Evaporation of the ether extract of the acidified sodium bicarbonate solution left a small (about 0.5 g.) residue which was taken up in alcohol and treated with the 2,4-dinitrophenylhydrazine reagent.[12] The resulting 2,4-dinitrophenylhydrazone, recrystallized from alcohol, m.p. 257–259 dec., gave no depression of melting point when mixed with an authentic sample.[13]

2-Carbethoxy-2-(3-chloroallyl)cycloheptanone.—Carbethoxycycloheptanone (31.3 g., 0.17 mole) was added to a hot solution of sodium (3.19 g., 0.17 g.-atom) in 100 ml. of absolute alcohol. After half an hour of heating, 1,3-dichloropropene (18.9 g., 0.17 mole) was added, and the mixture was left to reflux overnight. The usual work up followed by distillation gave 21 g. (47.7%) of colorless liquid boiling at 135–150° (4 mm.). Careful fractionation through the stainless steel sponge-packed column gave a chromatographically pure liquid boiling at 129° (1 mm.), $n^{23}\text{D}$ 1.4858.

Anal. Calcd. for $C_{13}H_{19}ClO_3$: C, 60.36; H, 7.34. Found: C, 60.42; H, 7.65.

2-(3-Chloroallyl)cycloheptanone.—Cycloheptanone (112 g., 118 ml., 1 mole) was added to a well stirred mixture of sodium amide (40 g., 1.02 moles) in 500 ml. of anhydrous ether. The mixture was refluxed for 4 hr. and then cooled in ice–water, with nitrogen flowing through the system, and treated with a solution of 1,3-dichloropropene (111 g., 1 mole) in 100 ml. of anhydrous ether. When the initial exothermic reaction had subsided, the mixture was left to reflux overnight. The mixture was then cooled and 500 ml. of water was added. The ether solution was washed with water and dried over magnesium sulfate. Distillation gave 25 g. of unchanged cycloheptanone and 86.8 g. (59.2%) of liquid boiling at 125–130° (10 mm.). Careful fractionation gave a chromatographically pure analytical sample boiling at 96° (2 mm.), $n^{22}\text{D}$ 1.4978.

Anal. Calcd. for $C_{10}H_{15}OCl$: C, 64.36; H, 8.04. Found: C, 64.46; H, 8.09.

Bicyclo[4.3.1]dec-7-en-10-one.—(a) 2-Carbethoxy-2-(3-chloroallyl)cycloheptanone (41.6 g., 0.16 mole) was added dropwise with stirring to 50 ml. of concentrated sulfuric acid. After the mixture had been stirred for 1 week at room temperature, the reaction was stopped by the addition of 500 ml. of cold water and the product was taken up in ether. The ether was washed with sodium bicarbonate solution[14] and water and dried over magnesium sulfate. Chromatographic analysis after removal of the ether revealed the presence of a little 2-(3-chloroallyl)cycloheptanone but no bicyclo[4.3.1]dec-7-en-10-one. Fractionation yielded 5.25 g. (21.7%) of bicyclo[4.3.1]dec-7-en-10-one,[15] boiling 100–105° at (4 mm.), $n^{24}\text{D}$ 1.5020, 2,4-dinitrophenylhydrazone m.p. 136–138, containing only a trace of 2-(3-chloroallyl) cycloheptanone and 10.9 g. of an inseparable[16] mixture[17] of starting material and 1-carbethoxybicyclo[4.3.1]dec-7-en-10-one boiling at 145–150° (4 mm.), $n^{24}\text{D}$ 1.4896.

(b) 2-(3-Chloroallyl)cycloheptanone (49 g., 0.263 mole) was added to 50 ml. of concentrated sulfuric acid and worked up as before. Chromatographic analysis of the product before distillation indicated approximately an equal mixture of unchanged starting material and product. Distillation gave 5.5 g. (14%) of good quality bicyclo[4.3.1]dec-7-en-10-one[18] boiling at 85–91° (2 mm.), $n^{23}\text{D}$ 1.5050, 2,4-dinitrophenylhydrazone, m.p. 136–138°. There was no depression of melting point on mixture with the 2,4-dinitrophenylhydrazone obtained from method a.

Acknowledgment.—This research was supported by a grant from The Alfred University Research Foundation.

---

[12] Shriner and Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948, p. 171.

[13] Reported (ref. 2) 259–261°, dec.

[14] Only a trace of gummy material was obtained by acidifying the sodium bicarbonate solution.

[15] Bicyclo[4.3.1]dec-7-en-10-one begins to polymerize after only a few days at room temperature.

[16] With the available fractionating equipment.

[17] No trace of either 2-(3-chloroallyl)cycloheptanone or bicyclo[4.3.1]-dec-7-en-10-one was present in this fraction. A second distillation, with a purposely prolonged total reflux, however, resulted in contamination from both these materials.

[18] An 18.3-g. sample (46.4%) of liquid (of which the 5.5 g. was the best), slightly contaminated with 2-(3-chloroallyl)cycloheptanone, was actually isolated. Greater yields of highly pure product would be possible with better fractionating equipment.

Cyanoethylation of Butadiene Sulfone

RICHARD P. WELCHER

Industrial Chemicals Division,
American Cyanamid Company, Stamford, Connecticut

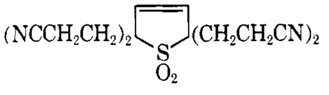
Received December 26, 1962

Although cyanoethylation of aryl sulfones[1] and 1,3,5-trimethylene trisulfones[2] has been described, the reaction of butadiene sulfone with acrylonitrile was reported to take another course.[3]

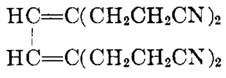
In this last study no definite crystalline addition compounds were found, but instead distillable products which appeared to be low-molecular weight polymers of acrylonitrile and butadiene sulfone. Copolymers of acrylonitrile and cyclic sulfones, containing at least 85% acrylonitrile, also have been claimed.[4]

This paper reports the preparation of a crystalline adduct by the base-catalyzed reaction of butadiene sulfone and four moles of acrylonitrile. It was postulated to be 2,2,5,5-thiophenetetrapropionitrile 1-dioxide (I) on the basis of analysis, infrared spectrum, and chemical behavior. Unlike previous products,[3] our product decomposed at the melting point, with evolution of gas, to form a new crystalline solid. Analysis, infrared and ultraviolet spectra, showed the new compound to be 1,4-tetrakis(2′-cyanoethyl)-1,3-butadiene [better name: 4,7-bis(2′-cyanoethyl)-4,6-decadienedinitrile] (II). The thermal decomposition of I into II constitutes strong evidence of the postulated structures, in view of the known[5] breakdown of simple diene sulfones into 1,3-dienes upon heating.

This two-step procedure provides a new method of preparing 1,4-substituted 1,3-dienes.



I



$$\begin{array}{l} HC{=}C(CH_2CH_2CN)_2 \\ | \\ HC{=}C(CH_2CH_2CN)_2 \end{array}$$

II

Experimental[6]

2,2,5,5-Thiophenetetrapropionitrile-1,1-dioxide (I).—To a solution of 11.8 g. (0.10 mole) of butadiene sulfone (from the Phillips Petroleum Co.), 23.3 g. (0.44 mole) of acrylonitrile, and 50 ml. of acetonitrile was added a mixture of 1 g. of acetonitrile and 2 g. of a 40% solution of benzyltrimethylammonium hydroxide in methanol over a period of 3.5 hr. at 0–10°. The mixture was neutralized with acetic acid and filtered. The product (20% yield) was recrystallized from acetonitrile to give white crystals melting at 209.5–210°, decomposing with the evolution of gas.

Anal. Calcd. for $C_{16}H_{18}N_4O_2S$: C, 58.16; H, 5.49; N, 16.96; S, 9.70. Found: C, 58.40; H, 5.72; N, 17.53; S, 9.57.

Its infrared spectrum showed bands at 2255 cm.$^{-1}$ (nitrile), 1425 cm.$^{-1}$ (–CH_2CN), 1295 and 1130 cm.$^{-1}$ (sulfone), 958 and

---

[1] H. A. Bruson (to the Resinous Products and Chemical Co.), U. S. Patent 2,435,552 (February 3, 1948).

[2] H. T. Hookway and E. M. Evans (to British Resins Products Ltd.), U. S. Patent 2,468,015 (April 19, 1949).

[3] R. Wegler and H. Lafos (I. G. Leverkusen), 1944; referred to by O. Bayer, *Angew. Chem.*, **61**, 229 (1949).

[4] (a) A. Fournet and H. Lemoine (to Societe des Usines Chimiques Rhone-Poulenc) U. S. Patent 3,017,397 (January 16, 1962); (b) NOTE ADDED IN PROOF.—After this manuscript had been accepted, news of the preparation of compound I was received [Derwent, British Patent, Abstract 3, no. 5, Gp. 1, 2 (February 1, 1963)].

[5] (a) Badische Anilin- and Soda-Fabrik, German Patent 236,386; *Chem. Zentr.*, **II**, 316 (1911); (b) O. Grummitt, A. E. Ardis, and J. Fick, *J. Am. Chem. Soc.*, **72**, 5167 (1950).

[6] Melting points are corrected.

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).

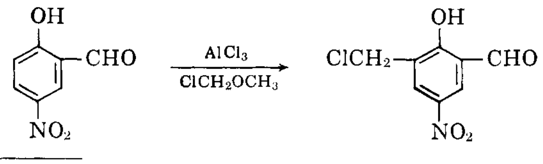
The Chloromethylation of 5-Nitrosalicylaldehyde

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.



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]

---

[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.

[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

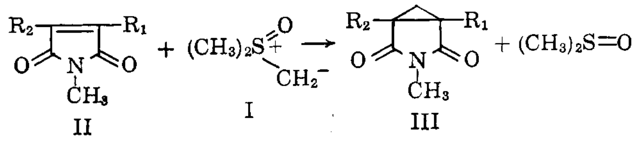
Patrick T. Izzo

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



---

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