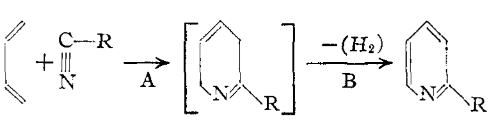


The dihydro-cyclic intermediate has never been isolated, the loss of hydrogen being a spontaneous process under the reaction conditions. The beneficial effect of the aromatization-type catalysts reported in the earlier work,[3] and observed again in the present study, undoubtedly can be attributed to promotion of the dehydrogenation step (B) in the over-all process.

The mode of action of the alumina itself must be basically different from the aromatization catalysts. Aluminum oxide is known to be an amphoteric substance, having the properties of an acid or base depending on its environment. Under the condition of the present work (400–500°) the structure is predominantly the γ-alumina structure. The properties of the silica–alumina cracking catalysts have been interpreted on a chemical basis to the existence of aluminum ions (γ-alumina) with the characteristic of a Lewis acid.[12] The surface is active to electron donors from the gas phase to form complexes with the Lewis acid. In the present work, the cracking of propionitrile over pure alumina (A-3), and the lower catalytic activity of the alumina containing the basic oxide rather than the acidic oxide (*i.e.*, A-1 and A-2, respectively) are in accord with some acidic properties of this surface. Comparison of the relative surface areas when nitriles alone, and butadiene, were passed over the pure alumina (Table II, no. 1, 7, 8 and 5, respectively) indicates that the decrease in area is much smaller for the nitriles than the dienes (*i.e.*, the $C{\equiv}N$ and $CH{=}CH_2$) groups. This and the temperature rise indicate a more selective adsorption of the olefinic group. The data for acrylonitrile are interpreted as reaction through the olefinic group, the polar nature of the nitrile group promoting the double bond to a more reactive state.

The formation of some ammonium carbonate in the pyrolyses of the nitriles over pure alumina, and reported as a by-product in the nitriles–dienes reaction[3,13,14] can be attributed to a secondary reaction occurring in the alumina surface. The γ-alumina structure is formed from boehmite by dehydration at temperatures above 350°. The water thus expelled hydrolyzes the nitrile in these systems leading to the ultimate formation of ammoniacal products. Preliminary work in this Laboratory indicated that this reaction can be minimized by exhaustive high vacuum drying of the alumina at 500° prior to use in the nitriles–dienes reaction.

The preferential formation of certain isomers[13,14] and the enhanced rates in the heterogeneous reactions have been interpreted[13] in the light of a Diels–Alder reaction mechanism. Wassermann and coworkers[15] have reported that the Diels–Alder type reaction is susceptible to a general acid catalysis. In the present work, the activity of the alumina in promoting the rate of the nitriles–dienes cyclization is best understood as another example of the general acid catalysis of diene addition reactions.

Acknowledgment.—The authors wish to thank Miss Sonja Krause of this Laboratory for the measurements of surface areas. This work was made possible by grants-in-aid from Research Corporation of New York and the Research Grants Committee of Rensselaer Polytechnic Institute.

TROY, N. Y.

[12] A. G. Oblad, T. H. Milliken and G. A. Mills, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 231.

[13] G. J. Janz and S. C. Wait, Jr., THIS JOURNAL, **76**, 6377 (1954).

[14] G. J. Janz and W. J. G. McCulloch, *ibid.*, **76**, 3143 (1954).

[15] A. Wasserman, *J. Chem. Soc.*, 618 (1942); W. Rubin, H. Steiner and A. Wassermann, *ibid.*, 3046 (1949).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

Sulfur-containing Pivalic Acid Derivatives. I. Sulfonyldipivalic Acid

BY JOSEPH L. GREENE, JR.,[1] AND HUGH J. HAGEMEYER, JR.[2]

RECEIVED DECEMBER 15, 1954

Bromopivalic acid was synthesized from hydroxypivalic acid. The synthesis of thiodipivalic acid in excellent yields was accomplished by the reaction of bromopivalic acid with sodium sulfide; the ease with which this neopentyl halide is converted without rearrangement is unusual. Oxidation of thiodipivalic acid with hydrogen peroxide led to sulfonyldipivalic acid. A number of new sulfur-containing pivalic acid derivatives were synthesized. The preparation and properties of these compounds are described.

The literature contains relatively few references to aliphatic sulfonyldicarboxylic acids. The first member of the series, sulfonyldiacetic acid, also was the first prepared.[3]

It has been shown that α-sulfonylcarboxylic acids are analogous to α-keto acids in that they are decarboxylated readily by heat.[4] A general discussion of acids having the type formula $HOOCCHR$-$SO_2CHRCOOH$ has been published.[5] Since the advent of nylon, dicarboxylic acids have been of growing general interest as intermediates for polyamides and other condensation polymers. Since sulfonyldipivalic acid contains neither an α-sulfonyl group nor an α-hydrogen atom, it is thermally very stable, being unaffected by heating for 4 hours at a temperature 30° above its melting point. Hence it is of interest as an intermediate in the preparation of polyesters, polyamides, plasticizers, and other useful products.

The purpose of this paper is to describe the pro-

[1] Chemistry Department, Emory University, Emory University, Georgia.

[2] Texas Eastman Company, Longview, Texas.

[3] J. M. Loven, *Ber.*, **17**, 2817 (1884).

[4] R. Otto, *ibid.*, **21**, 89 (1888); R. Otto and W. Otto, *ibid.*, **21**, 992 (1888).

[5] J. M. Loven and R. Ahlberg, *ibid.*, **54B**, 227 (1921).

cedures and the intermediates involved in the conversion of hydroxypivalic acid to sulfonyldipivalic acid and some of its derivatives.

Attempts to prepare chloropivalic acid by the method of Kharasch and Brown[6] gave very low yields of the desired compound; however, excellent yields of bromopivalic acid were obtained from hydroxypivalic acid by a modification of the procedure reported by Kohn and Schmidt.[7]

As an intermediate in the synthesis of sulfonyldiacetic acid, Alden and Houston[8] prepared thiodiacetic acid by the reaction of two moles of sodium chloroacetate with one mole of sodium sulfide. Sodium bromopivalate was converted in an analogous manner to thiodipivalic acid, which was isolated and purified. The melting point and neutral equivalent of the product synthesized by the authors were the same as those reported for the compound obtained by the acid hydrolysis of thiodipivalonitrile.[9] The almost instantaneous reaction of this neopentyl halide with sodium sulfide is most unusual and deserves further study.

Following the procedure of Alden and Houston[8] for preparing sulfonyldiacetic acid, thiodipivalic acid was oxidized with alkaline permanganate to give sulfonyldipivalic acid. However, the yields obtained by this procedure were poor because the product was difficult to isolate and purify. A modification of a procedure employed by Hurd and Gershbein[10] to oxidize thiodinitriles to sulfonyldinitriles with hydrogen peroxide gave excellent yields of sulfonyldipivalic acid from thiodipivalic acid. Sulfonyldipivalic acid is a high-melting, crystalline solid which neither decomposes nor discolors when heated at 275° for 4 hours. It has been employed successfully as the acid constituent in high-molecular-weight polyesters.[11]

Several derivatives of thiodipivalic acid and sulfonyldipivalic acid were prepared. These are described in the Experimental section.

Experimental

Hydroxypivalic Acid.—This acid (m.p. 126–128°) was made from hydroxypivalaldehyde by the Cannizzaro reaction. The aldehyde was made by aldol condensation of formaldehyde and isobutyraldehyde.

Bromopivalic Acid.—Hydroxypivalic acid (1000 g.) was refluxed with 48% hydrobromic acid (10 kg.) for 20 hr., then the mixture was distilled slowly through a 24-in. Vigreux column. The distillate was led to the receiver through a condenser maintained at about 55°. When the vapor temperature reached 120°, bromopivalic acid started to co-distil with the hydrobromic acid and to crystallize in the receiver. The aqueous hydrobromic acid was decanted at intervals and returned to the still-pot and distillation was continued until no more organic material passed over. The solid bromopivalic acid was dissolved in a minimum quantity of ligroin and the small aqueous layer was discarded. The organic layer was dried over Drierite, then filtered into a large evaporating dish. The solvent was evaporated in a current of air, leaving white, flaky crystals of bromopivalic acid; yield 1255 g. or 82%, m.p. 46–48°.

Anal. Calcd. for $C_5H_9BrO_2$: Br, 44.20. Found: Br, 44.04.

Thiodipivalic Acid.—To a slurry of bromopivalic acid (1086 g.) and water (1000 ml.) a solution of sodium carbonate (300 g.) in water (960 ml.) was added slowly with vigorous stirring. When the neutralization reaction had subsided and the mixture had become homogeneous, a solution of sodium sulfide ($Na_2S{\cdot}9H_2O$, 852 g.) in water (450 ml.) was added in a fine stream with vigorous stirring. The temperature rose at once to 60° and the system was allowed to cool to room temperature before being filtered. The filtrate was treated (in a hood) with 50% sulfuric acid (900 g.) and stirred an additional 15 min. before being filtered. The product was first air-dried on the filter, then dried at 65° for 12 hr. and finally recrystallized from glacial acetic acid; yield 527 g. or 75%, m.p. 163–164°.

Anal. Calcd. for $C_{10}H_{18}O_4S$: C, 51.25; H, 5.02; neut. equiv., 117. Found: C, 51.41; H, 5.23; neut. equiv., 117.

Thiodipivalyl Chloride.—Thiodipivalic acid (24 g.) was refluxed with thionyl chloride (50 g.) for 1.5 hr. The excess thionyl chloride was removed under reduced pressure before the residual thiodipivalyl chloride was distilled; yield 24 g. or 88.5%, b.p. 156–157° (6 mm.).

Anal. Calcd. for $C_{10}H_{16}Cl_2O_2S$: C, 44.34; H, 5.95; Cl, 26.15; neut. equiv., 135.5. Found: C, 44.20; H, 5.78; Cl, 25.98; neut. equiv., 135.3.

Thiodipivalamide.—Thiodipivalyl chloride (10 g.) was poured slowly with stirring into NH_4OH (150 ml.) at 0° to give a white, granular precipitate of thiodipivalamide. The crude product was recrystallized from water; yield 7.1 or 82%, m.p. 174–175°.

Anal. Calcd. for $C_{10}H_{20}N_2O_2S$: C, 51.70; H, 8.67; N, 12.07. Found: C, 51.83; H, 8.92; N, 12.14.

N,N'-Di-(*p*-tolyl)-thiodipivalamide.—This compound was prepared from thiodipivalyl chloride by a standard procedure[12]; yield 72%, m.p. 139–140°.

Anal. Calcd. for $C_{24}H_{32}N_2O_2S$: C, 70.00; H, 7.83; N, 6.79. Found: C, 70.16; H, 8.12; N, 6.98.

Dimethyl Thiodipivalate.—Thiodipivalic acid (125 g.) was esterified with methanol, using the procedure of Clinton and Laskowski[13] for the preparation of methyl esters; yield 75 g. or 53.5%, b.p. 124–125° (1 mm.).

Anal. Calcd. for $C_{12}H_{22}O_4S$: C, 54.80; H, 8.44. Found: C, 54.69; H, 8.27.

Diethyl Thiodipivalate.—A mixture of thiodipivalic acid (468 g.), ethyl alcohol (550 g.), benzene (1200 ml.) and concentrated sulfuric acid (12 ml.) was refluxed through a 10-in. Vigreux column topped by a Dean–Stark water trap until no more aqueous layer collected. The reaction mixture was then washed successively with water and dilute sodium bicarbonate solution until excess acid was neutralized, then dried over calcium chloride. The benzene was removed and diethyl thiodipivalate was then distilled at reduced pressure; yield 510 g. or 88%, b.p. 135–136° (1 mm.).

Anal. Calcd. for $C_{14}H_{26}O_4S$: C, 57.85; H, 9.02. Found: C, 57.66; H. 8.87.

Sulfonyldipivalic Acid.—A mixture of diethyl thiodipivalate (500 g.), glacial acetic acid (1500 ml.) and acetic anhydride (1000 ml.) was stirred in a three-necked flask fitted with a thermometer, a mechanical stirrer and a reflux condenser. Hydrogen peroxide (30%, 460 g.) was added dropwise through the condenser over a 3-hr. period while maintaining the reaction temperature at 60–70° by external cooling. Stirring was continued until there was no further temperature rise. The reaction mixture was then transferred to a large evaporating dish on a steam-bath and heated in a strong current of air overnight. Hydrochloric acid (36%, 1500 ml.) was added, then heating and evaporation were continued until a thick slurry of crystals was obtained. An additional portion of hydrochloric acid (500 ml.) was added and evaporation over steam was continued until only a stiff paste of crystals remained. The crude product was cooled, then transferred to a sintered-glass funnel and dried by suction. The crude sulfonyldipivalic acid was recrystallized by dissolving it in boiling glacial acetic acid (900 ml.), cooling and adding benzene (300 ml.) when the solu-

---

[6] M. S. Kharasch and H. C. Brown, THIS JOURNAL, **62**, 925 (1940).

[7] M. Kohn and A. Schmidt, *Monatsh.*, **28**, 1056 (1907).

[8] J. P. Alden and B. Houston, THIS JOURNAL, **56**, 413 (1934).

[9] O. W. Cass, U. S. Patent 2,429,391 (1947).

[10] C. D. Hurd and L. L. Gershbein, THIS JOURNAL, **69**, 2328 (1947).

[11] Unpublished work of the Tennessee Eastman Company.

[12] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 158.

[13] R. O. Clinton and S. C. Laskowski, THIS JOURNAL, **70**, 3135 (1948).

tion temperature had fallen to 70°; yield 362 g. or 79%, m.p. 243–244° (acid was unchanged by heating at 275° for 4 hr.).

Anal. Calcd. for $C_{10}H_{18}O_6S$: C, 45.10; H, 6.81; neut. equiv., 133.1. Found: C, 45.16; H, 7.02; neut. equiv., 132.9.

Sulfonyldipivalyl Chloride.—Sulfonyldipivalic acid (30 g.) was refluxed with thionyl chloride (75 g.) for 16 hr. The excess thionyl chloride was removed under reduced pressure and the residue was dissolved in hot benzene (200 ml.). The benzene solution was cooled, then filtered directly into ligroin (500 ml.) at 0° with stirring. The crystals thus precipitated were collected on a filter and dried by suction in a current of dry air; yield 26 g. or 76%, m.p. 103–105°.

Anal. Calcd. for $C_{10}H_{16}Cl_2O_4S$: C, 39.65; H, 5.32; Cl, 23.40; neut. equiv., 151.6. Found: C, 39.49; H, 4.98; Cl, 23.57; neut. equiv., 151.3.

Sulfonyldipivalamide.—This compound was prepared as described above for thiodipivalamide; yield 85%, m.p. 205–206°.

Anal. Calcd. for $C_{10}H_{20}N_2O_4S$: C, 45.40; H, 7.62; N, 10.61. Found: C, 45.52; H, 7.85; N, 10.45.

N,N′-Di-(*p*-tolyl)-sulfonyldipivalamide.—This compound was obtained from sulfonyldipivalyl chloride by the standard method previously cited[12]; yield 69%, m.p. 212–213°.

Anal. Calcd. for $C_{24}H_{32}N_2O_4S$: C, 64.90; H, 7.27; N, 6.31. Found: C, 64.78; H, 7.62; N, 6.51.

Dimethyl Sulfonyldipivalate.—Sulfonyldipivalyl chloride (50 g.) was treated with methanol (400 ml.) in a large beaker. After the vigorous reaction had subsided, practically all excess methanol was removed by evaporation on a steam-bath. The crude ester which remained was recrystallized from a mixture of methanol (150 ml.) and benzene (50 ml.); yield 43.2 g. or 89%, m.p. 90–92°.

Anal. Calcd. for $C_{12}H_{22}O_6S$: C, 48.96; H, 8.14. Found: C, 49.06; H, 8.33.

Diethyl Sulfonyldipivalate.—This compound was prepared from the acid chloride and ethyl alcohol by the method described for the preparation of the methyl ester. The crude ester was recrystallized from a mixture of ethyl alcohol and ligroin (2:1 by vol.). In this case the solution was allowed to stand overnight at 0°; yield 83%, m.p. 53–54°.

Anal. Calcd. for $C_{14}H_{26}O_6S$: C, 52.15; H, 8.14. Found: C, 52.31; H, 8.41.

Acknowledgment.—The authors are grateful to Mr. D. C. Sievers and the staff of the analytical section of the Research Laboratories of Tennessee Eastman Co. for all elemental analyses.

KINGSPORT, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

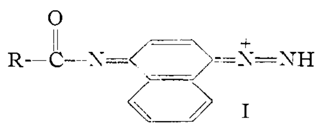
The Absorption Spectra of Some *p*-Acylaminobenzenediazonium Compounds

BY LEIGH C. ANDERSON AND B. MANNING[1,2]

RECEIVED JUNE 18, 1954

The marked stability of dry *p*-acylaminoaryldiazonium salts as compared to the high instability of simple diazonium compounds leads one to suggest different electronic structures for these two types of compounds. Two *p*-acylaminobenzenediazoimides and seven different *p*-acylaminobenzenediazonium salts and some of their metal complexes have been prepared and their quantitative visible and ultraviolet absorption spectral curves determined. The data indicate that a quinonoid configuration is the chief contributor to the structure of these diazonium compounds.

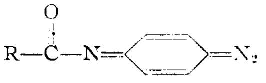
In this investigation, the absorption spectra of solutions of a number of *p*-acylaminobenzenediazonium salts have been compared to those of the benzenoid compounds from which they have been prepared and to those compounds of recognized quinonoid configuration. Hewitt, in 1907,[3] assuming a mobile hydrogen atom on the amide nitrogen, proposed a quinonoid structure for the 4-benzoylamino-1-naphthalenediazonium ion (I) to account for the color of the chloride. Other investigators opposed the assignment of this structure



I

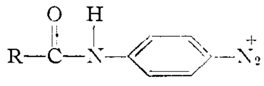
because the corresponding *p*-(alkylacylamino) compounds are colored also. The marked stability of the dry diazonium compound containing the *p*-acylamino group as compared to the high instability of simple diazonium compounds leads one to suggest different electronic structures for these two types of compounds. The imides of the *p*-acylaminobenzenediazonium compounds are colored also, but are quite unstable.

The classical formula for the neutral imide can only be postulated in the quinonoid form II

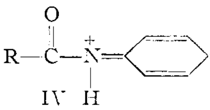


II

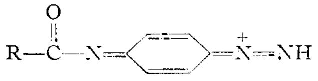
Three structures III, IV and V can be written for the *p*-acylaminobenzenediazonium ion



III



IV



V

Substitution of various acyl groups for a hydrogen atom of an amino group of *p*-phenylenediamine and also substitution of chlorine atoms for one or two of the hydrogen atoms of the benzene nucleus produce marked differences in the ultraviolet absorption spectrum as compared to that of *p*-phenylenediamine (Table I). The absorption of the predominantly benzenoid derivatives of the *p*-phenylenediamine molecules is altered markedly by the introduction of the various acyl groups and the

---

[1] The material presented in this paper represents a portion of a dissertation submitted by Bernard Manning to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, June, 1950.

[2] Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society at Boston, Mass., April 5, 1951.

[3] J. T. Hewitt, *Proc. Chem. Soc.*, **23**, 181 (1907).