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A NEW METHOD FOR THE SYNTHESIS OF TWO-EQUIVALENT COUPLERS IN COLOUR PHOTOGRAPHY

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Dedicated to Professor Matthias Pailer, formerly University of Vienna, on the occasion of his 85th birthday

Suitable sulfanes prepared from photographic colour couplers of the 1-naphthol, pyrazolo[5,1-*c*](1,2,4)triazole and 3-anilinopyrazol-5-one classes have been transformed into heteroatom-substituted transient sulfur(IV) species capable of arylating a triazolate or carboxylate ligand or an added 1*H*-triazole via ligand exchange and a subsequent process closely related to ligand coupling. This new reaction may be named *Sulfurane Contraction* and there is evidence for *thiophilic control* of the key steps involved. The syntheses are carried out preferably at about 0°C and provide access to photographic two-equivalent colour couplers which are inaccessible by known methods.

Key words: Colour photography, ligand coupling, sulfurane contraction, sulfuranes, sulfonium ylides, 1,2,3-triazoles, 4-triazolyl-1-hydroxy-2-naphthoic anilides, two-equivalent couplers.

CONTENTS

1. THE PHOTOGRAPHIC PROBLEM

Colour photography based on subtractive colour mixing has undergone major developments since its beginning in 1935. This particular branch of industrial research has, of course, produced a large variety of organic compounds useful for controlling the photographic process taking place on the silver halide microcrystals of photographic emulsions and also the related colour forming processes of *chromogenic development* and subsequent processing steps.

Sulfur as a constituent of organic additives in colour photographic materials or processes has proved highly valuable for influencing the results of the photographic process since sulfur—especially in its low valence states—strongly coordinates to the silver ion.

The present paper is concerned with another aspect of sulfur chemistry in photography—the use of special sulfur compounds as synthetic tools useful for the preparation of ingredients of colour photographic materials. One reaction for the preparation of certain colour couplers which is, according to our knowledge, new and displays many aspects of theoretical and practical importance, will be described in particular detail.

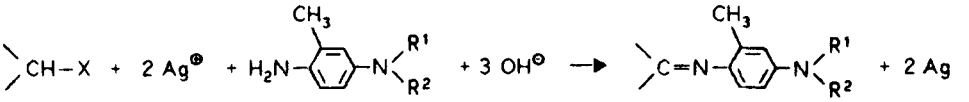
In colour photography—with the exception of special materials based on dye bleaching or dye diffusion—the dye image is generated by a chromogenic process commonly known as *colour development.* This process was devised by R. Fischer in 1914[1] and not put into industrial use until 1935 by Eastman Kodak and Agfa. The chemical aspects of colour photography are discussed elsewhere.[2,3]

Chromogenic coupling is a process in which the oxidation product of an *N,N*-disubstituted *p*-phenylenediamine reacts as a *soft nitrogen electrophile* with the anion of a colour coupler and initiates the formation of an azomethine or indoaniline dye. The main step in the process of colour coupling is commonly described as the electrophilic substitution of a carbanion species.[4] Depending on the structure of the colour coupler the overall process may liberate two to four electrons which are consumed by the developing silver halide. Thus, colour couplers are classified either as two-equivalent or four-equivalent couplers. The corresponding processes are defined by simplified equations (see Fig. 1).

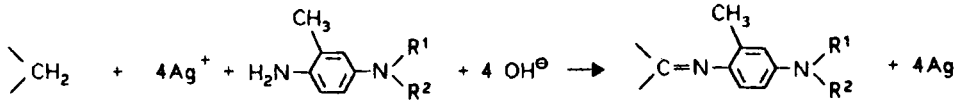
Two-equivalent coupling has proved to be not only the more convenient process but also—especially under the aspect of the reduction of the silver demand in photographic materials—the more economical process. In two-equivalent coupling a nucleophilic leaving group is split off from the colour coupler by the coupling process, and it is the nucleophilic leaving group which can be used as a tool for controlling the whole photographic process in the colour forming layers involved. In colour negative films the use of Development Inhibitor Releasing *DIR couplers* has proved to be one of the most important prerequisites for improving essential image qualities such as visual contrast, granularity, detail rendition and colour saturation.[5] Some common DIR couplers are depicted below.

The main objective of our investigations was to obtain new DIR couplers inaccessible by prior synthetic methods. In a DIR coupler the leaving group may be either a heterocyclic thiol such as a 5-mercapto-1-aryl- or 5-mercapto-1-alkyltetrazole or a condensed or substituted triazole of carefully balanced hydrophobicity which determines its diffusion range and its adsorption to developing silver halide emulsion grains.

Chromogenic Coupling on Active Methylene Compounds



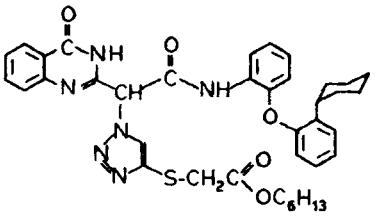
Two-equivalent Coupling X: Leaving Group Azomethine Dye



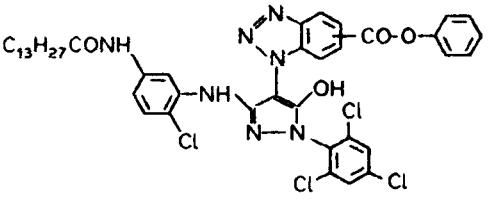
Four-equivalent Coupling

FIGURE 1 Chromogenic Coupling

Yellow DIR Coupler DIR C 1



Magenta DIR Coupler DIR C 2
two Isomers



Cyan DIR Coupler DIR C 3

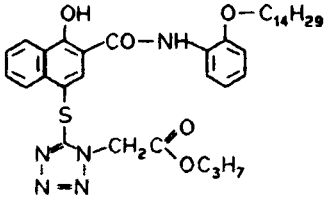
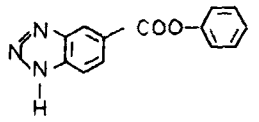


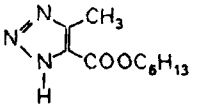
FIGURE 2 DIR Couplers DIR C 1, DIR C 2, DIR C 3

The choice of appropriate development inhibitors (see Fig. 3) and appropriate coupler backbones has been a major area for inventions, but the available methods of synthesis impose restrictions on arbitrarily combining coupler and inhibitor moieties. Other restrictions result from the effect of the leaving group on the coupling activity of the resulting two-equivalent coupler, i.e. the acidity of the coupler and the nucleophilicity of the coupler anion. Monocyclic 1,2,3-triazoles of moderate hydrophobicity have proved to be highly effective and diffusible development inhibitors.

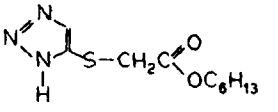
Development Inhibitors Containing an Acidic NH-Group: Triazoles



D-I 1

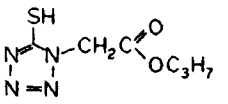


D-I 2

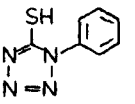


D-I 3

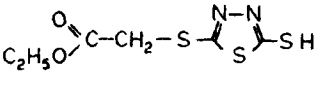
Development Inhibitors Containing a Heterocyclic Thiol Group



D-I 4



D-I 5



D-I 6

FIGURE 3 Typical Development Inhibitors

2. THE CHEMICAL PROBLEM

Two basic methods for directly introducing nucleophilic leaving groups into the strongly electron-donating coupler species have been used:

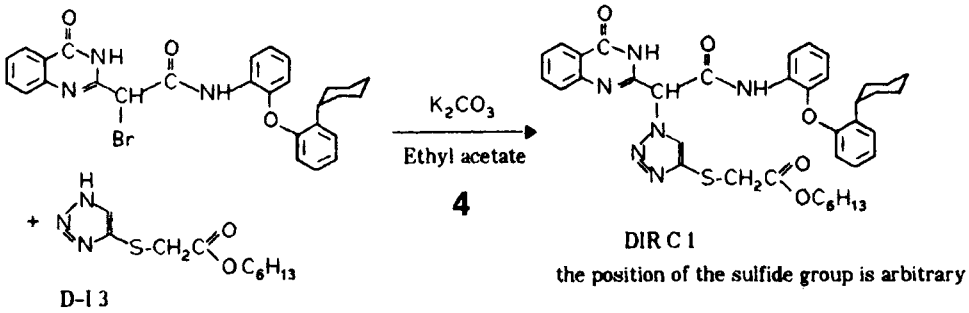
— nucleophilic substitution by the leaving group at an electrophilic center generated at the coupling position (method A),
— electrophilic substitution at the nucleophilic coupling position by an electrophilic center temporarily generated on the leaving group (method B).

Method A is preferred for modifying open chain ketomethylene type couplers such as common *yellow couplers* of the acylacetanilide or malonanilide types. By this method nucleophilic leaving groups of the cyclic imide type such as hydantoins or of the azole type such as imidazole derivatives are introduced by a halogenation-substitution sequence. Since the nucleophilic character of the coupler moiety can prevent the electrophilic center from reacting it may be necessary to deactivate the nucleophilic center throughout the synthesis by electron-accepting protective groups. Thus, for example, acylation of the amino group of 3-aminopyrazol-5-ones stabilizes the monohalogenated coupler against disproportionation into a mixture of a dibrominated and a bromine free four-equivalent coupler and makes it more reactive.

Method B is preferred for introducing thiol leaving groups into common *magenta couplers* of the pyrazolone and pyrazolotriazole classes and into *cyan couplers* of the naphthol class. Thiol leaving groups are easily transformed into electrophilic sulfenic acid derivatives by halogenation or oxidative processes, and appropriate methods for synthesizing two-equivalent couplers carrying a thiol leaving group consist of applying an oxidant to a mixture of the thiol leaving group and the four-equivalent coupler, optionally in the presence of a weak base.

Occasionally method A gives good results when it is applied to halogenated pyrazolotriazoles or α-naphthols as couplers and certain thiols or the thiocyanate ion as leaving groups.[6] In such

Synthesis of Yellow DIR Coupler DIR C 1 by Method A



Synthesis of Cyan DIR Coupler DIR C 3 by Method B

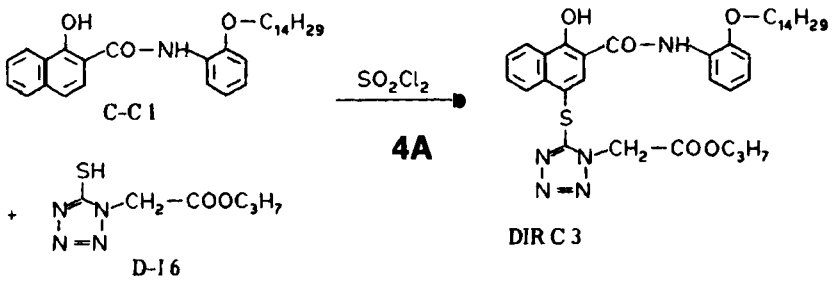


FIGURE 4 Examples of DIR Coupler Syntheses

cases, where the aromaticity of the molecule prevents it from directly replacing the strongly bound halogen atom by a nucleophilic azolate anion, single electron transfer can be assumed to be the driving force and to permit the indirect replacement of the halogen by a thiolate.

Method A does usually not succeed when phenols or naphthols are used as the coupler structures and triazoles as the leaving groups. On the other hand, certain halogenated 3-acylamino-5-pyrazolones are capable of replacing the halogen atom by nucleophilic azoles such as pyrazoles or imidazoles provided the reaction conditions are carefully optimized and the use of strong auxiliary bases is avoided.[7] In the field of phenolic or naphtholic cyan couplers methods for directly replacing a halogen atom or another leaving group at a coupler by an azole moiety are unknown.

In recent years we have discovered new reactions for introducing a triazole substituent into various types of colour couplers. These reactions have overcome many limitations of prior methods of syntheses and have provided new alternatives for two-equivalent couplers. A reaction based on the introduction of an *auxiliary selenium(IV) electrophile* into the nucleophilic position of the coupler was disclosed in 1990 and two useful methods were described in a brief report.[8]

These reactions may be typical for higher chalcogen elements. They may provide new routes for the arylation of heteroatom ligands in general and especially by electron donor substituted aromatic and heteroaromatic molecules. The most promising of these reactions makes use of an apparently unknown reactivity of *hypervalent sulfur*.[9] It is one of the aims of the present paper to report this highly valuable and variable reaction.

Synthesis of DIR Coupler DIR C 3 (Two Isomers)
Disclosed in DE 40 40 472

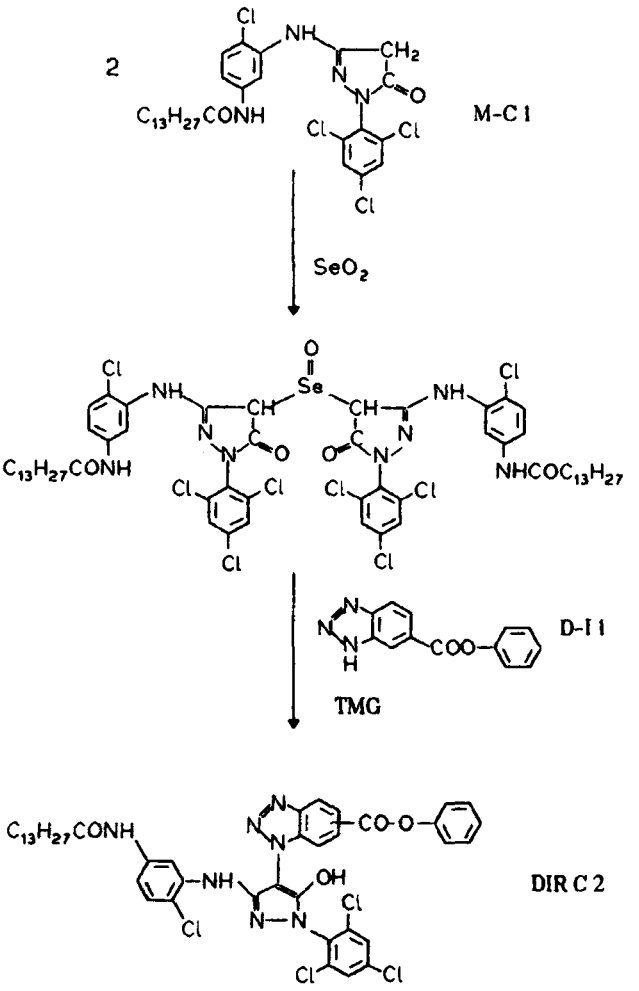


FIGURE 5

In a tentative interpretation of selenium mediated arylations it was assumed that the auxiliary selenium(IV) electrophiles formed coupler selenuranes which collapsed by a mechanism very similar to ligand coupling. In the case of 1-hydroxy-2-naphthoic anilide the 4,4-bisnaphthol coupler dimer resulting from *ligand coupling* as a competing process was isolated as one of the products of the reaction.

The benzotriazole substituted cyan coupler C-C 2 found in the reaction mixture was clearly identified as the N(1) isomer by its ^1H NMR spectrum. The N(2) isomer C-C 3 was not found. This was the first evidence of what we regard as kinetic control of the process in which the 4-(benzotriazol-1-yl)naphthol derivative is formed. Thermodynamic control

Synthesis of Two-equivalent Cyan Coupler C-C 2 from Coupler C-C 1 via a Selenurane Intermediate

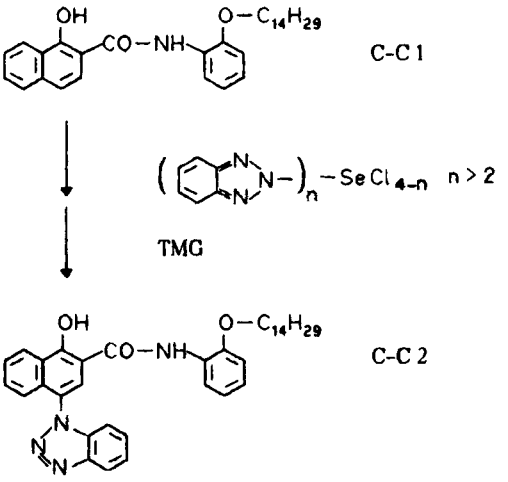


FIGURE 5A

as it is observed in many cases of nucleophilic substitution of benzotriazole[10] would have led to the preferential formation of the 4-(benzotriazol-2-yl)naphthol derivative. Since σ selenuranes in most cases are stable compounds favouring thermodynamic control we decided to investigate the generally higher reactivity of the analogous 6-sulfuranes.

Our next experiments (see Fig. 6) were carried out with couplers substituted by a benzeneselenenyl group which were prepared from benzeneselenenyl chloride and a four-equivalent coupler and subsequently chlorinated with *N*-chlorobenzotriazole, followed by treatment with auxiliary bases. These experiments were unsuccessful with one exception in which a magenta coupler of the 7-(benzotriazol-1-yl)pyrazolo[5,1-*c*](1,2,4)triazole type was formed in 1% yield from a 7-benzeneselenenylpyrazolo[5,1-*c*](1,2,4)triazole derivative. What we present now are the results of our efforts to use this new selenium(IV) chemistry to find methods using less toxic and more easily obtainable sulfur compounds and more easily controlled reactions.

3. THE ARYLATION OF TRIAZOLES BY 1-HYDROXYNAPHTHOIC ANILIDE CYAN COUPLERS VIA SULFUR(IV) INTERMEDIATES

In our first experiments we treated two-equivalent couplers containing a benzenesulfenyl substituent as the leaving group with *N*-chlorobenzotriazole.[11] None of these experiments succeeded. Thus, as our next choice, we decided to investigate the more promising thiobis coupler derivatives resulting from the reaction of 2 mol of (unsubstituted) four-equivalent coupler with 1 mol of sulfur dichloride, preferably in the presence of small amounts of Lewis acids such as $AlCl_3$ or $ZnCl_2$. It is well known that the result of this reaction depends strongly on the quality of the unstable SCl_2.

Atypical Synthesis of Benzotriazole substituted Pyrazolo[5,1-*c*][1,2,4]triazole by Collapse of a Heterocyclic Sulfurane and a Selenurane

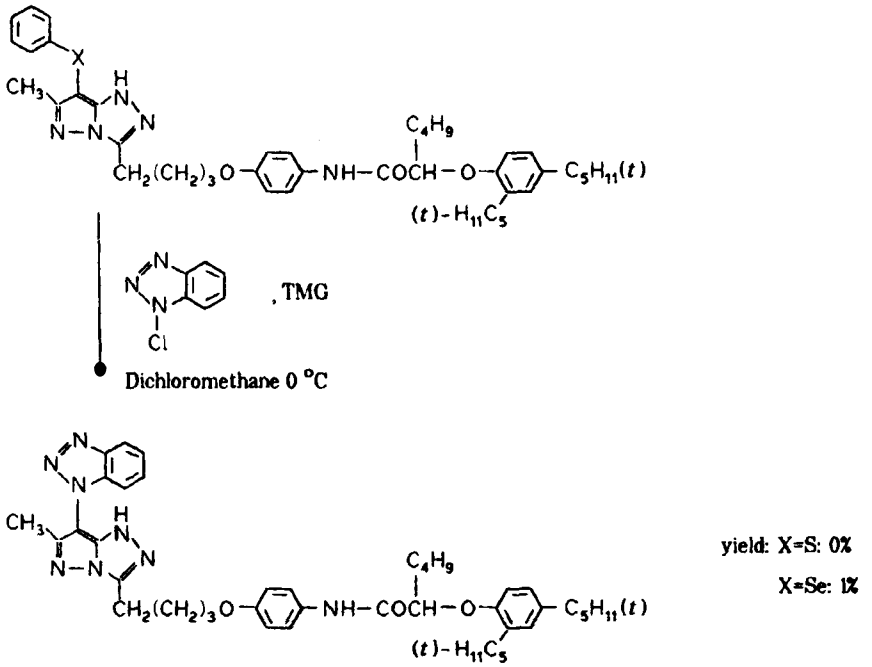


FIGURE 6 Atypical Sulfurane Contraction

We had to take into account that this process generally yields impure thiobis coupler as exemplified by the 4,4-thiobis-1-hydroxy-2-naphthoic anilide C-C 4, and in some cases we found up to 20% of the dithiobis compound C-C 5 and also a small quantity of the trithiobis compound C-C 6. The crude products were used for the next step and found to be almost as useful as the pure thiobis couplers. Since we detected dithiobis-(1-hydroxy-2-naphthoic anilides) in the product mixtures of all the subsequent reactions of the corresponding thiobis(1-hydroxynaphthoic anilides) the role of the dithiobis compound was not clear for some time. Meanwhile it appears that the dithiobis coupler is generally not involved in the desired reaction, but instead destroyed by a side reaction and regenerated by a consecutive process which will be discussed later.

On treating C-C 4 with *N*-chlorobenzotriazole in dichloromethane at 0°C the mixture immediately darkened and a very complex mixture was obtained from which after standing for 24 hours 4-(benzotriazol-1-yl)-1-hydroxy-2-naphthoic anilide C-C 2 was isolated by column chromatography in yields up to 25 mol %. Notably the same isomer was formed as in the selenurane experiment. As was found later the reaction conditions employed are highly important in determining whether the 4-(benzotriazol-1-yl)-1-naphthol derivative is formed alone or together with the strongly fluorescent 4-(benzotriazol-2-yl)-1-naphthol derivative C-C 3 which may be formed predominantly in the presence of strong base. In these experiments the theoretical yield was erroneously calculated on the basis of the unsubstituted 1-hydroxy-2-naphthoic anilide.

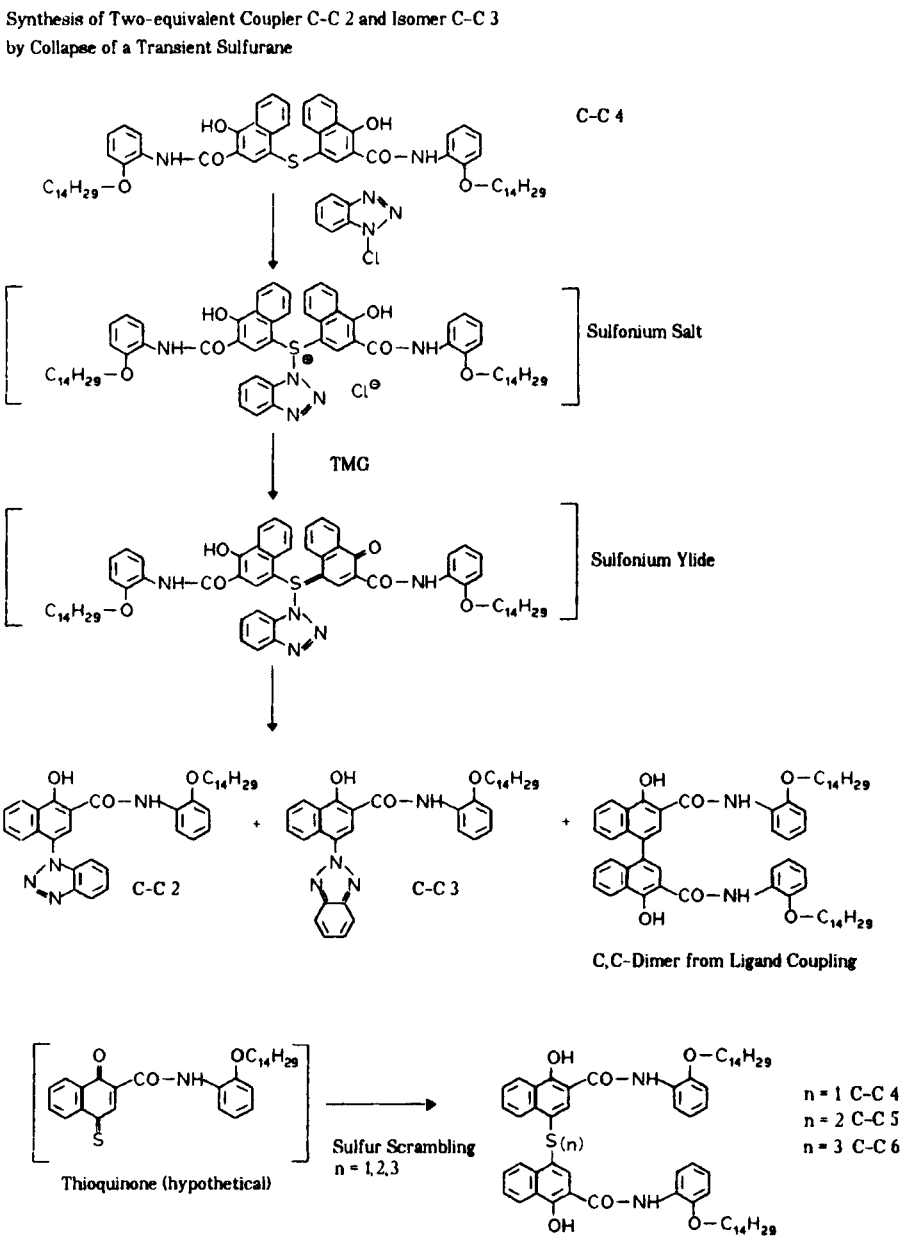


FIGURE 7 Synthesis of the Two-equivalent Couplers C-C2 and C-C3 by Collapse of a Transient Sulfurane

In our next experiments we replaced the *model nucleophile* benzotriazole by well-known development inhibitors of the 1,2,3-triazole series such as phenyl benzotriazole-5-carboxylate D-I 1[12] and *n*-hexyl 5-methyl-1,2,3-triazole-4-carboxylate D-I 2.[13] To avoid problems with the preparation and stability of unknown *N*-chlorotriazoles we decided to carry out our experiments on the thiobisnaphthol C-C 4 with *t*-butyl hypochlorite, *N*-chlorosac-

charin, *N*-chlorosuccinimide or other reagents known for their capability of producing heteroatom substituted sulfonium salts and we relied on the high tendency for heteroatom ligand exchange exhibited by all sulfurane species.[14] The reactions were carried out under essentially the same conditions as before except that *N,N,N',N'*-tetramethylguanidine (TMG) was used as an auxiliary base and cooling to 0 °C was maintained for about 6 hours only. By chromatographic separation of the crude products the triazole substituted 1-hydroxy-2-naphthoic anilides were isolated in yields between 20 and 35% based on the unsubstituted four-equivalent coupler C-C 1. Surprisingly neither the saccharin-substituted nor the succinimide-substituted two-equivalent coupler were identified among the reaction products. Thus it was taken for evident that all primarily formed transient sulfurane species were stable enough to undergo ligand exchange before they collapsed. We were also surprised to find only traces of the 4-chlorinated naphthol coupler. It is noteworthy that the benzotriazole moiety is predominantly bound to the naphthol group via its N(2) atom when phenyl benzotriazole-5-carboxylate D-I 1 is introduced as a leaving group. An isomer containing a naphthol group bound to its N(1) or N(3) atom is formed to a lesser extent.

This isomer distribution greatly differs from the isomer distribution resulting from the selenium(IV)-mediated reaction in which benzotriazole is exclusively bound to the coupler residue via N(1).[8] In model experiments with benzotriazole as the added nucleophile and *t*-butyl hypochlorite as the sulfurane-generating reagent it was found that in the absence of an auxiliary base the N(1)-substituted benzotriazole derivative is formed predominantly at low conversion rates and in lower yields while the presence of a strong base enhances the formation of the 4-(benzotriazol-2-yl)-1-hydroxy-2-naphthoic anilide, at higher conversion rates. Since—for photographic reasons—we were more interested in the N(1)- or N(3)-substituted isomer the results were not promising.

As reported in Ref. 15 ligand exchange in sulfuranes proceeds at high rates via an addition-elimination equilibrium between sulfonium salt and π-sulfurane. Bearing this in mind, we assumed that the reaction would proceed via a sulfonium ylide intermediate (a π-sulfurane) and without further proof we concluded that it was the relative stability of the π-sulfuranes which determines the result of the reaction and particularly the isomer distribution.

Recently sulfonium ylides (π-sulfuranes) based on arylsulfinyl-substituted active methylene compounds were investigated by Koval and Panasenko[16] and the results demonstrate that their hydrolysis proceeds with formation of arylsulfinylsuccinimides. We carried out our experiments under essentially aprotic conditions and came to a different conclusion. In analogy to the results of Koval, the formation of a 1-naphthol-4-sulfinylsuccinimide and an unsubstituted 1-naphthol derivative (i.e. the 4-equivalent coupler) was expected, but none of these products were identified in the reaction mixture. Instead we found throughout our experiments on C-C 4 and different triazole derivatives that the sulfur(IV) intermediates split to form a substituted naphthol and what we regard as secondary products of an extremely unstable sulfene species (thioquinone). The sulfene was apparently generated by the decay of a 1-hydroxynaphthalene-4-sulfenate fragment and subsequently underwent *sulfur scrambling*.[17] A better explanation for the formation of the thiobis-, dithiobis- and trithiobisnaphthol derivatives could not be found. The formation of a C,C-dimerized 1-hydroxy-2-naphthoic anilide apparently results from ligand coupling.[18] Thus, the new reaction differs clearly from ligand coupling and also from the sulfonium ylide fragmentation reported by Koval.

Further experiments were then conducted with C-C 4 and other triazole derivatives and also with carboxylate transferring oxidants such as lead tetraacetate, iodosobenzene diac-

Synthesis of Cyan DIR Coupler DIR C 4 by Lead Tetraacetate Induced Sulfurane Contraction

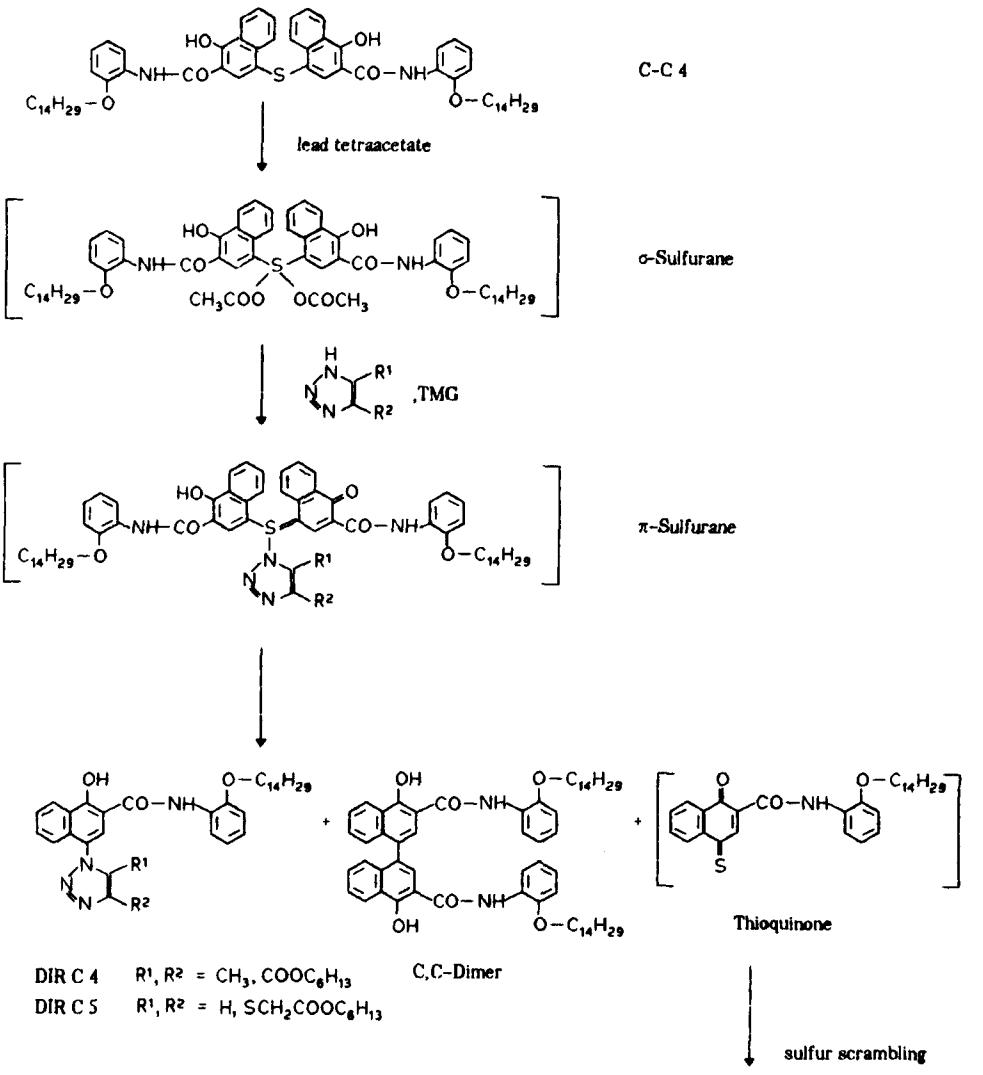


FIGURE 8 Synthesis by Use of Lead(IV) Acetate

etate and iodosobenzene bis(trifluoroacetate). Optimum results were obtained at −10 to −20°C with lead tetraacetate uncontaminated with acetic acid in dichloromethane as the solvent and in the presence of 2 mol TMG per mol of lead tetraacetate. Lead tetraacetate, the triazole derivative and the auxiliary base were used in excess of up to 50%. Under these reaction conditions even triazole derivatives containing a readily oxidized sulfide group as a photographically useful substituent, e.g. D-I 3, were induced to react with the primary sulfurane—or sulfonium ylide—and to produce the triazole-substituted 1-hydroxy-2-naph-

thoic anilide DIR C 5 in yields up to 66%. The yield of the corresponding 1-hydroxy-2-naphthoic anilide DIR C 4 substituted by an *n*-hexyl 5-methyl-1,2,3-triazole-4-carboxylate moiety (D-I 2) was 86% determined by HPLC. The different yields can be explained by the undesired attack of lead tetraacetate on the sulfide group of the triazole derivative. The position of the naphthol moiety on the 1,2,3-triazol ring of DIR C 4 and DIR C 5 has not been ascertained beyond doubt.

The calculated yield of two-equivalent coupler is based on the thiobis(1-hydroxy-2-naphthoic anilide) and it is important to note that only one of the two naphthol moieties of the coupler can be transformed into DIR coupler while the other is undergoing sulfur scrambling. The yield of undesired C,C-dimerized naphthol as the result of C,C-ligand coupling varies, but is greatly reduced when the reaction is carried out at the lowest possible temperature.

When these concepts were applied to the synthesis of heterocyclic magenta couplers such as the 1-phenyl-3-anilinopyrazol-5-ones or the pyrazolo[5,1-*c*](1,2,4)triazoles the results were less convincing, but as a whole the method proved reliable if the introduced leaving group was sufficiently acidic and the corresponding anion exhibited sufficient nucleophilic character. The yield of the two-equivalent coupler was found to drop below 50%, in nonoptimized systems and procedures.

4. SEARCH FOR A REACTION MECHANISM

Industrial colour couplers are usually highly sophisticated materials, and economical synthesis is an important requirement determining their quality and performance. Therefore the most unsatisfactory aspect of our syntheses based on thiobis couplers was considered to be the high loss of coupler, since only one of both ligands could be bound to the desired nucleophilic moiety while the other had to draw off the undesired sulfur atom. We therefore had to find a *dummy* substituent capable of forming a sulfur(II) fragment, and it was this aspect of our investigation which provided some surprising insight into the path by which the sulfur(IV) intermediate is most probably decomposed. Originally we had assumed that a coupler sulfenate species left behind after formation of the two-equivalent coupler would be capable of entering another sulfur(IV)-mediated process leading to the formation of a second molecule of two-equivalent coupler, but this assumption proved incorrect. In spite of the observation that yields are improved by increasing the amount of lead tetraacetate, triazole derivative and base, no clear evidence of the formation of more than one molecule of two-equivalent coupler from one molecule of thiobis coupler was obtained.

Moreover, our experiments with coupler sulfenamide derivatives as starting materials demonstrated the instability of these species—at least in the presence of base—and led us to conclude that the sulfur(II) fragment of the sulfurane collapse was either short-lived or too unreactive to allow the addition of an oxidant such as lead tetraacetate in sufficient quantities. This remains unclear, however.

Two methods have been used for preparing unstable 1-hydroxy-2-naphthoic-anilide-4-sulfenamides as intermediates which, however, have not been clearly identified:

1) In the first series of experiments a bis(dialkylamino)disulfane[19] was chlorinated in dichloromethane at low temperature and the crude dialkylaminosulfenyl chloride

Synthesis of DIR C 4 via a 1-Hydroxy-2-naphthoic Anilide 4-sulfenamide

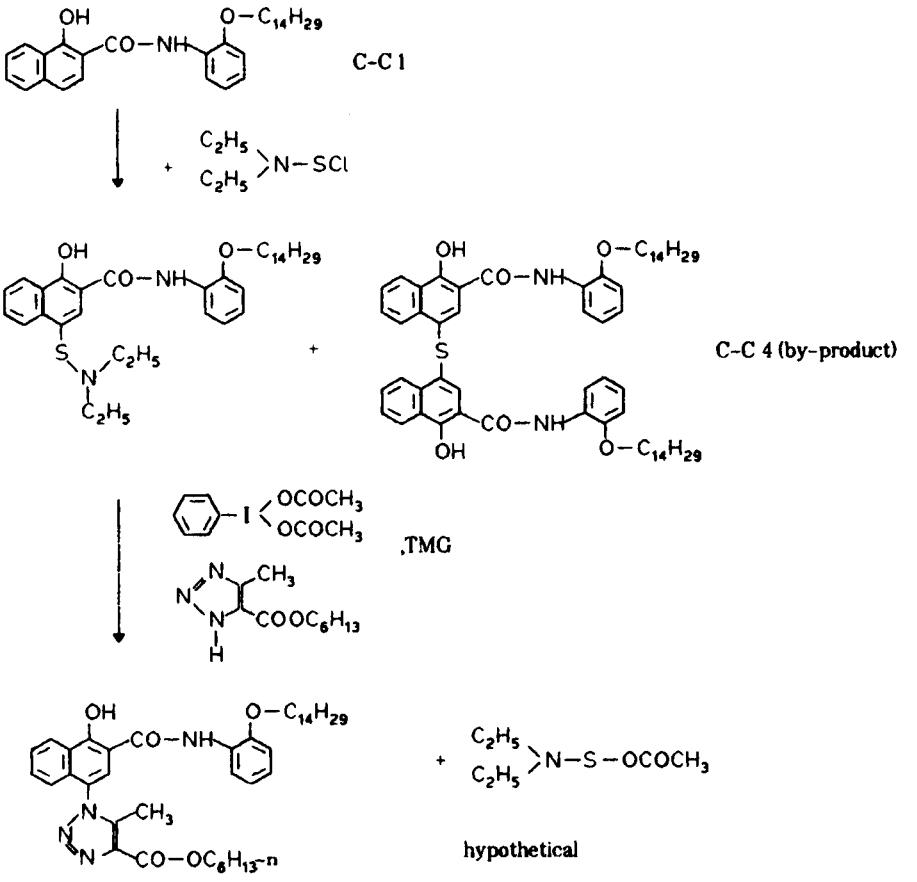


FIGURE 9 Sulfurane Contraction in 1-Hydroxy-2-naphthoic Anilides Containing a 4-Sulfenamide Group

treated with C-C 1 at 0 °C. The course of the reaction was far from uniform and a complex mixture of unstable and mostly unidentified products including thiobis- and dithiobisnaphthol derivatives was obtained. On attempted workup impure C-C 4 was isolated from the reaction mixture. Oxidation started before C-C 1 was consumed completely. The successive addition of lead tetraacetate, triazole derivative (D-I 2) and the auxiliary base induced the usual darkening which indicates the formation of the sulfur(IV) intermediate, and after 12–24 hours the triazole-substituted two-equivalent naphthol coupler DIR-C 5 was isolated from the reaction mixture by column chromatography in 60% yield based on C-C 1. No 4-dialkylamino-1-hydroxy-2-naphthoic anilide was isolated at all. With crude diimidazol-1-yldisulfane[20] as the starting material similar results were obtained and no trace of 4-(imidazol-1-yl)-1-hydroxy-2-naphtoic anilide was detected in the reaction mixture.

2) In a second series of experiments pure dithiobis-1-hydroxy-2-naphthoic anilide, C-C 5, was prepared from the corresponding 1-hydroxy-4-thiocyanato-2-naphthoic anilide and hydrazine hydrate in ethanol by a known procedure[21] and subjected to chlorination at low temperature, optionally in the presence of 1-(trimethylsilyl)pyrazole. In the absence of (trimethylsilyl)pyrazole a 4-chlorosulfenyl-1-hydroxy-2-naphthoic anilide can be isolated. In the presence of (trimethylsilyl)pyrazole the reaction seemed to reach a state of equilibrium in which the mixture contained con-

Sulfurane Contraction by Lead Tetraacetate on a
1-Hydroxy-2-naphthoic Anilide 4-sulfenylphthalimide

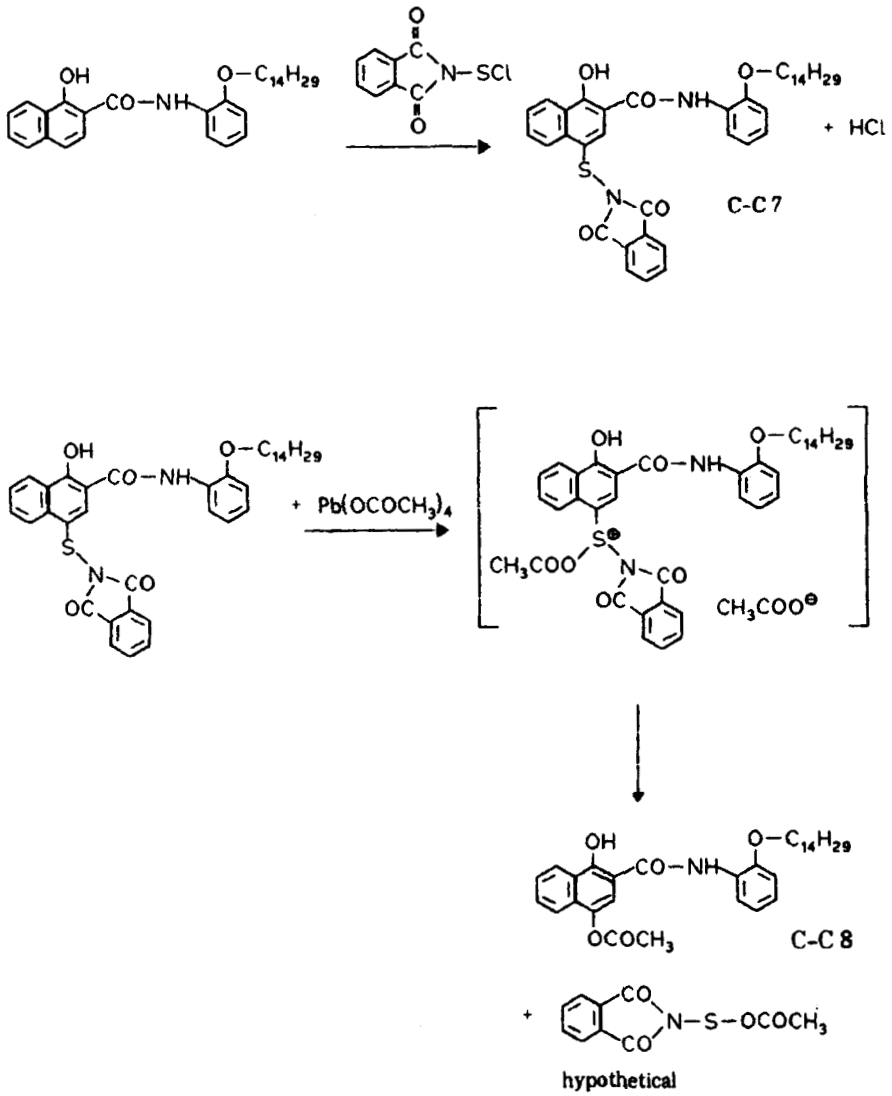


FIGURE 9a

siderable amounts of thiobis coupler. By addition of lead tetraacetate, triazole derivative (D-I 2) and TMG it was terminated to induce the formation of the sulfur(IV) intermediate before C-C5 was totally consumed. After 2 hours the mixture again contained DIR C 5 in yields of up to 60% and no trace of pyrazole substituted coupler was found in the reaction mixture.

A special case was the 1-hydroxy-4-phthalimidosulfenyl-2-naphthoic anilide C-C 7 resulting from C-C 1 and phthalimide-*N*-sulfenyl chloride in dichloromethane which was immediately destroyed when it was exposed to base—apparently with formation of secondary products of the hypothetical thioquinone. Addition of lead tetraacetate to the cyan coupler C-C 7 in the presence of the triazole D-I 2 at 0 °C caused immediate darkening and after 10 minutes a new coupler was found which, according to its R_f value on the TLC plate, was believed to be DIR-C 4. It showed almost the same melting point (80–82 °C, compared to 82–84 °C for DIR C 4), but the ^1H NMR spectrum made clear that we had synthesized the 4-acetoxy-1-hydroxy-2-naphthoic anilide C-C 8. The value of this new acetoxylation method is limited by the moderate yields and the necessity of working up a complex reaction mixture. Apparently the strongly electrophilic transient sulfurane from C-C 7 collapsed immediately after its formation and in the absence of a base the neutral triazole did not undergo ligand exchange: the coupler residue had trapped the less nucleophilic acetate ligand.

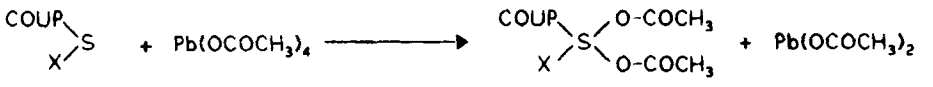
As clearly seen in this figure it is the less nucleophilic of two heterocyclic ligands which is bound to the coupler moiety while the more nucleophilic ligand remains on the electrophilic sulfur atom. At this stage of the experimental work all the evidence was in favour of the hypothesis that the course of the reaction was determined by *thiophilic control.* Therefore it is suggested that the new reaction be named *Sulfurane Contraction* to emphasize that it is the binding ability of the transient sulfur(IV) species as an electrophile which determines the fate of the reactants.

Once a transient sulfurane is formed from a starting sulfane containing two carbon atom ligands of different nucleophilic character the sulfurane can be expected to collapse in such a way that the less thiophilic of the two carbon atoms—as a result of a reversal in polarity—will trap the less thiophilic heteroatom ligand while the ligand containing the more nucleophilic carbon atom will remain on the sulfur atom—possibly together with the more thiophilic heteroatom ligand. The nomenclature sulfurane contraction was chosen in analogy to the *sulfide contraction* of Eschenmoser and coworkers.[22]

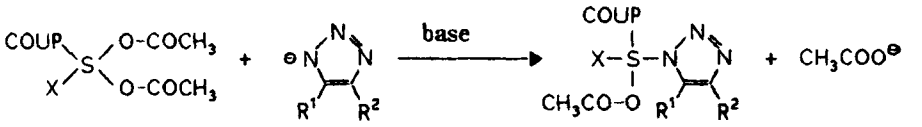
In more general terms: apart from cases where preformed cyclic structures may influence the course of the reaction it will be controlled by the binding capacity of the hypervalent sulfur atom which determines its preference for certain heteroatom ligands and carbon atom ligands in the sulfur(IV) coordination sphere and the choice of the ligands to be coupled to a leaving carbon ligand. By more general criteria, the reaction could be classified as "hetero atom ligand coupling", an extension of the known ligand coupling scheme. It must be emphasized that in the systems under investigation C,C-ligand coupling as a side reaction proceeds in contrast to thiophilic control. There is no proof for the conclusion that the activation energy of this reaction might be higher than that of the sulfurane contraction.

According to the most likely course of events the nucleophilic sulfur atom of the sulfane species is *oxidized* to an electrophilic transient sulfurane which induces a carbon atom lig-

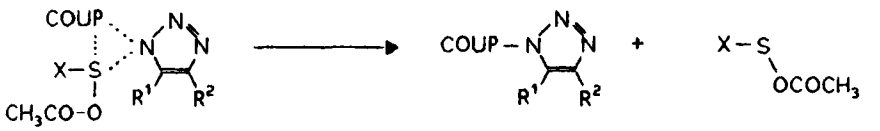
Sulfurane Contraction: General Reaction Scheme (COUP = Coupler)



X: COUP or Dummy Nucleophile — Diacetoxysulfurane



Ligand Exchange on Sulfurane



Collapsing Sulfurane — Two-equivalent Coupler — Sulfane

FIGURE 10 General Reaction Scheme

and to undergo *umpolung* and to strip a weakly bound apical heteroatom ligand from the sulfur(IV) atom. If the principle of thiophilic control applies strictly the best explanation for our results is provided by the hypothesis that the sulfurane species undergoing heteroatom ligand coupling with high selectivity is the hetero-sulfonium ylide, a π-sulfurane.

Hypothetical reaction path:

coupler sulfane $\xrightarrow{\text{oxidation}}$ heterosulfonium salt $\xrightarrow{\text{ligand exchange}}$ heterosulfonium ylide $\xrightarrow{\text{ligand coupling}}$ two-equivalent coupler

In our experiments normal ligand coupling leads to the formation of C,C-dimerized couplers which are easily identified by their inability to form azomethine dyes and by smooth oxidation to dark quinonoid compounds. The formation of coupler dimer is favoured by temperatures above 10 °C, e.g. when the slowly oxidizing iodosobenzene diacetate[23] is used as the oxidant and it is the preferred escape reaction for those systems where a sulfurane contraction is discriminated by the choice of unfavorable ligands, i.e. heteroatom ligands of highly thiophilic[24,25] or nucleophilic character which lead to a diminished electrophilic character of the transient sulfurane.

One exception may be worth mentioning: From C-C 1 and 2-*p*-toluenesulfonylbenzo-1,2-thiazol-3-one,[26] a moderately reactive sulfenylating agent, an unsymmetric 1-hydroxy-2-naphthoic anilide coupler sulfane containing a chelating ortho substituent of weakly thiophilic character was obtained. When the sulfane was treated with lead tetraacetate and D-I 2 in dichloromethane under cooling DIR C 4 was formed rapidly, but in low yield (generally below 5% as determined by HPLC) and apparently without participation of an auxiliary base. The main reaction, however, led to the formation of secondary products of the hypothetical thionaphthoquinone intermediate and unidentified fragments.

5. CONCLUSION

The goal of this investigation was preparative in nature and its framework was restricted to new compounds useful in colour photography. A new reaction was found which could turn out to be a general method for the arylation of sufficiently acidic azoles. Considerations concerning reaction mechanisms resulted primarily from efforts to improve yields and selectivity and also from the constraints to explain the formation of certain by-products.

At present the proposed reaction mechanism is based primarily on an extrapolation of known sulfurane reactivity:[27] all oxidants of the carboxylate transferring type and all halogenating agents used are well known sulfurane generating reagents capable of forming sulfonium salts under appropriate conditions, at least from suitable highly nucleophilic sulfides.[28,29] Since our experiments were not designed to isolate or even identify sulfurane intermediates it needs further proof.

The high reactivity of sulfuranes has occasionally been compared to that of diazo compounds.[15] The electrophilic reactivity of donor substituted aromatic or heteroaromatic sulfuranes observed in coupler syntheses may be superior to that of comparable quinone diazides and—as in many reactions of the Sandmeyer type—poor yields can be related to abundant reactivity.

At this stage of our investigations it is, however, not possible to rule out categorically the possibility of an SET mechanism which could start the new reaction from a radical cation. Stereochemical investigations which could provide insight into the ligand arrangement of hypothetical transient sulfuranes and also into the process of bond breaking in the course of the reaction were outside the scope of our investigations. What the reaction can provide is a deeper understanding of thiophilic reactivity which has hitherto been examined from the point of view of the binding step while our experiments provide insight into the bond breaking process.

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7. EXPERIMENTAL PART

Melting points are uncorrected. TLC: silica gel, toluene or cyclohexane-acetone 8:2, (spots are made visible as green or cyan indoaniline dyes by spraying with colour developer CD-4 and alkaline potassium peroxidisulfate solution).

7.1. *Synthesis of C-C 2*

1-Chlorobenzotriazole 1.7 g, (0.011 mol) and 2.5 g *N,N,N',N'*-tetramethylguanidine are added to 9.8 g (0.01 mol) C-C 4 (see below) in 100 ml dichloromethane at 0 °C. After 24 h the mixture is evaporated to dryness under reduced pressure, taken up in 200 ml ethyl acetate and 100 ml water and the organic phase washed with additional water. After drying with anhydrous sodium sulfate it is again evaporated to dryness, taken up in toluene and chromatographed over 150 g silica gel. After elution of dimer, C-C 4, C-C 5 and C-C6 the two-equivalent coupler C-C 2 is eluted by adding up to 50% by volume ethyl acetate. The fractions containing C-C 2 are concentrated, the residue digested with methanol and recrystallized from acetonitrile.

Yield:2.1–3.0 g (35–50 %), m.p. 112–113 °C.

7.2. *Synthesis of the Thiobis Coupler C-C 4*

Aluminium chloride (0.3 g) and 10.5 g (0.102 mol) sulfur dichloride are added to 95 g (0.2 mol) 1-hydroxy-2-naphthoic (2-tetradecyloxy)anilide[9] in 250 ml chlorobenzene at 10 °C. The temperature rises to 20 °C and hydrogen chloride is evolved. After 2 h the mixture is evaporated to dryness under reduced pressure, digested with 400 ml ethyl acetate, filtered by suction and dried in air.

Yield: 100 g, m.p. 110–114 °C (compared to pure C-C 4, m.p. 118 °C, from 1,2-dichloroethane).

7.3. *Synthesis of DIR C 4*

n-Hexyl 5-methyl-1,2,3-triazole-4-carboxylate (D-I 2) (3 g), 6.7 g lead tetraacetate and 3.5 g *N,N,N',N'*-tetramethylguanidine are added to 9.8 g (0.01 mol) C-C 4 in 100 ml dichloromethane at –10 °C. After stirring for 6 h at –10 °C the mixture is kept in the refrigerator for another 15 h and worked up by addition of 10 ml 25% by weight sulfuric acid, separation of the organic phase, concentration under reduced pressure and subsequent column chromatography over 150 g of silica gel with toluene containing increasing amounts of ethyl acetate as the eluent. The main fractions containing DIR C 4 are collected, evaporated to dryness, digested with hexane-ethanol 5:1 and recrystallized from ethyl acetate-methanol.

Yield: 4.9 g (71%; the crude yield of DIR C 4 was 5.8 g, determined by HPLC); m.p. 82–84 °C.

^{1}H NMR (200 MHz), $CDCl_3$, TMS: δ = 14.3 (s, OH), 8.41 (s, NH), 8.28–8.30 (d, CH), 8.19–8.21 (d, CH) 8.03–8.06 (d, CH), 7.93 (s, CH), 7.60–7.76 (q, CH), 7.26 (s, CH), 6.9–7.16 (m, CH), 4.38–4.46 (t, CH_2), 4.04–4.14 (t, CH_2), 2.72 (s, CH_3), 1.78–1.96 (m, CH_2), 1.16–1.5 (m, CH_2), 0.82–0.94 (m, 2 × CH_3).

From the earlier eluates the following by-products were isolated in order of their relative polarity:

the C,C-dimer, m.p. 100–101°C, C-C 4 and C-C 5 in a mixed fraction, and C-C 6, m.p. 99–100 °C.

C-C 6: $C_{62}H_{80}N_2O_6S_3$, calc. S: 9.2%, found S: 9.2%.

^{1}H NMR (200 MHz), $CDCl_3$, TMS: δ = (OH not registered), 8.05–8.35 (m, CH), 6.82–7.5 (m, CH + s, NH), 3.92–4.07 (t, CH_2), 2.84–2.96 (q, CH_2), 1.06–1.58 (m, CH_2), 0.83–0.92 (t, CH_3).

7.4. *Synthesis of DIR C 5*

Aluminium chloride (0.3 g) and 10.5 g (0.102 mol) sulfur dichloride are added to 95 g (0.2 mol) 1-hydroxy-2-naphthoic (2-tetradecyloxy)anilide in 250 ml chlorobenzene at 10 °C. The temperature rises to –20 °C and hydrogen chloride is evolved. After 2 h the mixture is evaporated to dryness under reduced pressure, 1000 ml trichloroethene, 36 g *n*-hexyl-1,2,3-triazole-4-thioglycolate (D-I 3, 0.15 mol) and 11 g *N,N,N',N'*-tetramethylguanidine are added and the mixture cooled to –15 °C. While the temperature is maintained between –10 °C and –20 °C 66.5 g lead tetraacetate and 23 g *N,N,N',N'*-tetramethylguanidine are added and the mixture kept in the refrigerator at 0 °C for 16 h. Then 100 ml dilute sulfuric acid (25% by weight) are added, the dark organic phase decanted from the white slurry of lead(II) sulfate, washed with water and evaporated to dryness under vacuum at 40–50 °C. The residue is dissolved in 300 ml toluene, diluted with 1200 ml hexane and chromatographed over 750 g silica gel. C-C 4 and C-C 5 are separated with the non-polar fractions, the trisulfide and another by-product are eluted by addition of increasing amounts of toluene to the eluent and DIR C 5 is eluted by a 50:50 toluene-ethyl acetate mixture. The fractions containing the main portion of DIR C 5 are concentrated at 50 °C under reduced pressure, digested with hexane-ethanol for 48 h and filtered by suction. After drying, the white powder is recrystallized from ethanol at 70 °C.

Yield: 35 to 39 g (50–55%), m.p. 47–50 °C.

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