yellow color appeared immediately and slowly faded on standing. From this point two procedures were used: (a) 16.0 g. (0.2 moles) of pyridine was added and the mixture was heated for four hours on the steam-bath or (b) the mixture (without added pyridine) was allowed to stand at room temperature overnight. In each case the resultant mixture was poured into 500 ml. of water and stirred until the oily lower layer solidified. The solid was collected on the buchner funnel, washed with 10% hydrochloric acid, 5% sodium bicarbonate, 10% potassium hydroxide, and with water in that order, and recrystallized from 95% ethanol, giving 16–18.5 g. (73–83%) of phenyl cinnamate, m.p. 75–76°. This procedure compares favorably with respect to yields (reported 56–75%) and with respect to the manipulations required with that reported in reference 11.

2,6-Dimethylphenyl Cinnamate.—To 24.5 g. (0.1 mole) of cinnamoylpyridinium chloride was added 12.2 g. (0.1 mole) of 2,6-dimethylphenol (DPI 1772). A bright yellow-orange color appeared briefly then disappeared. To the mixture was added 8.0 ml. of pyridine and it was allowed to stand overnight. The reaction mixture was worked up as described for phenyl cinnamate (above), giving 19 g. (76%) of 2,6-dimethylphenyl cinnamate, m.p. 91–92°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.39; H, 6.32.

AVERY LABORATORY
UNIVERSITY OF NEBRASKA
LINCOLN 8, NEBRASKA

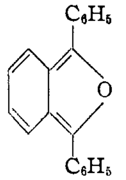
Reactions of 1,3-Diphenylisobenzofuran with Acetylenic Dienophiles

BY JEROME A. BERSON

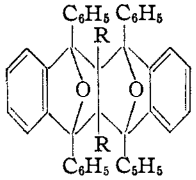
RECEIVED OCTOBER 17, 1952

Although additions of 1,3-diphenylisobenzofuran (I) to a number of ethylenic dienophiles have been reported,[1–4] the literature does not seem to contain any examples of reactions of this interesting substance with acetylenic dienophiles. In connection with a separate study, we have had occasion to carry out such reactions. The preparation and properties of the adducts and their derivatives are reported here.

The reaction of I with acetylenedicarboxylic acid (II) produced the bis-adduct (III) in near-quantitative yield. Even in the presence of a large excess of II, only III could be isolated, albeit in smaller yield.

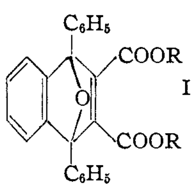


I



III, R = COOH

Diene addition of I to ethyl acetylenedicarboxylate afforded a 1:1 adduct (IVa) in excellent yield. The ester (IVa) was readily reduced to the corresponding dihydro adduct (V). Saponification of IVa yielded the very unstable unsaturated acid IVb, isolated only as the monohydrate. This acid suffers partial retrograde diene addition in alkaline solution and consequently, the saponification of the ester (IVa) yielded a small quantity of I, identified as the autoxidation product, *o*-dibenzoylbenzene. Pyrolysis of IVb at the melting point (140°) resulted in virtually quantitative conversion to the bis-adduct (III), presumably by retrograde diene addition and recombination of the addends. The facile dissociation of V and especially of IVb



IV a, R = C_2H_5
b, R = H

---

(10) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 72.

(11) *Org. Syntheses*, **20**, 77 (1940).

(1) R. Weiss, A. Abeles and E. Knapp, *Monatsh.*, **61**, 162 (1932).

(2) E. de B. Barnett, *J. Chem. Soc.*, 1326 (1935).

(3) C. Dufraisse and R. Priou, *Bull. soc. chim.*, [5] **5**, 502 (1938).

(4) A. Etienne and A. Spire, *Compt. rend.*, **230**, 2030 (1950).