8-107 SR CROSS REFERENCE SEARCH ROOM
FIP8309 XR 3,101,333

United States Patent Office 3,101,333
Patented Aug. 20, 1963



# 3,101,333
# STILBYL-ACENAPHTHENOTRIAZOLE BRIGHTENERS

Dennis Arthur William Adams, Leeds, and Asim Kumar Sarkar, Adel, England, assignors to Hickson & Welch Limited, Castleford, England, a British company

No Drawing. Filed Aug. 4, 1960, Ser. No. 47,399
Claims priority, application Great Britain Oct. 9, 1956
4 Claims. (Cl. 260—240)

This invention is concerned with improvements in or relating to optical whitening agents and is particularly concerned with certain new compounds of use as optical whitening agents. This application is a continuation-in-part of our application Serial No. 688,427, filed October 7, 1957, and now abandoned.

Optical whitening agents have in recent years found extensive use in the treatment of textiles particularly during washing and are designed to counteract the yellow or off-white colour which white textiles, particularly cellulosic textiles, may possess, especially after repeated washing. Such optical whitening agents also tend to improve coloured textiles as they impart a general brightness to them. They are also widely used to impart whiteness to other cellulosic material, particularly paper.

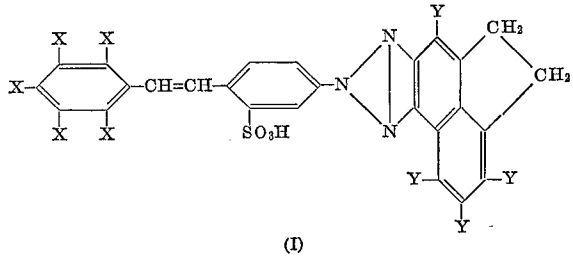
Optical whitening agents in general absorb light in the ultra-violet range of the spectrum and emit in the visible spectrum, usually in the bluish-green to bluish-violet. Thus, the fluorescence of such compounds in white material tends to counteract any yellowing as, for example that resulting upon repeated washing of a white cotton, linen or polyamide textile. The compounds used as optical whitening agents must be substantive to the material being treated, and must be substantially stable when "dyed" on the material being treated.

In general best results are obtained with optical whitening agents which give a shade of fluorescence which is complementary to that of the aged fibre, so that the colours will cancel out each other. Since, in general, the most common off-white shade of textiles resulting from aging or repeated washing is yellow, the most desirable optical whitening agent is one that fluoresces blue.

It is also of importance that the optical whitening agent should not be destroyed or removed by bleaching agents; that is, it should be bleach-fast. Thus, fluorescent optical whitening agents are generally incorporated into soaps and synthetic detergents, which are marketed for household use and articles washed therewith are often subjected to bleaching with various bleaching agents, for example sodium hypochlorite. It is therefore desirable that the optical whitening agents already on the fibre or in the treating solution should be affected as little as possible by the action of any bleaching agent which may be present.

It is an object of the present invention to provide optical whitening agents having improved properties in the foregoing respects.

We have now found that certain new compounds represented by the general formula:



(I)

in which X and Y are each a member selected from the group consisting of hydrogen, halogen, lower alkyl, lower alkoxy and sulphonic acid groups, as well as water soluble salts thereof, in particular the alkali metal, ammonium and amine salts, can be used with advantage as optical whitening agents in that they possess favourable properties from the point of view of the above-mentioned desiderata for the ideal optical whitening agents.



Accordingly the invention comprises such compounds together with water-soluble salts thereof in particular alkali metal, e.g. sodium or potassium, ammonium and amine salts.

The term "water soluble salts" is used in the sense in which it is commonly employed in the art relating to optical whitening agents that is to mean those salts which have a sufficient solubility in water to make possible their application from aqueous media onto material being treated. As is known, optical whitening agents of the stilbyl-triazole type have in general a comparatively low solubility in water, but it is usual to classify those compounds in this art which can be applied from aqueous media as water-soluble. This is, in general, because optical whitening agents are normally applied at very low concentrations so that even a compound which has a very low absolute solubility may well, for the purpose of its use as an optical whitening agent, be classified as water-soluble.

The compounds of the present invention show a good affinity for cellulosic material and exhibit a blue fluorescence, giving to the fibre a particularly pleasant hue. They also have a good affinity for various polyamide fibres. They show in general good resistance to bleaching agents and have good "build-up" qualities; that is—due to well-balanced substantivity—on repeated treatments with a bath of the same concentration the whiteness of the fabric being treated continually increases up to a maximum, which maximum does not in general cause unpleasant visible colour or hue, as is often the case. The amine salts show excellent substantivity to cellulosic fibres such as cotton under neutral conditions and thus are particularly suitable for application to such fibres from neutral treating solutions. The alkanolamine salts also show a particularly good dispersibility.

The compounds according to the present invention can with advantage be incorporated in compositions normally used for the treatment of textiles, for example detergents and soaps in solid or liquid form. They may also be incorporated in baths for the treatment of cellulosic or polyamide materials during their production or for treatment of finished textile articles. In addition, the new compounds may also be incorporated in compositions for the treatment of paper and photographic paper where high whiteness is necessary.

There is provided therefore according to a feature of the invention a composition adapted for the treatment of textile material, in particular cellulosic and polyamide materials composing one or more compounds of the general formula I above or water soluble, in particular alkali metal, ammonium and amine salts thereof. The invention also includes cellulosic and other textile materials when treated with the above compositions, in particular cotton or linen textiles, and nylon.

Preferred amine salts of the compounds of the general formula I include those formed with primary, secondary and tertiary alkylamines and primary, secondary and tertiary alkanolamines, in particular those formed with lower alkylamines (primary, secondary and tertiary) and those formed with lower alkanolamines (primary, secondary and tertiary). Representative amines within these classes include the following:

| | |
|---|---|
| Ethylamine | Ethanolamine |
| Diethylamine | Diethanolamine |
| Triethylamine | Triethanolamine |
| n-Propylamine | n-Propanolamine |
| Di-n-propylamine | Di-n-propanolamine |
| Tri-n-propylamine | Tri-n-propanolamine |

Illustrative preferred new compounds according to the invention include the following compounds together with their alkali metal, ammonium, alkylamine and alkanolamine salts,

2-(4''-styryl - 3'' - sulphophenyl)(acenaphtheno - 6':7'-4:5)-1:2:3-triazole.

2-(4''-(4'''-methoxy styryl) - 3'' - sulphophenyl)(acenaphtheno-6':7'-4:5)-1:2:3-triazole.

2-(4''-styryl-3''-sulphophenyl)(3' - sulpho - acenaphtheno-6':7'-4:5)-1:2:3-triazole.

2-(4''-styryl-3''-sulphophenyl)(5' - chloro - acenaphtheno-6'7'-4:5)-1:2:3-triazole.

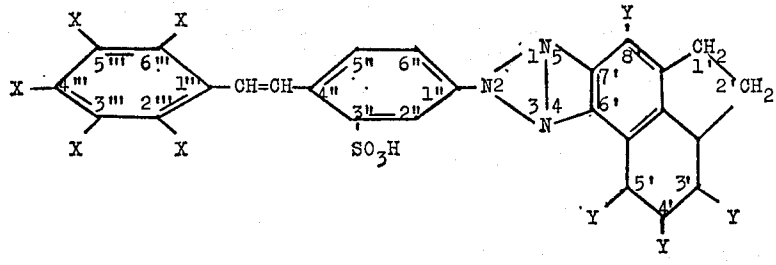
2-(4''-(4'''-chlorostyryl) - 3'' - sulphophenyl)(acenaphtheno-6':7'-4:5)-1:2:3-triazole.

2 - (4'' - (2'' - chlorostyryl - 3'' - sulphophenyl)(acenaphtheno-6':7'-4:5)-1:2:3-triazole.

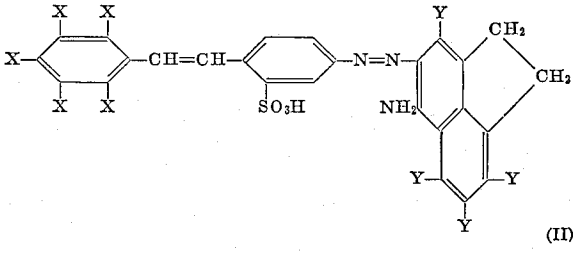
2-(4''-(2'''-sulphostyryl) - 3'' - sulphophenyl)(acenaphtheno-6':7'-4:5)-1:2:3-triazole.

A particularly preferred new compound is 2-(4''-styryl - 3'' - sulphophenyl)(acenaphtheno - 6':7' - 4:5)-1:2:3-triazole.

In the above compounds the nomenclature adopted is based on the numbering shown below:



The new compounds of the general Formula I according to the invention can conveniently be prepared by oxidising an o-amino azo dye of Formula II given below, and according to a further feature of the invention therefore there is provided a process for the preparation of the compounds of the general Formula I above by oxidising an o-amino azo dye of the general formula

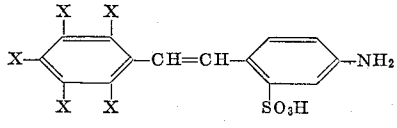


(II)

(where X and Y have the above-stated meanings).

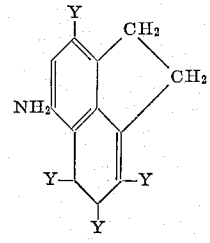
Mild oxidising agents are preferred for effecting the above reaction such as an alkali-metal hypochlorite, for example sodium hypochlorite; cuprammonium sulphate or copper sulphate in the form of a soluble complex with pyridine as well as thionyl chloride and sulphuryl chloride may also be used. The oxidation is preferably effected at elevated temperature.

The o-amino azo dye above-mentioned may be prepared in any convenient manner, such as, for example, by diazotizing a compound of the formula:



(where X has the above-stated meaning), and coupling the resultant diazotized compound with a compound of the formula:





where Y has the above stated meaning. The intermediate compound may if desired be isolated before being coupled.

The water soluble salts according to the invention may be prepared in general by the reaction of the parent acid with an appropriate base. In the case of the alkali-metal salts these may conveniently be prepared by using, as starting material, an alkali-metal salt of the stilbene sulphonic acid for diazotization and coupling with the aminoacenaphthene moiety, the stilbyl triazole product, after oxidation of the o-amino azo dye being then isolated in the form of its alkali metal salt. Alternatively one may react the free acid with an alkali-metal hydroxide, or carbonate thereby obtaining the alkali metal salt. The ammonium salt may be prepared in an analogous manner.

The amine salts can conveniently be prepared by direct reaction of the free acid with the amine for example by dissolving the acid in an excess of the amine, the reaction if desired being carried out at an elevated temperature. Isolation of the reaction product may be effected in any convenient manner.

In order that the invention may be more fully understood that the following examples are given by way of illustration only:

## EXAMPLE 1

*2-(4''-Styryl-3''-Sulphophenyl)(Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

A solution of 16.32 parts of the sodium salt of 4-aminostilbene-2-sulphonic acid (91% pure) and 3.45 parts of sodium nitrite in 150 parts water is indirectly diazotized at 8–10° C. with 20 parts of concentrated hydrochloric acid. The diazo compound is isolated, suspended in aqueous alcohol and mixed with a solution of 10.3 gms. of 5-amino-acenaphthene hydrochloride in acidified aqueous alcohol. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is complete the o-amino azo dyestuff obtained is filtered off at 25–30° C.

The o-amino azo dyestuff is dissolved in aqueous alcohol and refluxed with an excess of diethanolamine and copper sulphate (20 gms.). On completion of the oxidation the desired product is obtained by acidification of the hot filtrate. The compound is slurried with aqueous alcohol, made alkaline and treated with sodium hydrosulphite for a few hours at 90–100° C. to remove the last traces of coloured impurities. Finally the compound is crystallised from aqueous alcohol.

The compound so obtained is a brownish yellow pow-

der which in dilute solution gives vivid blue fluorescence and when a piece of cotton is washed in a detergent solution containing a small amount of this compound the material acquires a much whiter appearance than before treatment. The compound as the sodium salt has λ max. 370 mμ.

The compound may also be prepared as follows:

A solution of 16.32 parts of sodium salt of 4-aminostilbene-2-sulphonic acid (91% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotized at 8–10° C. with 20 parts concentrated hydrochloric acid. The diazo compound is isolated, suspended in water and mixed with a solution of 10.3 parts of 5-amino-acenaphthene hydrochloride in dilute hydrochloric acid. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is completed the o-amino azo dyestuff obtained is filtered off at 25–30° C.

The o-amino azo dyestuff is dissolved in butanol and refluxed with an excess of ammonia and 20 parts of copper sulphate.

On completion of the oxidation the product is obtained by acidification of the hot solution. The compound is recrystallised from aqueous pyridine. In the form of the sodium salt it has λ max. 370 mμ.

## EXAMPLE 2

*2-(4''-(4'''-Methoxy Styryl)-3''-Sulphophenyl)(Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

A solution of 16.68 parts of the sodium salt of 4'-methoxy-4-aminostilbene-2-sulphonic acid (98% pure) and 3.45 parts of sodium nitrite in 150 parts of water is directly diazotized at 8–10° C. with 20 parts of concentrated hydrochloric acid. The diazo compound is isolated, suspended in water and mixed with a solution of 5-aminoacenaphthene hydrochloride in dilute hydrochloric acid. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is complete the o-amino azo dyestuff obtained is filtered off at 25–30° C. The o-amino azo dyestuff is dissolved in aqueous pyridine and refluxed with an excess of ammonia and 20 parts of copper sulphate. On completion of the oxidation the product is obtained by acidification of the hot solution. The compound is recrystallised from aqueous pyridine. In the form of the sodium salt it has λ max. 375 mμ.

## EXAMPLE 3

*2-(4''-Styryl-3''-Sulphophenyl)(3'-Sulphoacenaphtheno-6':7'-4:5)-1:2:3-Triazole*

A solution of 16.32 parts of the sodium salt of 4-aminostilbene-2-sulphonic acid (91% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotized at 8–10° C. with 20 parts concentrated hydrochloric acid. The diazo compound is isolated, suspended in water and mixed with a solution of 14.73 parts of sodium salt of 5-amino-acenaphthene-8-sulphonic acid in water. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is complete the o-amino azo dyestuff obtained is filtered off at 25–30° C.

The o-amino azo dyestuff is dissolved in water and refluxed with excess of ammonia and 20 parts of copper sulphate.

On completion of the oxidation the product is obtained by acidification of the hot solution. The compound is recrystallised from aqueous pyridine. The sodium salt has λ max. 370 mμ.

## EXAMPLE 4

*2-(4''-Styryl-3''-Sulphophenyl)(5'-Chloro-Acenaphtheno-6':7-4:5)-1:2:3-Triazole*

A solution of 16.32 parts of the sodium salt of 4-aminostilbene-2-sulphonic acid (91% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotized at 8–10° C. with 20 parts of concentrated hydrochloric acid. The diazo compound is isolated, suspended in water and mixed with a solution of 13.79 parts 6-chloro-5-aminoacenaphthene hydrochloride in dilute hydrochloric acid. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is completed the o-amino azo dyestuff obtained is filtered off at 25–30° C.

The o-amino azo dyestuff is dissolved in pyridine and refluxed with an excess of ammonia and 20 parts of copper sulphate.

On completion of the oxidation the product is obtained by acidification of the hot solution. The compound is recrystallised from aqueous pyridine. The sodium salt has λ max. 372 mμ.

## EXAMPLE 5

*2-(4'''-Chlorostyryl-3''-Sulphophenyl)(Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

A solution of 18.41 parts of the sodium salt of 4' - chloro - 4 - aminostilbene - 2 - sulphonic acid (90% pure) and 3.45 parts of sodium nitrite in 150 parts water is indirectly diazotized at 8–10° C. with 20 parts concentrated hydrochloric acid. The diazo compound is isolated, suspended in water and mixed with a solution of 10.3 parts of 5-aminoacenaphthene hydrochloride in dilute hydrochloric acid. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is complete the o-amino azo dyestuff obtained is filtered off at 25–30° C.

The o-amino azo dyestuff is dissolved in pyridine and refluxed with an excess of ammonia and 20 parts of copper sulphate. On completion of the oxidation the product is obtained by acidification of the hot solution. The compound is recrystallised from aqueous pyridine. The sodium salt has λ max. 371 mμ.

## EXAMPLE 6

*2-(4''-(2'''-Chlorostyryl)-3''-Sulphophenyl)(Acenaphtheno-6':7'-4:5)1:2:3-Triazole*

This is prepared as in Example 5 replacing 4'-chloro-4-aminostilbene-2-sulphonic acid by 2'-chloro-4-aminostilbene-2-sulphonic acid. The sodium salt has λ max. 370 mμ.

## EXAMPLE 7

*2-(4''(-2'''Sulphostyryl)-3''-Sulphophenyl)(Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

A solution of 28.1 parts of the sodium salt of 4-aminostilbene-2:2'-disulphonic acid (71% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotized at 8–10° C. with 20 parts of concentrated hydrochloric acid. The diazo compound is isolated, suspended in water and mixed with a solution of 10.3 parts of 5-aminoacenaphthene hydrochloride in dilute acetic acid. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When the coupling is complete the o-amino azo dyestuff obtained is filtered off at 25–30° C.

The o-amino azo dyestuff is dissolved in dilute sodium hydroxide solution and refluxed with an excess of ammonia and 20 parts copper sulphate. On completion of the oxidation the product is obtained by acidification of the hot solution.

The compound is obtained by recrystallising from aqueous alcohol. The sodium salt has λ max. 370 mμ.

## EXAMPLE 8

A piece of aged white poplin (slightly yellow) was washed with a detergent solution containing 0.05 g. per litre of the compound obtained in Example 1. After rinsing and drying the cloth showed a brilliant white appearance.

EXAMPLE 9

Cotton or nylon is washed at 80° C. at a goods/liquor ratio of 1:40 in a bath containing a 3% solution of a washing product of the following composition, 29.0% dodecyl benzene sulphonate, 20.95% sodium sulphate, 25.0% sodium metasilicate pentahydrate, 25.0% tetra sodium pyrophosphate, and 0.05% of the product of Example 1. The material is then rinsed in plain water and dried. The material so treated has a much whiter appearance than when washed with a washing preparation not containing the product of Example 1.

EXAMPLE 10

*Monoethanolamine Salt of 2-(4''-Styryl-3-Sulphophenyl) (Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

10 gms. of 2 - (4'' - styryl - 3 - sulphophenyl) (acephtheno-6':7'-4:5)-1:2:3-triazole, are dissolved in 50 gms. of monoethanolamine by heating to 120°. The solution is cooled and then added to 600 ccs. of water with stirring.

The precipitated monoethanolamine salt is filtered and washed with hot water. The compound on drying has a decomposition point of 298° C.

EXAMPLE 11

*Diethylamine Salt of 2-(4''-Styryl-3-Sulphophenyl) (Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

10 gms. of 2 - (4'' - styryl - 3 - sulphophenyl) (acenaphtheno-6':7'-4:5)-1:2:3-triazole, are dissolved in 100 gms. of diethylamine and then in 250 ccs. of 80% aqueous dioxan, in the manner of Example 10.

The solution is cooled, diluted with water and filtered. The residue is re-slurried in 90% alcohol, filtered and washed with hot water. The diethylamine salt on drying has a decomposition point of 250° C.

EXAMPLE 12

*Triethanolamine Salt of 2-(4''-Styryl-3-Sulphophenyl) (Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

10 gms. of 2 - (4'' - styryl - 3 - sulphophenyl) (acenaphtheno-6':7'-4:5)-1:2:3-triazole, are dissolved in 100 gms. of triethanolamine and a little water by warming. The solution is cooled, drowned in water and the precipitate filtered. The precipitate is re-crystallised from 95% alcohol. The decomposition point of the triethanolamine salt is 200–203° C.

EXAMPLE 13

*Morpholine Salt of 2-(4''-Styryl-3-Sulphophenyl) (Acenaphtheno-6':7'-4:5)-1:2:3-Triazole*

10 gms. of 2-(4''-styryl-3-sulphophenyl) (acenaphtheno-6':7'-4:5)-1:2:3-triazole are dissolved in 200 gms. of morpholine and a little water by warming. The solution is drowned in water as before. The precipitate is filtered and re-slurried with hot 90% alcohol. The slurry is filtered and the solid dried in the usual manner. The decomposition point of morpholine salt is 293–6° C.

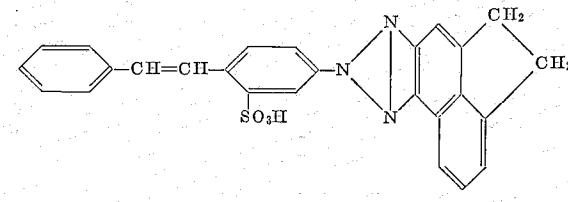
It will be appreciated that although only compounds in which the groups X and Y are hydrogen, chloro, methoxy and sulphonic acid groups have been exemplified in the foregoing examples, the nature of these groups is not restricted thereby. Thus, for example it will be clear to those skilled in the art that the groups X and Y can be other halogen or lower alkoxy groups or lower alkyl groups and need not necessarily be restricted to the groups specified in the examples. Other possibilities for the groups X and Y will be further apparent to those skilled in the art.



We claim:

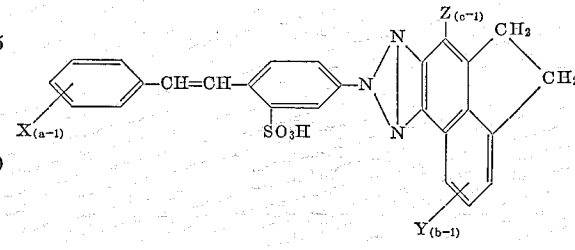
1. 2 - (4'' - styryl - 3'' - sulphophenyl) (acenaphtheno-6':7'-4:5)-1:2:3-triazole.

2. A compound selected from the group consisting of (1) a compound of the formula



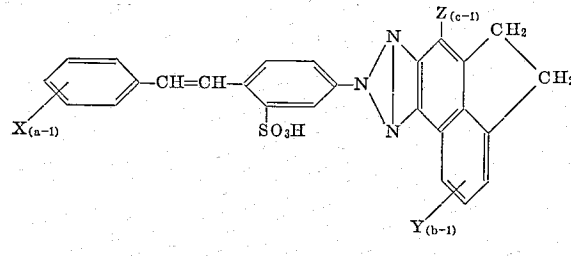
and (2) a water-soluble salt of said compound selected from the group consisting of alkali metal, ammonium, lower alkylamine and lower alkanolamine salts.

3. A compound selected from the group consisting of (1) a compound of the formula



in which X, Y and Z are each halogen, *a* is an integer from 1 to 5, *b* is an integer from 1 to 4 and *c* is an integer from 1 to 2, at least one of said integers being at least 2, and (2) a water-soluble salt of said compound selected from the group consisting of alkali metal, ammonium, lower alkylamine and lower alkanolamine salts.

4. A compound selected from the group consisting of (1) a compound of the formula



in which X, Y and Z are each lower alkyl, *a* is an integer from 1 to 5, *b* is an integer from 1 to 4 and *c* is an integer from 1 to 2, at least one of said integers being at least 2, and (2) a water-soluble salt of said compound selected from the group consisting of alkali metal, ammonium, lower alkylamine and lower alkanolamine salts.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,784,183 | Keller et al. | Mar. 5, 1957 |
| 2,784,184 | Zweidler et al. | Mar. 5, 1957 |
| 2,972,611 | Zweidler et al. | Feb. 21, 1961 |

OTHER REFERENCES

Charrier et al.: Gazz. Chim. Ital., volume 55, pages 745 to 754 (1925).

Beilstein's Handbuch der Org. Chem., volume 26, 4th edition EII (System No. 3812), pages 47–48 (1954).