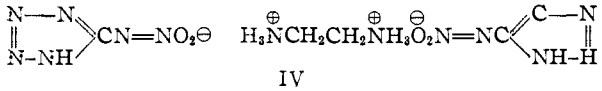
have combined in a 1:1 stoichiometric ratio. This precludes a bis-monoacid structure (IV), although one cannot distinguish the salt as being mono- or



IV

diacid. Since 5-nitroaminotetrazole does form salts with very weakly basic amines it has been assumed that the salt is diacidic.

Experimental

Nitroguanyl Azide.—This was prepared as previously described.[3] The product obtained by evaporation of the combined ether extracts, m.p. 79°, was sufficiently pure and was not recrystallized further.

Amines.—C.P. grade reagents were purified by distillation or recrystallization until they met the reported values for physical constants.

General Procedure for Reaction of Amines with Nitroguanyl Azide.—Specific illustrative examples for the preparation of the mono- and diacid salts of 5-nitroaminotetrazole have been described elsewhere.[2] In general the compounds noted in Table I were prepared by dissolving the nitroguanyl azide in ether (15 ml. for 0.01 mole) and adding the amine, in two molar proportions, also dissolved in ether (10 to 15 ml. for 0.02 mole of amine). Deviations from the use of anhydrous ether as solvent are noted in Table I. The amine salt of 5-nitroaminotetrazole, generally, immediately precipitates. However, the reaction mixture may be allowed to stand, at room temperature, for periods from 30 minutes or overnight. The crystals are removed by filtration, washed with anhydrous ethyl ether and recrystallized. The choice of solvent for recrystallization varies with the individual preparation. This has been noted in Table I.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS

S-Benzylthiuronium Salts of Nitroalkyl Hydrogen Sulfates

BY A. C. MCINNIS, JR., AND L. G. TOMPKINS

RECEIVED APRIL 9, 1951

We have prepared as derivatives for the characterization of several low molecular weight nitroalcohols the crystalline S-benzylthiuronium salts of their sulfate esters. The latter are prepared by the addition of the nitroalcohol to a mixture of chlorosulfonic acid and dioxane.[1]

The 3,5-dinitrobenzoates of two of these nitroalcohols also have been prepared. Benzenesulfonates, *p*-toluenesulfonates[2,3] and α-naphthylurethans[4] have previously been used to characterize nitroalcohols.

Pertinent data are tabulated herewith. Melting points were determined with a Fisher–Johns apparatus which was calibrated over the 50–160° range.

TABLE I

Nitroalcohol	S-Benzylthiuronium salt M.p., °C.	Nitrogen, % Calcd.	Found
2-Nitro-1-propanol	114–115	11.96	11.81
2-Nitro-1-butanol	100–101	11.50	11.54
2-Nitro-2-methyl-1-propanol	145–146	11.50	11.46
3-Nitro-2-butanol	105–106	11.50	11.69
3-Nitro-2-pentanol	127–128	11.08	11.15
3-Nitro-3-methyl-2-butanol	119–120	11.08	11.05

(1) R. K. Bair and C. M. Suter, THIS JOURNAL, **64**, 1978 (1942).
(2) P. J. Baker, U. S. Patent 2,395,386 (Feb. 26, 1946).
(3) J. L. Riebsomer, *J. Org. Chem.*, **11**, 182 (1946).
(4) D. Nightingale and J. R. Janes, THIS JOURNAL, **66**, 352 (1944).

Experimental

2-Nitro-2-methylpropyl 3,5-Dinitrobenzoate.—One gram of 2-nitro-2-methyl-1-propanol was dissolved in 3 ml. of anhydrous pyridine and 0.5 g. of 3,5-dinitrobenzoyl chloride was added to the stirred solution. The mixture was heated on the steam-bath for 15 minutes and then poured into 10 ml. of distilled water and stirred vigorously. The solid was collected on a filter and washed with 5 ml. of 5% sodium carbonate solution. It was recrystallized twice from 95% ethanol: m.p. 126–127°; N calcd., 13.42; N found, 13.39.

3-Nitro-3-methyl-2-butyl 3,5-Dinitrobenzoate.—Two milliliters of 3-nitro-3-methyl-2-butanol was added to 0.5 g. of 3,5-dinitrobenzoyl chloride contained in a dry test-tube. Dry pyridine was added dropwise to the mixture, allowing about five minutes for the addition of ten drops. The resulting mixture was heated over a steam-bath for 15 minutes. The reaction mixture was cooled to room temperature, and 10 ml. of distilled water was added with stirring. The product was collected and washed with 10 ml. of 2% sodium carbonate solution. Three recrystallizations from 50% aqueous ethanol gave a flaky product which melted sharply at 140°; N calcd., 12.48, N found, 12.79.

S-Benzylthiuronium 2-Nitro-1-propyl Sulfate.—Five drops of 2-nitro-1-propanol was added to a mixture of 5 drops of dry dioxane and 4 drops of chlorosulfonic acid. Hydrogen chloride was evolved immediately on shaking the test-tube. After standing 10 to 15 minutes the mixture was diluted with 1 ml. of water and added to 1 ml. of saturated aqueous S-benzylthiuronium chloride. After five minutes in an ice-bath the product precipitated, and was recrystallized three times from 10% ethanol and dried in a vacuum desiccator. The fine white needles melted at 114–115°. Analysis is given in Table I.

Acknowledgment.—The authors express their appreciation to The Commercial Solvents Corporation for supplies of nitroalkanes used in this work.

DEPARTMENT OF CHEMISTRY
STETSON UNIVERSITY
DELAND, FLORIDA

Some Diels–Alder Reactions of Chloroprene[1]

BY JOHN S. MEEK AND WALTER B. TRAPP

Chloroprene has been condensed with acrolein,[2] methyl vinyl ketone,[2] methyl ethynyl ketone,[2] acrylonitrile,[3] methacrylic acid[4] and methyl methacrylate.[4]

Methyl methacrylate and methacrylic acid gave mixtures which were not separated.[4] The structure of the chloroprene–methyl ethynyl ketone adduct was shown by dehydrogenation to be *p*-chloroacetophenone.[2] The structures of the remaining adducts were not proven. However, the adducts of acrylonitrile and acrolein were converted into the same acid which was believed by Petrov and Sopov to be 4-chloro-1,2,5,6-tetrahydrobenzoic acid (I) by analogy with the chloroprene–methyl ethynyl ketone adduct.

In our work, we have shown this to be correct. This same acid, 4-chloro-1,2,5,6-tetrahydrobenzoic acid, was prepared by condensing chloroprene with acrylic acid. The adduct was brominated with N-bromosuccinimide and then dehydrohalogenated with triethylamine to give *p*-chlorobenzoic acid. Compound I was also synthesized in low yield from

(1) This work was supported by the Office of Naval Research.
(2) A. A. Petrov and N. P. Sopov, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 1295 (1947).
(3) A. A. Petrov and N. P. Sopov, *ibid.*, **17**, 2228 (1947).
(4) A. A. Petrov and N. P. Sopov, *ibid.*, **18**, 1781 (1948).

4-oxocyclohexanecarboxylic acid by treatment with first phosphorus pentachloride and then potassium hydroxide. Chloroprene was condensed with methyl acrylate, ethyl acrylate, acrylyl chloride and acrylamide. Hydrolysis of these adducts in each case gave I. So far, no isomeric 3-chloro-1,2,5,6-tetrahydrobenzoic acid, or a derivative, has been isolated although the low melting point of various preparations indicated that both isomeric adducts may have been formed in some cases. In each case this indicates that the major adduct of chloroprene with a monosubstituted dienophile of the acrylic acid type was a 1,4-disubstituted cyclohexene as has been found to be the case with other 2-substituted dienes.

Attempts to condense chloroprene with anthracene and vinyl ethyl ether failed to give isolable adducts. It was hoped that with anthracene, chloroprene would act as a dienophile and the structure of the adduct would indicate which was the more reactive double bond of chloroprene.

Experimental

Starting Materials.—The authors wish to thank E. I. du Pont de Nemours and Co., Inc., for gifts of chloroprene, Rohm and Hass Co. for methyl and ethyl acrylate and acrylic acid, American Cyanamid Co. for acrylamide, Arapahoe Chemical Co. for N-bromosuccinimide and Carbide and Carbon Chemicals Co. for ethyl vinyl ether.

Acrylic Acid-Chloroprene Adduct (I).—A mixture of 35.4 g. (0.4 mole) of distilled chloroprene, 28.8 g. (0.4 mole) of glacial acrylic acid and 0.1 g. of hydroquinone was heated at 120° for 20 hours in a sealed glass tube.

The product was extracted with a 10% sodium hydroxide solution. Acidification of the extracts gave 44 g. (68%) of acid, m.p. 90–100°. Upon recrystallization from water and sublimation of a 2-g. portion of the crude adduct, 1.18 g. was recovered, m.p. 113–114° (lit. for the acid from the adduct of acrylonitrile and chloroprene, 109.5–110°[4]).

A 1.25-g. (0.0078 mole) sample of the chloroprene-acrylic acid adduct (I) was heated at reflux with 3.0 g. (0.0190 mole) of N-bromosuccinimide and 0.1 g. of benzoyl peroxide in 30 ml. of benzene for 6 hours. Upon cooling, the precipitated succinimide was removed by filtration and the solution was washed with two 20-ml. portions of 10% aqueous pyridine. After drying over sodium sulfate, the solution was heated at reflux with 17.2 g. (0.17 mole) of triethylamine for 4 hours. The mixture was allowed to cool and solid triethylammonium bromide was removed by filtration. The filtrate was subjected to partial evaporation in an air stream and acidified with 50% sulfuric acid. Solid *p*-chlorobenzoic acid precipitated and after sublimation, 0.51 g. (41%) was recovered, m.p. 219–221° (uncor.).

For further purification, 0.24 g. of this product was converted to the S-benzylthiuronium salt according to the procedure of Donleavy.[5]

The resulting complex was recrystallized from ethanol, m.p. 194.5–195.5°.

Anal. Calcd. for $C_{15}H_{15}ClN_2O_2S$: N, 8.70. Found: N, 8.48.

Upon alkaline hydrolysis of this salt, followed by drying and sublimation, 0.15 g. (26% over-all yield) of material was recovered, m.p. 241–242° (lit., 241.5°[6]). This material showed no depression of its melting point when mixed with an authentic sample of *p*-chlorobenzoic acid. The anilide of dehydrogenated I melted at 192–194° (lit., for the anilide of *p*-chlorobenzoic acid, 194°[7]).

m-Chlorobenzoic acid is reported to melt at 154.5°[8] and its anilide at 122°.[9]

(5) J. J. Donleavy, THIS JOURNAL, **58**, 1004 (1936).

(6) N. V. Sidgwick and E. K. Ewbank, *J. Chem. Soc.*, **119**, 979 (1921).

(7) O. Emmerling, *Ber.*, **8**, 880 (1875).

(8) N. V. Sidgwick, *J. Chem. Soc.*, **117**, 396 (1920).

(9) A. Hantzsch, *Ber.*, **24**, 31 (1891).

Preparation of I from 4-Oxocyclohexanecarboxylic Acid.[10]—Four-tenths of a gram (0.0028 mole) of 4-oxocyclohexanecarboxylic acid was added to 1.2 g. (0.0058 mole) of phosphorus pentachloride in 25 ml. of ether. The solution was refluxed at 31° for 2 hours and then allowed to stand for 12 hours. The ether was evaporated and the residue was made basic with 10% potassium hydroxide in order to hydrolyze the acyl chloride. This solution was then acidified with dilute sulfuric acid and extracted with ether. The ether was evaporated and the residue was sublimed *in vacuo* at 90°. Twenty-two milligrams (5%) of acid was recovered, m.p. 111–111.5°, mixed m.p. with I prepared from chloroprene and acrylic acid 111.5–112.0°.

Methyl Acrylate–Chloroprene Adduct.—Eighteen grams (0.20 mole) of chloroprene, 22 g. (0.25 mole) of methyl acrylate and 0.1 g. of hydroquinone were heated in a sealed glass tube at 125° for 44 hours. The product was distilled giving a crude yield of 23.2 g. (62%) of material (II), b.p. 106–108° (10 mm.). This was redistilled through a 40-cm. column packed with glass helices, 3 mm. i.d., to give 19.2 g. (54.5% of adduct, b.p. 65° (2 mm.), $n^{20}D$ 1.4860).

Anal. Calcd. for $C_8H_{11}ClO_2$: C, 55.02; H, 6.35; sapon. equiv., 174.6. Found: C, 54.93; H, 6.27; sapon. equiv., 175.

Petrov and Sopov had previously prepared this methyl ester from I and reported a boiling point of 117.5–118.5° (20 mm.), $n^{20}D$ 1.4878. A 5.0-g. (0.0286 mole) sample of II was placed in a glass-stoppered bottle containing 3.2 g. of potassium hydroxide dissolved in 16 ml. of ethylene glycol and 16 ml. of water. This was allowed to stand for 2 days and then heated for 5 minutes. Cooling and acidification led to 2.7 g. (65%) of acid I, m.p. 109.5–110.5°, mixed m.p. 110.5–112°. In addition, 1.65 g. of an acidic oil was obtained.

Ethyl Acrylate–Chloroprene Adduct.—Eighteen grams (0.20 mole) of chloroprene, 25 g. (0.25 mole) of ethyl acrylate and 0.1 g. of hydroquinone were heated together at 125° for 22 hours in a sealed glass tube. A 45.5% crude yield of adduct (III) was obtained, b.p. 75–90° (3 mm.). This was redistilled through the column used in distilling II to give 14 g. (37%) of adduct, b.p. 75° (2 mm.), $n^{20}D$ 1.4782.

Anal. Calcd. for $C_9H_{13}ClO_2$: C, 57.29; H, 6.94; sapon. equiv., 189. Found: C, 57.32; H, 7.04; sapon. equiv., 190.

Acidification of the saponification mixture gave 1.6 g. (100%) of acid melting at 86–94°. Recrystallization of the acid (I) from aqueous alcohol gave 1.17 g. of acid, m.p. and mixed m.p. 113–114°.

Acrylyl Chloride–Chloroprene Adduct.—Eight grams (0.091 mole) of chloroprene, 9.5 g. (0.105 mole) of acrylyl chloride and 0.1 g. of hydroquinone were heated at 110° for 19 hours in a sealed glass tube. A 39% yield of adduct (IV) was obtained by distillation, b.p. 55° (2 mm.), $n^{20}D$ 1.5122, d^{23}_4 1.2791; *MR* (calcd.) 41.99, *MR* (found) 41.60.

Anal. Calcd. for $C_7H_8Cl_2O$: C, 46.95; H, 4.50. Found: C, 46.73; H, 4.32.

Solvolysis of 1.28 g. of IV by warming with 9.6 g. of 98–100% formic acid gave after purification a 74% yield of acid (I), m.p. and mixed m.p. 113–114°.

Acrylamide–Chloroprene Adduct.—Twenty grams of 50% chloroprene–xylene solution (0.10 mole of chloroprene), 7 g. (0.10 mole) of acrylamide and 7 ml. of benzene were heated in a sealed glass tube at 110° for 24 hours. The solid product was extracted with 95% ethanol. Upon evaporation of the solvent and recrystallization of the solid from nitromethane, a 51% yield of adduct (V) was obtained, m.p. 185–188°. By recrystallization and sublimation, a final yield of 38% of V, m.p. 189.5–191° was obtained.

Anal. Calcd. for $C_7H_{10}ClNO$: N, 8.78. Found: N, 8.93.

Hydrolysis of V was carried out by heating at reflux for 45 minutes 0.20 g. of V, 3 ml. of water and 0.15 g. of sodium hydroxide. The solution was cooled, acidified and filtered. The crude yield of dried precipitate was 80%, m.p. 105–109°. This upon recrystallization from water gave a 60% yield of material (I), m.p. and mixed melting point 112.5–113.5°.

Attempted Condensations of Chloroprene with Anthracene and Ethyl Vinyl Ether.—Excess ethyl vinyl ether was heated

(10) The authors are indebted to Dr. H. E. Ungnade for a sample of this compound. For its preparation see H. E. Ungnade and F. V. Morriss, THIS JOURNAL, **70**, 1898 (1948).

with a 50% xylene solution of chloroprene in a sealed glass tube for 5 hours at 150°. The contents of the tube gradually blackened and only a viscous mass was obtained. Extraction of this material with ether, acetone and benzene failed to give any material corresponding to an adduct. Hydroquinone, du Pont "terpene B" and *t*-butylcatechol did not appear to inhibit the formation of the viscous material.

A 1.8-g. sample of anthracene, 8.4 g. of chloroprene in 50% xylene solution using "terpene B" polymerization inhibitor was heated for 24 hours at 130° in a sealed glass tube. At the end of this time the anthracene was recovered unchanged.

Acknowledgment.—The carbon hydrogen analyses were performed by the Galbraith Laboratories and the nitrogen analyses by Mrs. Patricia Ramey.

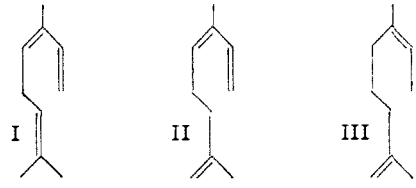
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO RECEIVED OCTOBER 1, 1951

The Structure of Ocimene

BY MAURICE D. SUTHERLAND

RECEIVED OCTOBER 9, 1951

The hydrocarbon which has been named ocimene was first isolated by van Romburgh[1] from the essential oil of *Ocimum basilicum* and has since been identified in many other essential oils. Formula II although generally accepted[2] appears to be incorrect and should be replaced by I.



Jones and Smith[3] isolated from the oil of flowering *Tagetes glandulifera* a substance closely similar in various physical and chemical properties to van Romburgh's ocimene and regarded these two substances as identical. The ocimene from this source has now been submitted to quantitative ozonolysis and found to yield 95–96% of the acetone expected on Formula I. This may be compared with acetone yields (96–97%) obtained from pure β-citronellol phenylazophenylurethan[4] prepared from β-citronellol, the infrared spectrum[5] of which indicated the presence of less than 1% of α-citronellol. As acetone in this case can result only from the isopropylidene group, the ocimene examined must be I, although the presence of a few per cent. of II is not excluded. In possessing the isopropylidene structure this sample of ocimene resembles the samples of myrcene, citronellol, geraniol, linalol and other acyclic terpenoids so far examined.[6]

(1) P. van Romburgh, *Proc. K. Acad. Wetensch. Amsterdam*, **3**, 454 (1900).

(2) (a) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. I, University Press, Cambridge, 1947, p. 19. (b) Maria Lipp in "Richter's Chemistry of the Carbon Compounds," Vol. II, edited by R. Anschutz, T. W. J. Taylor and A. F. Millidge, Elsevier, Amsterdam, 1938, p. 200. (c) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 2nd Ed., 1950, p. 1013.

(3) T. G. H. Jones and F. B. Smith, *J. Chem. Soc.*, **127**, 2530 (1925).

(4) M. D. Sutherland, THIS JOURNAL, **73**, 2385 (1951).

(5) R. Werner and M. D. Sutherland, accompanying paper.

(6) (a) Y. R. Naves, G. Brus and J. Allard, *Compt. rend.*, **200**, 1112 (1935); (b) J. Doeuvre, *Bull. soc. chim.*, [5] **3**, 613 (1936); (c) M. F. Carroll, *Perfumery and Essential Oil Record*, **38**, 226 (1947); (d) D. Barnard, *et al.*, *J. Chem. Soc.*, 915 (1950); (e) M. F. Carroll, R. G. Mason, H. W. Thompson and R. C. S. Wood, *ibid.*, 3457 (1950); (f) Y. R. Naves, *Bull. soc. chim.*, [5] **18**, 506 (1951).

The structure II for ocimene from *O. basilicum* is due to Enklaar who worked almost alone on the problem for about twenty years. Enklaar[7] at first suggested I in accordance with the 27% yield of acetone obtained from ocimene ozonide but later preferred II although the strongest evidence for this was a color reaction indicating a γ-dicarbonyl compound amongst the ozonolysis products. In 1938 Dupont and Desreux[8] after examining Raman spectra concluded that a sample of van Romburgh's ocimene was rich in I and that the dihydro ocimene obtained by sodium and alcohol reduction was free from III.

These results of Enklaar and of Dupont and Desreux show that ocimene from *O. basilicum* contains at least a substantial proportion of I. On the other hand, there is no very satisfactory evidence that II is present in any proportion and the results of Dupont and Desreux speak strongly for the absence of II. The close correspondence in physical properties between the ocimene of Eklaar and that of Jones and Smith also favors an identity in structure and an absence of II. Thus no acceptable evidence for the existence of II in essential oils has yet been put forward and the name ocimene should be reserved for the hydrocarbon of structure I first isolated from *Ocimum basilicum*.

Experimental

A sample of crude ocimene from *Tagetes glandulifera* (kindly provided by Professor T. G. H. Jones) was redistilled at 10 mm. pressure and a fraction of b.p. 63° (10 mm.), d^{25}_4 0.7947, $n^{25}D$ 1.4836 and $[\alpha]D$ +0.12° selected. The ozonolysis procedure of Kuhn and Roth[9] was modified principally by the use of 15–20 mg. samples, an ozonation period of 15 minutes at an oxygen flow rate of 20 ml. per minute, (ozone concentration 8% by weight) and a sufficient excess of $M/5$ $KMnO_4$ (20 ml.) to ensure that some remained unreduced at the end of the distillation. Under these conditions samples of ocimene yielded 94.9, 95.4 and 96.0% of the acetone calculated on formula I. Levulinic and pyruvic acids (10 mg.) processed separately resulted in iodine consumption equivalent to less than 1% of the acetone resulting from 15 mg. of ocimene.

(7) C. J. Enklaar, *Rec. trav. chim.*, **26**, 157 (1907); **27**, 422 (1908); **36**, 215 (1917); **45**, 337 (1926).

(8) G. Dupont and V. Desreux, *Bull. soc. chim.*, [5] **5**, 337 (1938).

(9) R. Kuhn and H. Roth, *Ber.*, **65**, 1285 (1932).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF QUEENSLAND,
ST. LUCIA, BRISBANE, AUSTRALIA

The Infrared Spectrum of α-Citronellol

BY R. L. WERNER AND MAURICE D. SUTHERLAND

RECEIVED NOVEMBER 1, 1951

In the published reports[1,2] of the infrared spectrum of various samples of citronellol, the absence of the bands characteristic of the isopropenyl group has been taken as proof of the virtual absence of α-citronellol, which itself has not been available for infrared examination.

The infrared spectrum of the previously de-

(1) D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

(2) M. F. Carrol, R. G. Mason, H. W. Thompson and R. C. S. Wood, *ibid.*, 3457 (1950).