853 cm.$^{-1}$ (distinctive finger-print bands for this material), and 780 and 740 cm.$^{-1}$ (probably *cis* olefin). The expected cyclic olefin band at 1615 cm.$^{-1}$ was very weak.

4,7-Bis(2′-cyanoethyl)-4,6-decadienedinitrile (II).—When 8.9 g. (0.027 mole) of 2,2,5,5-thiophenetetrapropionitrile 1-dioxide was heated at 195–205°, 0.1-mm. pressure, for 4 hr., gas evolved leaving a crystalline solid (90% yield). After recrystallization from acetonitrile it melted at 150–151°.

Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.15; H, 6.81; N, 21.04; mol. wt., 266. Found: C, 72.21; H, 6.47; N, 20.72; mol. wt., 253 (thermistor micromethod[7] with acetonitrile as the solvent).

Its infrared spectrum showed bands at 2250 cm.$^{-1}$ (nitrile), 1605 cm.$^{-1}$ (conjugated diene), and 1425 cm.$^{-1}$ (—CH_2CN). There were no sulfone bands at 1295 and 1130 cm.$^{-1}$. The ultraviolet spectrum (in acetonitrile solution) showed bands at 243 mμ (sh, ε 27,500), 247 mμ (ε 28,900), and 255 mμ (sh, ε 20,200). This pattern is typical of a poly-substituted linear conjugated diene.

Acknowledgment. The author wishes to thank Mr. N. B. Colthup, Dr. R. C. Hirt, and Mr. R. G. Schmitt for their interpretation of the infrared and ultraviolet spectra, and Mr. R. J. Francel for his cooperation in the analyses.

---

[7] A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961).

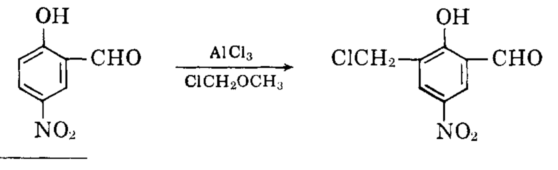
The Chloromethylation of 5-Nitrosalicylaldehyde

LLOYD D. TAYLOR AND ROBERT B. DAVIS

Chemical Research Laboratories, Polaroid Corporation, Cambridge 39, Massachusetts

Received December 10, 1962

Recently we have had occasion to prepare 3-chloromethyl-5-nitrosalicylaldehyde. We decided to try the direct chloromethylation of 5-nitrosalicylaldehyde, although the aromatic ring is somewhat inactive. After several unsuccessful conventional reactions,[1] a Friedel–Crafts type reaction with aluminum chloride and chloromethyl methyl ether was tried, although aluminum chloride usually is much too active a catalyst for this type of reaction, yielding diphenylmethane compounds. We now have found that chloromethylation of 5-nitrosalicylaldehyde is accomplished in yields of 90% by employing four equivalents of aluminum chloride (one for each oxygen atom) plus a 10% catalytic excess and by carrying out the reaction in pure chloromethyl methyl ether. Several reactions in chloromethyl methyl ether, with zinc chloride or with only one equivalent of aluminum chloride, yielded only starting material. The success of this reaction may be aided by the noticeable solubility of the salicylaldehyde–aluminum chloride complex in chloromethyl methyl ether. The literature does not mention the application of the halo ether as the solvent and it is possible that other highly oxygenated compounds may be successfully chloromethylated by means of this method.



---

[1] R. C. Fuson and C. H. McKeever, "Organic Reactions," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 66–71.

Experimental

Into a 2-l, three-necked, round-bottom flask, fitted with a mechanical stirrer, addition tube, 1 Allihn condenser surmounted by a Friedrichs condenser fitted with a calcium chloride drying tube, were placed 95 g. (0.57 mole) of 5-nitrosalicylaldehyde (m.p. 126–127°, Eastman product) and 1 l. of chloromethyl methyl ether (b.p. 58°, Eastman product). To this solution, cooled to 5°, was added with stirring 312 g. of aluminum chloride (2.3 moles) over a 1-hr. period. This slurry was brought to room temperature and then allowed to reflux for 80 hr. until evolution of hydrogen chloride ceased. The viscous solution was cooled to room temperature and then poured with stirring into 3 l. of crushed ice. The resulting brown tar was stirred with ice–water for ~30 min.

$$ClCH_2OCH_3 + H_2O \longrightarrow H_2O + HCl + CH_3OH$$

The brown solid was filtered and the filtrate extracted with ether. The ether extract was dried with sodium sulfate and the ether was removed by evaporation. The brown solid was added to that previously obtained and the product was recrystallized from carbon tetrachloride using charcoal. In this manner 108 g. (89%) of a tan solid (m.p. 89–90°) was obtained. A small portion was recrystallized from hexane (needles), m.p. 90.5–91.5°.

Anal. Calcd. for $C_8H_6ClNO_4$: C, 44.6; H, 2.8; N, 6.5; Cl, 16.5. Found: C, 44.4; H, 2.8; N, 6.6; Cl, 16.7.

An n.m.r. spectrum of the product is in accord with the assigned structure. The compound, run in deuteriochloroform, showed the following bands: one hydroxyl hydrogen at 12.1 p.p.m., one aldehyde hydrogen at 10.1 p.p.m., two aromatic hydrogens at 8.60 p.p.m., and two methylene hydrogens at 4.70 p.p.m. The only band split was that of the aromatic hydrogens, revealing an AB system with a coupling constant of 3 c.p.s., characteristic of aromatic protons in the *meta* position.[2]

---

[2] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.

The Preparation of 1-Aryl-1,2-cyclopropanedicarboximides. An Application of Dimethylsulfoxonium Methylide

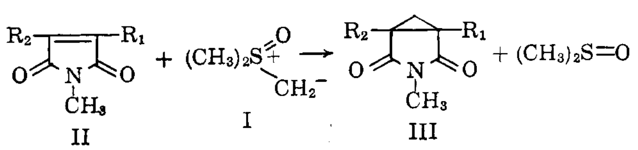
PATRICK T. IZZO

Organic Chemical Research Section, Lederle Laboratories, Division of American Cyanamid Company, Pearl River, New York

Received January 21, 1963

The interest, in these laboratories, in 1-aryl-1,2-cyclopropanedicarboximides as pharmacologically interesting compounds prompted an investigation of new methods for the preparation of some members of this class of substances.

Recently Corey and Chaykovsky[1] have reported on a new synthesis of cyclopropanes based on Michael addition of dimethylsulfoxonium methylide (I) to appropriate α,β-unsaturated ketones. The purpose of this paper is to describe an application of this reaction in which some N-methyl-2-arylmaleimides (II) were the substrates for the action of the ylide. In



II I III

---

[1] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).