the molecules of these compounds of one or more hydrogen atoms would both lower the molecular weight and raise the boiling point due to the introduction of an electric moment. This would place the compounds far above the curve.

The authors wish to acknowledge gratefully the assistance in the preparation and separation of these compounds of the following Graduate Students at the Pennsylvania State College: R. L. Bond, J. W. Ford, R. E. McArthur, D. I. Randall, T. K. Sloat, and A. C. Werner.

Summary

A continuous reaction between fluorine and carbon without explosions has been accomplished.

Compounds corresponding in molecular weight to octafluoropropane, two isomers of decafluorobutane, decafluorocyclopentane, a dodecafluorohexane, and a tetradecafluoroheptane have been isolated in addition to carbon tetrafluoride and hexafluoroethane.

The properties of these compounds have been determined. A mixture of fluorocarbons boiling from 25 to 160° has been obtained.

STATE COLLEGE, PENNA. RECEIVED NOVEMBER 2, 1938

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

The Action of *p*-Tolyl Isothiocyanate on Ethyl Acetonedicarboxylate

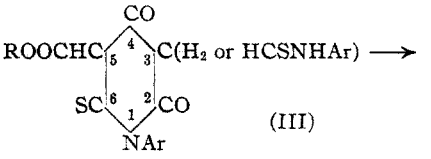
BY DAVID E. WORRALL

In connection with a study of the chemistry of isothiocyanates it seemed desirable to investigate their reactivity toward molecules containing two active methylene groups. Ethyl acetonedicarboxylate (I), a relatively common substance which contains such a system, was selected for this purpose. It quickly became apparent that this ester does not follow the pattern of substances previously studied,[1] but reacts in a highly characteristic manner.

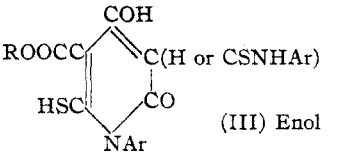
Through the sodium derivative I probably does form the expected thiotoluide, either with one or two equivalents of tolyl isothiocyanate. An additional reaction follows in which the elements of ethyl alcohol are lost. Ring closure suggests itself, particularly as the product contains a nucleus comparatively stable toward acid or alkali which remains intact through certain transformations. Sulfur is labile in the monosulfo derivative; therefore it is concluded that a piperidine ring is formed.

$$ROOCCH_2COCH(COOR)CSNHAr \longrightarrow OCCH_2COCH(COOR)CSNAr\ (II) + ROH$$

The same reaction takes place, using two equivalents of metal and isothiocyanate, although the second methylene group is converted into a thioamide producing III. Sulfur in the side chain is comparatively non-reactive. These pyridones are sufficiently acidic to decompose alkali carbonates forming salts stable toward acetic acid, thus functioning as hydroxypyridines. Because of the presence of tertiary nitrogen, isomerization is restricted to the introduction of two double bonds.



(III)



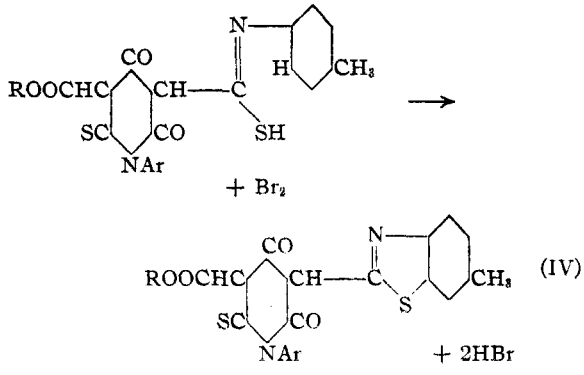
(III) Enol

II and III obviously form thio ethers with methyl iodide in alkaline solution, for the products contain inactive sulfur, whereas the parent substances readily lose this element. Hence one double linkage is located between positions 5 and 6 in the pyridine ring. Further alkylation is possible since the mono methyl ethers still are capable of forming metal derivatives. It is believed that these changes involve the shifting of hydrogen to position 4 rather than 2 which contains oxygen more completely neutralized. With dimethyl sulfate a third hydrogen, that attached to the amide nitrogen is replaced. Ethyltoluidine and a dimethylpyridine dicarboxylate, result from secondary reactions. The carbethoxy group is easily lost both with II and III.

II forms a stable bromine derivative. The methyl ether does likewise, therefore bromine is

(1) Worrall, THIS JOURNAL, 46, 2834 (1924).

present at position 3. Although III also reacts spontaneously with bromine, liberating hydrogen bromide, the product (IV) contains no bromine and a pair of hydrogen atoms are missing from the molecule. The physical but not the chemical properties have altered considerably. IV is colorless, much less soluble in the usual organic solvents, and much higher melting than III. Sulfur is more mobile, but IV is still soluble in alkali and easily alkylated. The carbethoxy group is more readily hydrolyzed. One of the missing hydrogen atoms must have come from the substituted thioamide group; the other may have originated in either the aniline or the pyridone ring. Despite the fact that a similar reaction apparently takes place with an analogous compound prepared from methyl isothiocyanate,[2] the aniline ring probably is concerned in the reaction. Hugershoff[3] has shown that benzothioazoles result from the action of bromine on arylated thioureas. Moreover, the thioamide obtained by the addition of phenyl isothiocyanate to malonic ester reacts with bromine and definite proof has been found that the product is a thiazole.[2] Therefore, thiazole formation has been assumed here, a reaction in which intermediate bromine derivatives doubtless are formed.



(IV)

Experimental

1-*p*-Tolyl-2,4-dioxo-5-carbethoxy-6-sulfopiperidine.—To 0.25 g. mole of pulverized sodium suspended in ether was added cautiously one equivalent of I. A brisk reaction ensued, following which one equivalent of *p*-tolyl isothiocyanate was dropped into the clear ether solution. The pasty precipitate that formed was dissolved eventually in water containing crushed ice and slowly poured with stirring into cold dilute hydrochloric acid. A bulky solid separated, but on standing it changed into a compact, somewhat pasty mass that was digested with a small volume of cold alcohol; yield 14.3 g. The product was crystallized twice from alcohol, separating finally in bundles of colorless narrow plates, m. p. 174–175° dec.

Anal. Calcd. for $C_{15}H_{15}NO_4S$: C, 59.1; H, 4.9. Found: C, 59.0; H, 5.2.

II is soluble in aqueous sodium carbonate and is precipitated from the alkaline solution by hydrochloric acid, but not by acetic acid. An alkaline solution of II neutralized with acetic acid produces a blue green precipitate with ferric chloride. It is gradually decomposed by long heating with glacial acetic acid, slowly evolving hydrogen sulfide, the formation of which is speeded up by the presence of phenylhydrazine. In both reactions amorphous residues are produced.

1-*p*-Tolyl-2,4-dioxo-6-sulfopiperidine.—One gram of II heated for thirty minutes under a reflux condenser with concd. alcoholic potassium hydroxide was diluted with water, filtered and added dropwise with stirring to cold water containing hydrochloric acid. A bulky amorphous precipitate formed that was filtered with difficulty, thoroughly washed, and dried at room temperature. The resulting grayish powder was used directly for analysis m. p. 158–159°, dec.

Anal. Calcd. for $C_{12}H_{11}NO_2S$: C, 61.8; H, 4.7. Found: C, 61.4; H, 4.8.

1-*p*-Tolyl-2,4-dioxo-5-carbethoxy-6-sulfomethoxypiperidine.—To 2 g. of II dissolved in warm alcohol was added an excess of methyl iodide. A crystalline precipitate almost instantly formed in excellent yield.

Anal. Calcd. for $C_{16}H_{17}NO_4S$: C, 60.2; H, 5.3. Found: C, 59.9; H, 5.5.

It separates from alcohol as slender needles, m. p. indefinite with dec. above 250°. No hydrogen sulfide is liberated on heating with glacial acetic acid either alone or with phenylhydrazine, but the substance retains the property of dissolving in sodium carbonate solution. It forms a sparingly soluble salt with sodium hydroxide which can be recrystallized from a small volume of water. An analysis indicated the presence of one equivalent of sodium.

1-*p*-Tolyl-2,4-dioxo-3-bromo-5-carbethoxy-6-sulfopiperidine.—A small portion of II was brominated in glacial acetic acid, heated for a few minutes on a water-bath and recrystallized from alcohol, separating as tiny pale yellow needles, m. p. 238–239°, dec.

Anal. Calcd. for $C_{15}H_{14}BrNO_4S$: C, 46.9; H, 3.6; Br, 20.8. Found: C, 46.9; H, 3.4; Br, 20.9.

It still is soluble in sodium carbonate solution and reprecipitated unchanged by acid.

1-*p*-Tolyl-2,4-dioxo-3-bromo-5-carbethoxy-6-sulfomethoxypiperidine.—After bromination of the methyl ether of II the product obtained by pouring the mixture into water was recrystallized twice from a small volume of alcohol. Long colorless needles appeared which apparently contained alcohol of crystallization, as on drying at 100° a powder resulted; m. p. 165.5–166.5°.

Anal. Calcd. for $C_{16}H_{16}BrNO_4S$: Br, 20.1. Found: Br, 20.0.

1-*p*-Tolyl-2-oxo-4-methoxy-5-carbethoxy-6-sulfomethoxypiperidine.—A portion of II dissolved in sodium hydroxide solution was shaken with dimethyl sulfate. The

(2) Unpublished results.

(3) Hugershoff, *Ber.*, **36**, 3121 (1903).

product, insoluble in the alkaline solution, was crystallized from dilute alcohol, separating as slender silky needles, m. p. 166°.

Anal. Calcd. for $C_{17}H_{15}NO_4S$: C, 61.3; H, 5.7. Found: C, 61.1; H, 5.9.

This dimethyl derivative is not only insoluble in both aqueous sodium carbonate and sodium hydroxide but does not react with bromine.

1-*p*-Tolyl-2,4-dioxo-5-carbethoxy-6-sulfopiperidine-3-thioformo-*p*-toluide.—Using the customary technique, 0.1 g. mole of I was converted into the metal derivative with two equivalents of sodium. The second equivalent reacted slowly and incompletely even on the application of heat. The clear solution after several hours was poured from unchanged sodium into another flask containing two equivalents of tolyl isothiocyanate. A bulky solid separated after a time from the new mixture. The next morning the entire batch was mixed with ice water, the aqueous layer separated and run carefully with stirring into cold, well-diluted hydrochloric acid. The resulting flocculent precipitate coagulated on standing into a somewhat pasty ball-like mass. It was filtered and thoroughly washed with warm alcohol, yield 18 g.

Anal. Calcd. for $C_{23}H_{22}N_2O_4S_2$: C, 60.8; H, 4.9. Found: C, 61.0; H, 5.0.

III is practically insoluble in alcohol, but dissolves readily in benzene, separating from a mixture of these solvents as shining yellow needles, m. p. 182–184°, dec. It is easily dissolved by alkaline solutions, including concd. ammonia, from which the ammonium salt separates in a few minutes. No reaction takes place with hydroxylamine beyond partial hydrolysis of the ester group. Slow evolution of hydrogen sulfide occurs on long heating with glacial acetic acid. The substance is unchanged on long standing with dilute sodium hydroxide solution. Although unaffected by concd. hydrochloric acid, it is dissolved by cold concd. sulfuric acid, the solution acquiring a blue fluorescence on warming.

1-*p*-Tolyl-2,4-dioxo-6-sulfopiperidine-3-thioformo-*p*-toluide.—A solution containing 2 g. of III dissolved in concd. alcoholic potash was heated for an hour under a reflux condenser, diluted with water and carefully mixed with an excess of acid. The product separated from a large volume of alcohol as lustrous pale yellow irregular plates, m. p. 205–208°, dec.

Anal. Calcd. for $C_{20}H_{18}N_2O_5S_2$: C, 62.8; H, 4.7. Found: C, 62.6; H, 5.0.

It is less soluble than the parent substance in benzene, but more so in alcohol. It is soluble in sodium carbonate solution and reacts with bromine.

1-*p*-Tolyl-2,4-dioxo-5-carbethoxy-6-sulfomethoxypiperidine-3-thioformo-*p*-toluide.—On heating under a reflux condenser 5 g. of III suspended in alcohol containing methyl iodide, the solid rapidly disappeared. An excellent yield of bright yellow needles formed on cooling, m. p. 151–152°.

Anal. Calcd. for $C_{24}H_{24}N_2O_4S_2$: C, 61.5; H, 5.1. Found: C, 61.3; H, 5.1.

The methyl ether slowly dissolved by sodium carbonate solution is precipitated unchanged by acetic as well as by hydrochloric acid. It is readily dissolved by warm alcohol. No hydrogen sulfide is liberated on heating with glacial acetic acid either alone or with phenylhydrazine.

1-*p*-Tolyl-2,4-dioxo-5-carboxy-6-sulfomethoxypiperidine-3-thioformo-*p*-toluide.—A small portion of the monomethyl ether heated for an hour under a reflux condenser with concd. alcoholic potash was isolated in the usual manner. It crystallized from glacial acetic acid in the form of glittering yellow plates, m. p. 232–233° dec.

Anal. Calcd. for $C_{22}H_{20}N_2O_4S_2$: C, 60.0; H, 4.5. Found: C, 60.2; H, 4.6.

Hydrolysis but not decarboxylation took place.

1-*p*-Tolyl-2-oxo-4-methoxy-6-sulfomethoxypiperidine-3-thioformo-*p*-toluide.—The sodium derivative of the monomethyl ether of III was prepared using dilute sodium hydroxide and recrystallizing the colorless needles from a small volume of water. It was then heated to 100° in a sealed tube with alcohol containing methyl iodide for nearly two hours. On pouring the contents after cooling into water, an oil separated. This product dissolved in a small volume of warm alcohol formed tiny snow-white crystals, m. p. 153°.

Anal. Calcd. for $C_{22}H_{22}N_2O_5S_2$: C, 64.4; H, 5.4. Found: C, 64.1; H, 5.3.

It is insoluble in sodium hydroxide solution, and does not react with bromine.

1-*p*-Tolyl-2-oxo-4-methoxy-6-sulfomethoxypiperidine-3,5-dicarboxylate.—A suspension prepared by dissolving 4 g. of III in 150 ml. of warm dilute sodium hydroxide solution and then cooling was shaken with a few ml. of dimethyl sulfate. The sodium salt rapidly disappeared to be replaced by a precipitate that became increasingly pasty. Simultaneously a strong amine-like odor became noticeable. The product, heated on a water-bath for several hours, hardened into a crystalline mass that was repeatedly recrystallized from alcohol. Finally clusters of tiny colorless plates separated, m. p. 177–178°.

Anal. Calcd. for $C_{16}H_{15}NO_6S$: C, 55.0; H, 4.6. Found: C, 55.2; H, 4.7.

A qualitative test revealed the presence of sulfur. While insoluble in aqueous sodium hydroxide the substance is very soluble in alcoholic alkali, remaining in solution on mixing with a large volume of water. It is promptly precipitated from these solutions by acid. The original filtrate contained monomethyl-*p*-toluide, which was isolated by steam distillation from an alkaline mixture. The resulting oil dissolved in acid and formed a nitroso derivative with nitrous acid.

1-(1-*p*-Tolyl-2,4-dioxo-5-carbethoxy-6-sulfopiperidyl)-5-methyl-benzothiazole.—A molar equivalent of bromine was added to 5 g. of III suspended in a small volume of glacial acetic acid. The mixture, which immediately began to yield hydrogen bromide, was heated for an hour on a water-bath. The mustard colored product, practically insoluble in the common organic solvents, was thoroughly washed with warm alcohol; yield 4.3 g. By beating under a reflux condenser with glacial acetic acid, most of the color could be removed.

Anal. Calcd. for $C_{23}H_{20}N_2O_4S_2$: C, 61.1; H, 4.4. Found: C, 61.0; H, 4.3.

IV may be recrystallized in small quantities from nitrobenzene, or better still, aniline, as tiny feathery needles

m. p. above 300°. It is easily dissolved by ammonium hydroxide or concd. sulfuric acid, producing on warming with the latter a bluish fluorescence. Hydrogen sulfide is set free rapidly on heating the substance suspended in glacial acetic acid with phenylhydrazine.

1 - (*p* - Tolyl - 2,4 - dioxo - 5 - carboxy - 6 - sulfopiperidyl)-5-methylbenzothiazole.—IV dissolved quickly in cold ammonium hydroxide, a solution which was slowly run into a large volume of water containing an excess of hydrochloric acid. A bright yellow gelatinous precipitate formed. It was filtered with difficulty, washed thoroughly and dried at room temperature. The color darkened considerably, m. p. 260–261° with dec. and foaming.

Anal. Calcd. for $C_{21}H_{16}N_2O_4S_2$: C, 59.4; H, 3.8. Found: C, 59.4; H, 3.7.

The new substance is soluble in sodium carbonate solution.

1 - (*p* - Tolyl - 2,4 - dioxo - 5 - carbethoxy - 6 - sulfomethoxypiperidyl) - 5 - methylbenzothiazole.—On shaking an ammonia solution of IV with alcohol containing methyl iodide a precipitate quickly formed. The mixture, concentrated to a small volume by distillation, gave a quantitative yield of the product which was recrystallized from a large volume of alcohol. Pale yellow needles separated, m. p. 282–283°, dec.

Anal. Calcd. for $C_{24}H_{22}N_2O_4S_2$: C, 61.8; H, 4.7. Found: C, 61.7; H, 4.8.

The methyl derivative does not react with bromine or phenylhydrazine. On destructive distillation the gases blacken lead acetate paper and have a strong pyridine odor. It still is soluble in ammonia, but this is due to hydrolysis of the carbethoxy group, as an analysis of the product indicated. The product was isolated by precipitation with acid as a semi-gelatinous solid which did not discolor on standing, m. p. 260–261°, dec. The same substance was obtained by the action of concd. nitric acid or warm sulfuric acid.

Summary

It has been shown that ethyl acetonedicarboxylate reacts with one or two equivalents of *p*-tolyl isothiocyanate forming pyridones, which are soluble in alkali and are readily alkylated. An oxypiperidyl benzothiazole apparently results from the action of bromine on the pyridone containing a thioamide group.

MEDFORD, MASS. RECEIVED JULY 11, 1939

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Aromatic Amines and 3-Nitro-6-bromonitrostyrene

BY DAVID E. WORRALL AND JACK FINKEL

It has been shown previously[1] that while the additive capacity of nitrostyrene toward the so-called organic bases is comparatively weak and even more so as a rule when substituents are introduced, the nitration of 2-chloronitrostyrene produced an unsaturated compound in which this reactivity is somewhat strengthened. As we wished to determine whether its effect were general, the corresponding bromostyrene has been prepared. The two substances have almost identical chemical properties.

Experimental

α-Nitro-β-(2-bromophenyl)-ethylene (I).—This compound was obtained by the action of triethylamine[2] on bromobenzaldehyde[3] and nitromethane at 25 to 30°; yield, after steam distillation, approx. 60%. It crystallized from ligroin in bundles of yellow needles, m. p. 84°.

Anal. Calcd. for $C_8H_6BrNO_2$: C, 42.1; H, 2.6. Found: C, 42.1; H, 2.8.

α-Nitro-β-(6-bromo-3-nitrophenyl)-ethylene (II).—The product from the nitration of I, using fuming nitric acid, separated from alcohol as small pale yellow needles, m. p. 144–145°.

Anal. Calcd. for $C_8H_5BrN_2O_4$: C, 35.2; H, 1.8. Found: C, 35.1; H, 2.1.

A small portion on oxidation with potassium permanganate produced a substance that crystallized from water as long needles, m. p. 178–179°. It did not depress the melting point of an authentic sample of 6-bromo-3-nitrobenzoic acid prepared from *m*-nitrotoluene, thus indicating that the nitro group is para to the halogen.[4]

α-Bromo - α - nitro - β - (6 - bromo - 3 - nitrophenyl) - ethylene (III).—Five grams of II after bromination was mixed with warm alcoholic potassium acetate. The product crystallized from alcohol in yellow needles, m. p. 146–147°.

Anal. Calcd. for $C_8H_4Br_2N_2O_4$: C, 27.3; H, 1.1. Found: C, 27.6; H, 1.3.

The corresponding chlorine derivative was obtained as yellow needles, m. p. 140–141°.

N,N'-(α,α'-Di-(2-bromophenyl)-β,β'-dinitrodiethyl)-*p*-phenylenediamine.—A small portion of I dissolved in hot alcohol was mixed with one-half the equivalent amount of the base. The yellow crystals were washed with warm alcohol, m. p. 146–147°.

(1) Worrall, THIS JOURNAL, **60**, 2845 (1938).
(2) Worrall, *ibid.*, **56**, 1556 (1934).
(3) Adams and Vollweiler, *ibid.*, **40**, 1737 (1918).

(4) Since the corresponding chlorine derivative must contain a similar arrangement of groups, the name previously assigned to it (ref. 1) is incorrect. The substance should be listed as 3-nitro-6-chloronitrostyrene and corresponding changes made in the names of the addition products.