[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

General Formation of Aryl Dithiolcarbonates and Ethyl Ethylxanthate in the Leuckart Thiophenol Synthesis[1]

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Study of the reactions of a variety of diazonium salts with potassium ethylxanthate showed that in addition to the aryl ethylxanthate previously considered to be the principal product, other important and general products are the corresponding diaryl dithiolcarbonate and ethyl ethylxanthate. Evidence is given for the structure of typical products and for the probability that the dithiolcarbonate is not formed from the aryl ethylxanthate, either during the Leuckart reaction or subsequently. The yield of a typical dithiolcarbonate was not improved by use of potassium isopropyl- or benzylxanthate. Both heterolytic and homolytic processes apparently occur, at least to some extent. Experiments are described which permit tentative generalizations and conclusions as to the nature of the Leuckart thiophenol synthesis.

The Leuckart reaction for the preparation of thiophenols involves addition of a neutralized solution of a diazonium salt to a hot aqueous solution of potassium ethylxanthate (I). The product, assumed in the past to be an aryl ethylxanthate (II), ordinarily is not purified but is hydrolyzed directly to the thiophenol, as shown by the equations.[3,4]

$$\mathrm{ArN_2X} + \underset{\mathrm{I}}{\mathrm{KS{\cdot}CS{\cdot}OC_2H_5}} \xrightarrow{70^\circ} \underset{\mathrm{II}}{\mathrm{ArS{\cdot}CS{\cdot}OC_2H_5}} + \mathrm{N_2} + \mathrm{KX} \ldots (1)$$

$$\mathrm{II} \xrightarrow{\text{Aq. KOH}} \mathrm{C_2H_5OH} + \mathrm{KS{\cdot}CO{\cdot}OK} + \mathrm{ArSK} \xrightarrow{\mathrm{H^+}} \mathrm{ArSH}$$

In preparing 2,6-dimethylthiophenol (III) by this reaction, we found that the crude product before hydrolysis partially crystallized. The solid, surprisingly, was bis(2,6-dimethylphenyl) dithiolcarbonate (IV). Fig. 1 shows the evidence for its identity; the disulfide V was prepared because the thiol III had a refractive index higher than reported. Conversions of IV to V and III in yields exceeding 50% demonstrated that IV could not be the isomeric thionothiolcarbonate.

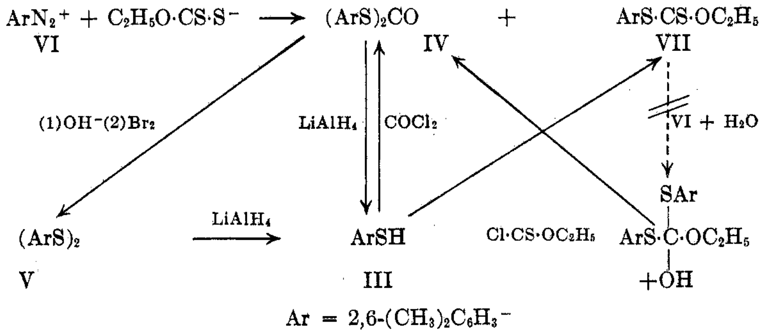

Fig. 1. Identification of bis(2,6-dimethylphenyl) dithiolcarbonate (IV)

Information as to how IV might have been formed was sought by an attempt to isolate all reaction products. Washing the crude product with acid removed negligible material, but aqueous alkali extracted a little 2,6-dimethylphenol and what appeared to be an azophenol, a type of compound which could account for the dark red color of the crude product.

Partial distillation of the neutral products then gave ethyl ethylxanthate (VIII), a finding which surprised us even more than had the isolation of IV, because of the evident transfer of an ethyl group from I and the necessarily concomitant cleavage of the bond in I between oxygen and a primary carbon atom. The identity of VIII was demonstrated by comparing its infrared spectrum with that of authentic VIII, itself characterized by derivatives. Potassium ethylxanthate (I) gave no VIII when heated in water and therefore its simple decomposition was not responsible for formation of VIII.

$$2\ \mathrm{ArN_2X} + 2\ \underset{\mathrm{I}}{\mathrm{KS{\cdot}CS{\cdot}OC_2H_5}} \longrightarrow \underset{\mathrm{IX(in\ IV,\ Ar=\ 2,6\text{-}(CH_3)_2C_6H_3^-)}}{\mathrm{(ArS)_2CO}} + \underset{\mathrm{VIII}}{\mathrm{C_2H_5S{\cdot}CS{\cdot}OC_2H_5}} + 2\mathrm{N_2} + 2\mathrm{KX} \ldots (2)$$

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[1] Largely abstracted from the M.A. thesis of J. R. C., December 1955, and the Ph.D. thesis of C. L. G., May 1959. Presented in part at the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14-16, 1957.

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[3] K. H. Saunders, *The Aromatic Diazo Compounds*, 2nd ed., Edward Arnold and Co., London, 1949, p. 324.

[4] E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. 1, Chemical Publishing Co., Inc., New York, N. Y., 1958, p. 31.

The yield of VIII was 44%, calculated using Equation 2, which later seemed likely to apply. For the sake of brevity, the ratio of the yield of ethyl ethylxanthate (VIII) to the yields of various diaryl dithiolcarbonates (IX) will be called the "VIII/IX ratio"; IX will be used to refer to diaryl dithiolcarbonates in a general sense, and II will be used in the same way for aryl ethylxanthates.

Since the dithiolcarbonate IV was isolated in 62% yield, the VIII/IX ratio in this instance was 0.7, rather than 1 as required by Equation 2. A plausible explanation for the discrepancy was that VIII had been destroyed in part, either during the reaction or the isolation. Since VIII was resistant to acid and base, as used in its isolation, an effort was made to approximate its destruction in the reaction (or the subsequent distillation) by determining that proportion of an extraneous amount of VIII which could be recovered after it had been added during the usual reaction; the assumption was made that the amount of VIII actually formed in the reaction would be unchanged. About 81% of the extraneous VIII survived. Correction for the loss suggested that about 55% of VIII had been formed in the conventional reaction. The VIII/IX ratio obtained using the corrected yield was 0.9, which thus rather strongly supports the validity of Equation 2.

Chromatographic separation of the residue from the distillation of VIII gave the aryl xanthate VII in 23% yield and the dithiolcarbonate IV in 62% yield (including IV which had crystallized earlier). VII was identified conclusively by independent synthesis from ethyl chlorothionoformate and the thiol III (Fig. 1); this type of reaction has been used with alcohols but seems to be novel with a thiol.

The effect of varied conditions next was explored in the hope of improving the yield of IV and of obtaining intimations as to the mechanism of its formation. It might be added here that yields as high as 75% of IV have been obtained but that occasionally, in the same procedure, they were as low as 53%. One possible explanation for this variation may be that an important part of the reaction occurs in the water-insoluble organic phase and that there is erratic diffusion of a necessary intermediate within this mass. Another explanation is suggested later. In any event, caution is dictated in the interpretation of results in the various reactions leading to aryl xanthates (II) and dithiolcarbonates (IX) which are to be considered.

In this study of conditions, the proportions of reagents were varied by adding the diazonium salt VI to three molar proportions (usually 1.25) of xanthate I. In an effort to have VI in excess, it also was added, both slowly and rapidly, to 0.5 molar proportion of I. The range of 40–54% in the yield of IV probably is not very significant but does suggest that better yields of IV are obtained with a ratio of VI to I which approximates unity.[5]

A feature of the reaction which undoubtedly plays a highly significant role, both theoretically and practically, is the solid which forms when VI is allowed to react with I in the cold. This solid presumably is a diazoxanthate,[3] $ArN_2S{\cdot}CS{\cdot}OR$, and ordinarily is decomposed immediately when the reaction is effected at 60° (an explosion may ensue if it is not).[3] Attempts to isolate this complex were thought to be hazardous because of its apparent explosive tendency. It was studied, however, *in situ*. When 0.52 molar proportion of the I was added to one equivalent of VI at 0° and the mixture then heated slowly to 60°, IV resulted but only in 25% yield. The same result ensued when the cold mixture of I and VI was added rapidly to water at 60°. It is noteworthy that when 2.1 proportions of I to 1 of VI were used, IV was isolated in only 1% yield. These results, more than those obtained only at 60°, point to the undesirability of a ratio of VI to I which differs much from unity, if IV is sought from the reaction.

The most obvious explanation for the formation of the dithiolcarbonate IV in the Leuckart synthesis was that the anticipated aryl xanthate VII is in fact a major initial product, but that it is attacked by VI and water and thus partially converted into IV, as shown by the cancelled arrow of Fig. 1.

Hölzle had previously isolated bis(5,8-dichloro-1-naphthyl)dithiolcarbonate in 34% yield in the appropriate Leuckart reaction (and the aryl xanthate in 46% yield).[6] In considering the mechanism of its formation, he rejected the aryl ethylxanthate as an intermediate on the ground of its insolubility in water; he also excluded its hydrolysis product, $ArS{\cdot}CO{\cdot}S^-$, on the basis that the aryl ethylxanthate could not be hydrolyzed under the conditions of the reaction and that, even if it were, the hydrolysis product would not be that indicated. We substantiated Hölzle's opinion as to simple direct attack upon the aryl xanthate by recovering the xanthate VII after it had been treated with VI in water. Since it was possible, however, that the VII formed in the Leuckart reaction would appear so finely dispersed that our experiment in bulk would not be representative, VII also was exposed to VI in methanol, which effected homogeneity. Again VII was recovered, despite the fact that a control reaction of VI with I in methanol gave IV in 25% yield. These observations suggest that VII is not an intermediate in the formation of IV, but they are by no means conclusive; for example, the xanthate I normally might function concertedly with VI

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[5] Owing to the rapidity of the reaction, I probably was in excess in *all* of these experiments, since the VI had to be added to it. The reverse addition to heated VI obviously is impracticable.

[6] K. Hölzle, *Helv. Chim. Acta*, 29, 1883 (1946).

upon the aryl xanthate VII in a manner that would be difficult to duplicate in a model situation. It might be added that Hölzle's exclusion of a hydrolysis product of VII also is reasonable, if our observation of the slow decrease in *p*H of an alkaline solution of VII indicates only slow hydrolysis.

Hölzle noted that the yield of his dithiolcarbonate was inversely proportional to the acidity of the medium,[6] and concluded that the reactive species was a diazonium hydroxide. His view, as we understand it, was that the xanthate ion, in the form of the mesomeric structure $C_2H_5\overset{+}{O}\cdot C\overset{-}{S}\cdot\overset{-}{S}$, upon simultaneous attack by the diazonium and hydroxide ions, followed by loss of alcohol, gave the intermediate $ArS\cdot CO\cdot\overset{-}{S}$, which then underwent attack by a second diazonium ion to give the dithiolcarbonate; attack of the xanthate ion in its usual form ($C_2H_5O\cdot CS\cdot\overset{-}{S}$) gave the aryl ethylxanthate. In both paths nitrogen was lost at appropriate points. The formation of VIII, however, cannot be accounted for by Hölzle's mechanism.

One of the most important questions connected with the Leuckart synthesis, and probably one of the most difficult to answer, is whether the reaction is heterolytic, homolytic, or some combination of the two (one path perhaps leading to the dithiolcarbonates IX and the other to the aryl xanthates II).[7] In a consideration of the uncatalyzed reactions of diazonium salts, Ingold has pointed out the probable importance of S_N1 decomposition into arylcarbonium ions, which subsequently react rapidly with nucleophilic species which are at hand;[9] decreased reactivity of the *p*-nitro compound (and perhaps of the *p*-methoxy) and enhanced reactivity of *ortho*-substituted systems are to be anticipated in such reactions (*vide infra*).[9] De Tar and Turetzky found that diazonium salts decomposed homolytically in acetate-buffered methanol[10] but stated their belief that decomposition in water up to about *p*H 7 occurred mainly by an ionic mechanism.[10b] In our reactions, the solution of diazonium salt was neutralized to Congo Red (*p*H 3–5)[11] and added to an essentially neutral solution of I. One is tempted therefore to conclude that the *p*H favors an ionic mechanism; however, the fact that the reaction mixture ultimately had a *p*H of about 7–7.5 makes such a conclusion seem somewhat injudicious.

In an effort to determine whether or not homolysis is involved in the Leuckart synthesis, the usual reaction with VI and I was effected in the presence of acrylamide. The formation of a considerable amount of presumed polyacrylamide was a strong indication that free radicals were in fact present. The yields of IV and VII differed little from that of a control reaction without acrylamide, but this result would be anticipated if the chain length of the polyacrylamide were sufficiently great so that relatively few initiating radicals were trapped. An interesting implication that radicals might form more readily with a hindered diazonium salt was obtained by warming both VI and a benzenediazonium salt in the presence of the diamine-precursor of Wurster's Blue; the deep blue color indicative of a free radical formed at 15–20° and 40–50° respectively. Enhanced reactivity has been noted with diazonium salts of *o-tert*-butylaniline which decompose above about −25°[12]; behavior of this kind, whether it depends upon homolysis or not, demonstrates enhanced reactivity for *ortho*-substituted systems which probably is quite important in relation to the varied yields of IX discussed presently. It is also noteworthy that neutralization at 0° of the solution either of VI or the benzenediazonium salt caused development of the Wurster color, suggesting that radicals may be generated rather easily from the unhindered salt, even though perhaps less easily than from the hindered one.

In probing further into the nature of the Leuckart reaction, it next became desirable to determine whether the formation of VIII and of dithiolcarbonates (IX) was general and, if so, the influence of steric and electronic factors on the ratio of the dithiolcarbonate IX to the aryl xanthate II; this ratio will be referred to subsequently as the "IX/II ratio."

No attention has been paid to the generality of formation of dithiolcarbonates (IX) in the Leuckart reaction, although in at least three instances, besides that of Hölzle,[6] they have been isolated in small or undeclared amounts using *p*-methyl-,[13] *o*-methoxy-,[14] and 2,4,6-tribromo-[15] benzenediazonium salts. Table I shows the results obtained when various representative diazonium salts were subjected to the Leuckart reaction. It is notable that the VIII/IX ratio seems to approximate unity closely enough to support the validity of Equation 2; the variations from unity probably reflect, in

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(7) It is worth mentioning that there is a rather suggestive similarity of the Leuckart synthesis to the Sandmeyer reaction, in that the facile oxidation of the cuprous ion[8] has a possible counterpart in the presumably facile oxidation of I to the disulfide.

(8) *Cf.* ref. 3, p. 282.

(9) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 799.

(10) (a) D. F. De Tar and M. N. Turetzky, *J. Am. Chem. Soc.*, **77**, 1745 (1955); (b) **78**, 3925 (1956); (c) **78**, 3928 (1956).

(11) O. Tomicek, *Chemical Indicators*, Butterworths Scientific Publications, London, 1951, p. 50.

(12) F. Greer, Ph.D. thesis, Vanderbilt University, 1955, p. 73.

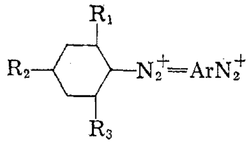
(13) R. Leuckart, *J. prakt. Chem.*, [2] **41**, 190 (1890); *J. Chem. Soc.* (*Abstracts*), **58**, 603 (1890).

(14) F. Mauthner, *Ber.*, **39**, 1347 (1906).

(15) W. H. Hunter and A. H. Kohlhase, *J. Am. Chem. Soc.*, **54**, 2425 (1932).

TABLE I

YIELDS,[a] FROM REPRESENTATIVE DIAZONIUM SALTS, OF ARYL DITHIOLCARBONATES (IX), ARYL ETHYLXANTHATES (II) AND ETHYL ETHYLXANTHATE (VIII)

				$(ArS)_2CO$ IX		$ArS\cdot CS\cdot OC_2H_5$ II		Ratio	$C_2H_5S\cdot CS\cdot OC_2H_5$ VIII	Ratio
No.	R_1	R_2	R_3	No.	Yield, %	No.	Yield, %	IX/II[b]	Yield, %[c]	VIII/IX[d]
VI	CH_3	H	CH_3	IV	62[e]	VII	23	2.7	55	0.9
X	C_2H_5	H	C_2H_5	XI	40	XII	29	1.4	33	0.8
XIII	CH_3	H	H	XIV	50	XV	42	1.2	45	0.9
XVI	H	H	H	XVII	30(11)	XVIII	50(36)	0.6	22	0.7
XIX	H	OCH_3	H	XX	20(12)	XXI	36	0.6	25	1.3[f]
XXII	H	NO_2	H	XXIII	27	XXIV	42	0.6	21[g]	0.8

[a] Yields are based on material before final purification. When substantial losses were incurred in purification, the yield of pure material follows in parentheses. [b] Crude yield % of the particular aryl dithiolcarbonate/crude yield % of the aryl ethylxanthate. [c] Corrected (see Experimental) for estimated decomposition after its formation. [d] Corrected yield %[c] of VIII/yield %, crude, of the particular aryl dithiolcarbonate. [e] 72% in a large-scale operation (see Experimental). [f] This unusually high value may simply be a result of greater loss than usual in the isolation of the XX. [g] Possibly an artifact.

part, differences in stabilities of products and ease of isolation in the various instances.

Consideration of most of the dithiolcarbonates which previously had been isolated from the Leuckart reaction suggested that steric hindrance about the diazonium function might have been an important factor in their formation and in the IX/II ratio. Table I shows that the yield of the dithiolcarbonate and the IX/II ratio are indeed greater when *ortho* substituents are present (*i.e.* with VI, X, and XIII). On the other hand, the isolation of IX after the reaction of XVI, XIX, and XXII, which contained no *ortho* substituents, shows that the formation of IX is general. The diazonium reagents XIX and XXII, containing a *p*-methoxy and a *p*-nitro group respectively, were used to determine the extent to which electron donation or withdrawal might affect the reaction; the rough similarity of these results to those obtained with the benzene-diazonium salt (XVI) indicates that electronic effects do not play a major role in determining the IX/II ratio.

The structures of the various dithiolcarbonates (IX) and aryl xanthates (II) probably need not be regarded with suspicion, since reactions of diazonium salts in which nitrogen is replaced appear invariably to result in entrance of the replacing group at the carbon atom which bore the nitrogen originally, irrespective of whether the reaction is heterolytic or homolytic.[16] Nevertheless, to obviate any possibility that the orientations of the products differed from those of the parent amines, the infrared spectra of all of the compounds of types IX and II were carefully scrutinized, especially in those regions which characterize the nature of aromatic substitution (1650–2000 cm.$^{-1}$, 950–1225 cm.$^{-1}$, and 670–1000 cm.$^{-1}$).[17] Correspondence of the spectra with expectation and with those of the parent amines appeared to support the validity of the various structures proposed.[18]

The experiments which led to the data of Table I were without notable incidents, except for those involving the benzene-(XVI) and *p*-nitrobenzenediazonium salts (XXII), which deserve some comment: (a) The melting points of the dithiolcarbonates XVII and XXIII differed from reported values. Evidence supporting our constants appears in the Experimental part (furthermore, absorption occurred in the infrared region[18] common to the other dithiolcarbonates). (b) Phenyl disulfide was obtained along with XVII and XVIII; XVII and XVIII seemed likely sources (*e.g.* dibenzyl dithiolcarbonate decomposes to the disulfide),[19] but, since both proved to be rather stable to heat, the origin of the disulfide still is unknown. (c) A red solid appeared when the nitro salt XXII was added to the I, even at 60°. This solid undoubtedly was a more stable counterpart of the presumed diazoxanthates. Another anomaly in this reaction was our inability to secure unequivocal evidence for the formation of VIII. As Table I shows, VIII was isolated, but the temperature required for distillation was sufficiently greater than usual to induce suspicion that VIII actually was an artifact; chromatography separated material which gave VIII upon distillation, but again

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(16) *Cf.* ref. 3, Chapter VIII.

(17) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., Methuen and Co., Ltd., London, 1958, Chap. 5. For the series from VI, the thiol III was used below 1000 cm.$^{-1}$ instead of IV and VII.

(18) The six dithiolcarbonates (IX) showed two medium (m) to strong (s) bands in the range of 830–880 cm.$^{-1}$ which accordingly may be characteristic of structure IX. The six xanthates (II), as well as VIII, showed six bands in the region of 1000–1300 cm.$^{-1}$ which may be characteristic: 1000–1015 cm.$^{-1}$ (m); 1020–1075 cm.$^{-1}$ (s; often as two overlapping bands); 1105–1110 cm.$^{-1}$ (m); 1139–1150 cm.$^{-1}$ (m); 1212–1235 cm.$^{-1}$ (s); 1265–1300 cm.$^{-1}$ (m).

(19) G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 666 (1945).

only with excessive heating. In the experiments with XXII, both VIII and XXIII conceivably could have formed according to Equation 3. This

$$2\ \underset{\text{XXIV}}{p\text{-}NO_2C_6H_4S\cdot CS\cdot OC_2H_5} \longrightarrow \underset{\text{XXIII}}{(p\text{-}O_2NC_6H_4S)_2CO} + \underset{\text{VIII}}{C_2H_5S\cdot CS\cdot OC_2H_5} \ldots \quad (3)$$

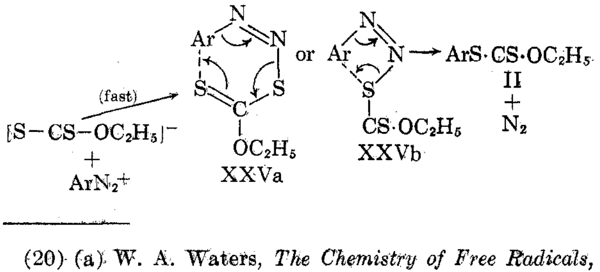
possibility was dismissed for the nitroaryl xanthate XXIV by demonstrating reasonable thermal stability for it. As a precaution, thermal stability under the conditions used to remove VIII also was established for the solid xanthates VII and XII. The other aryl xanthates (XV, XVIII, and XXI) were liquids which were considered to be stable, since no indication of behavior according to Equation 3 had been noticed when each was twice distilled for purification.

Since VIII evidently was an authentic product of the Leuckart reaction, an effort was worthwhile to determine the effect of using alkylxanthate salts other than I in the reaction, in order to facilitate the transfer of the alkyl group. The 2,6-diethyl compound X was found to give the dithiolcarbonate XI in a yield of between 50% (crude) and 18% (recrystallized) with potassium benzylxanthate, and of 37–28% with potassium isopropylxanthate (an effort to prepare potassium *tert*-butylxanthate was unpromising); both results thus approximate those obtained using I. No special effort was made to isolate products other than the XI, but 2,6-diethylphenyl benzylxanthate (43%) was isolated because it happened to crystallize nicely; the ratio of dithiolcarbonate XI to this xanthate resembles the IX/II ratio obtained with the ethyl xanthate I (approximately the same ratio resulted also with the isopropylxanthate if unpurified material which appeared at the expected point is considered to be the aryl isopropylxanthate).

Conclusions regarding the Leuckart process which now *seem* to be justified are these: (1) Formation is general of aryl xanthates (II), dithiolcarbonates (IX) and ethyl ethylxanthate (VIII; one possible exception); IX is not formed from II alone, in the reaction or subsequently. (2) Substituents in IX and II are oriented as in the parent amines. (3) The molar amount of VIII formed usually is smaller than of IX, but only slightly so. (4) Replacement of the ethyl group of I by isopropyl or benzyl has little effect on the yield of IX. (5) A diazonium salt and I at −5° give a solid diazoxanthate, which usually decomposes rapidly at 60°. (6) A 1:1 ratio of diazonium salt to I best produces IX. With solid diazoxanthate, excess I gives nearly no IX: excess diazonium salt produces IX, even though in low yield. (7) Free radicals are present. An unsubstituted diazonium salt yields radicals at 0° in neutral solution; a hindered salt probably does so more readily. (8) No biaryl coupling products were isolated (saponification of crude reaction product from XIX and steam distillation gave no 4,4′-dimethoxybiphenyl; however, aryl radicals may not survive long enough to couple). (9) Aryl carbonium ions are present, since a phenol was isolated. (10) Less IX forms in methanol than in water. Side reactions in methanol may be responsible but, since solvents of high dielectric constant favor heterolytic rather than homolytic processes,[20a] the result may signify that IX forms chiefly by a heterolytic path. (11) Substituents *ortho* to the diazonium function effect some increase in the yield of IX and in the IX/II ratio. (12) The yields of IX and II and the IX/II ratio are little affected by replacement of hydrogen by methoxy or nitro in the *para* position in the diazonium salt. (13) The yield of IX decreases with increasing acidity.[6] The reason may be that the diazotate anion is required,[6,20b] that a homolytic dissociation of the diazonium salt (known to be favored by a high *p*H) occurs, or simply that at low *p*H the concentration of ethylxanthate ion is reduced relative to the less nucleophilic free acid. Variation of *p*H may be a factor in the variable yields of IV which were mentioned earlier.

Mechanisms for the Leuckart synthesis cannot be offered now with much assurance. Thus, in addition to the quandary of heterolysis *versus* homolysis, the extent is unknown to which *syn*, *anti* stereoisomerism of diazoxanthates might determine whether IX or II predominates. Nevertheless, the fact that long-known reactions of diazonium reagents often are poorly understood leads us to believe that definitive evidence on the Leuckart process may appear only slowly and prompts us to suggest processes which may play a role. We wish to emphasize that these suggestions are quite speculative and are intended to be more provocative than definitive in explaining an unusual combination of reactions which results in the formation of a dithiolcarbonate and ethyl ethylxanthate along with the aryl xanthate.

An attractive pathway to the aryl ethylxanthates (II) involves the quasi-ring structures XXV A or XXV B for the diazoxanthate.



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(20) (a) W. A. Waters, *The Chemistry of Free Radicals*, 2nd ed., Oxford University Press, London, 1948, p. 16.

(20) (b) H. Zollinger, *Experientia*, **12**, 165 (1956); C. Wittwer and H. Zollinger, *Helv. Chim. Acta*, **37**, 1954 (1954).

Formation of the diaryl dithiolcarbonates (IX) might follow one or more of the sequences outlined in Fig. 2.

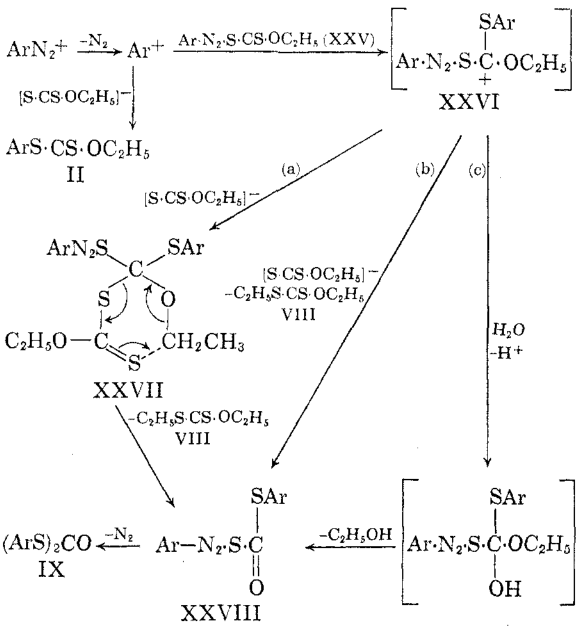

Fig. 2. Formation of the diaryl dithiolcarbonates (IX)[21]

EXPERIMENTAL[23]

Starting materials and general procedures. Potassium ethylxanthate (I)[24] was dried under vacuum and stored at 0–10°; no decomposition was evident after 3.5 years, the longest any was kept. Potassium isopropyl- (86%) and benzylxanthate (88%) were prepared in essentially the standard manner,[24] except that with the benzylxanthate the proportion of the alcohol was reduced by *ca.* one half and the product was precipitated with ether: both xanthates were completely soluble in acetone, showing the absence of potassium trithiocarbonate.

Amines used were purified commercial products. Sulfuric acid gave more soluble amine and diazonium salts with 2,6-dimethylaniline (XXIX) than did hydrochloric acid and accordingly was used for convenience in diazotizing all of the amines; hydrochloric acid, however, gave comparable results with XXIX. No explosions were encountered during the work, although the solids obtained by treating I with the nitro compound XXII or with the dimethyl salt VI in the low-temperature experiments gave indication of decomposing violently if handled incautiously in quantity; nevertheless care should be taken in the diazonium salt reactions generally, owing to the possibility of explosion.[25] In the Leuckart reactions, unless otherwise stated, the procedure of 1(a) was used with specified amounts of amines, and of other reagents in the molar proportions of 1(a), for diazotization, neutralization, reaction with I, and isolation of crude product by ether extraction; however, most diazotizations and neutralizations were done at 0–3° instead of at −5° to avoid solidification. Ether extracts of the reaction products usually were dried over anhydrous sodium sulfate and solvent then was removed under reduced pressure, most often by means of a rotating-flask evaporator (moist extracts in general were handled similarly); the term "red oil" refers to the residue left after removal of ether from the extract of the crude product of the Leuckart reaction. Chromatography was effected usually with a 3 × 32-cm. column of aluminum oxide ("Merck, Acid Washed, Suitable for Chromatographic Adsorption").

Yields in the Leuckart reaction were based on the amine, those of the aryl alkylxanthates being calculated on the basis of Equation 1 and those of the aryl dithiocarbonates (IX) and of ethyl ethylxanthate (VIII) on that of Equation 2. The identity of the samples of VIII isolated always was established by comparison of the infrared spectrum with that of authentic VIII.

1. *Reactions of the 2,6-dimethylbenzenediazonium salt* VI. (a) *Preparation of bis(2,6-dimethylphenyl) dithiolcarbonate* (IV). A solution of 60.5 g. of 2,6-dimethylaniline (XXIX) in 500 ml. of water containing 42 ml. of sulfuric acid (sp. gr., 1.84) was diazotized below −5° by dropwise addition of a cold solution of 34.5 g. of sodium nitrite in 200 ml. of water (unless a positive starch-iodide test resulted 1 min. after addition, more nitrite solution was added). The resulting solution of the diazonium salt VI was neutralized to Congo Red by adding 30% aqueous sodium carbonate below −5°; the color changed from light yellow to light brown.[26] The solution (containing some precipitated sodium sulfate) then was poured (*ca.* 1 min.) into a solution, kept at 50–60° of 100 g. of I in 500 ml. of water. Nitrogen evolved smoothly and oil separated. Upon completion of gas evolution at 60°, the mixture was cooled. An ether extract was washed with

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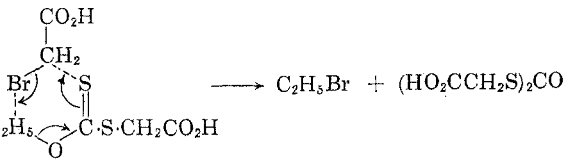
[21] In Fig. 2, ArN_2^+ (like Ar^+) could attack XXV, nitrogen being lost at once or subsequently. The formation of II shown could be competitive with or alternative to its formation *via* XXV A or XXV B. Paths (a), (b), and (c), shown for conversion of XXVI to IX, may be concomitant or alternative. In (a), XXVII is particularly speculative, since models are strained if the ring is coplanar; nevertheless, XXVII provides an attractive explanation for the unusual facile transfer of a primary alkyl group, especially since an otherwise rather puzzling reaction[22] can be formulated similarly:



In (b), the ethylxanthate anion is regarded as effecting nucleophilic displacement on the ethyl group of XXVI. Path (c) explains why the ratio of VIII/IX can be less than 1 [*cf.* (3)]. Compound XXVIII, however formed, may lose nitrogen essentially as in conversion of XXVB to II; loss of nitrogen is reserved to this point only for convenience. Fig. 2 rationalizes (6); with excess I, ArN_2^+ or Ar^+ presumably gave II, and hence negligible XXVI or IX; excess ArN_2^+ could produce IX *via* path (c), but in low yield since lack of I precluded paths (a) and (b).

[22] E. Bülmann, *Obersigt over det kgl. Danske Videnskabernes Selskabs Forhandlinger,* **1907** [2], 83; *Chem. Abstr.,* **2,** 1269 (1908).

[23] Melting points are corrected and boiling points are uncorrected. Analyses mainly were by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were obtained using a Perkin-Elmer Model 137 Infracord spectrophotometer; most substances, being liquid or low melting, were used as liquid films (XXIII in Nujol mull; XI, solid film; IV, VII in carbon tetrachloride).

[24] C. C. Price and G. W. Stacy, *Org. Syntheses,* **28,** 82 (1948).

[25] W. E. Bachmann and R. A. Hoffman, *Org. Reactions,* Vol. II, 224 (1944).

[26] In later Leuckart reactions, the *p*H was adjusted to *ca.* 5 using pHydrion test paper and was checked using Congo Red. Variations within the Congo Red transition range[11] may have been responsible for the variation in yields of IV mentioned in the discussion.

5% hydrochloric acid (100 ml.), 5% aqueous sodium hydroxide (200 ml.) and finally with water until neutral. Concentration of the dried extract to *ca.* 150 ml. and cooling gave the dithiolcarbonate IV, which was washed with cold petroleum ether; yield 35.2 g. (47%), m.p. 101–103.5°. Further concentration to *ca.* 75 ml. and chilling (Dry Ice-acetone) gave a second crop of 18.5 g. (25%), m.p. 98–101°. Recrystallization from ether (low yields) and carbon tetrachloride–methylcyclohexane gave colorless IV with a constant m.p. of 103–104.5°.

Anal. Calcd. for $C_{17}H_{18}OS_2$: C, 67.51; H, 6.00; S, 21.20. Found: C, 67.60; H, 6.06; S, 20.94.

(b) *Conversion of* IV *to 2,6-dimethylphenyl disulfide* (V) *and 2,6-dimethylthiophenol* (III). A mixture of 10 g. of IV and 20 g. of sodium hydroxide in 100 ml. of 1:1 water-ethanol was heated under reflux for 4 hr. The mixture was diluted with water and filtered. After removal of alcohol by distillation, bromine was added dropwise with shaking until its color persisted. Filtration removed 7.8 g. (86%) of the disulfide (V), m.p. 100–102°, which after recrystallization from aqueous alcohol and pentane had a constant m.p. of 103–104°; reported m.p., 105.5°–106°,[27] 103–104°.[28]

Anal. Calcd. for $C_{16}H_{18}S_2$: C, 70.03; H, 6.61. Found: C, 70.24; H, 6.76.

A solution of 1.52 g. of lithium aluminum hydride in 30 ml. of dry ether was added dropwise to 7.5 g. of IV in 50 ml. of ether. After 8 hr., moist ether was added, then dilute hydrochloric acid. The ether layer was washed with water and dried. Distillation gave 4.45 g. (64%) of the thiophenol III, b.p. 61–64° (2 mm.), n_D^{24} (each of four fractions) 1.5734; reported b.p. 91° (50 mm.),[28] 111° (25 mm.);[29] n_D^{20} 1.5712,[28] n_D^{25} 1.5712.[29] The thiol III also was obtained (75% yield) by reduction of V with lithium aluminum hydride,[30] b.p. 62–64° (2 mm.), n_D^{24} 1.5733.

Anal. Calcd. for $C_8H_{10}S$: C, 69.51; H, 7.29. Found: C, 69.32; H, 7.41.

(c) *Material balance in the reaction of* VI *with the xanthate* I. VI from 12.12 g. of XXIX was added in 2 min. and the ether extract of the product washed and dried (Extract XXX), all as usual.

In another experiment, with 60.5 g. of XXIX, the alkaline wash solution was strongly acidified and extracted with ether. This extract, dried and concentrated, left 0.98 g. of brown solid (XXXI). Sublimation of the XXXI gave 0.3 g. of 2,6-dimethylphenol, m.p. and mixture m.p. 45–47°. Reduction of the residue from this sublimation with aqueous sodium hydrosulfite resulted in an acid-soluble precipitate; since the precipitate apparently was an aminophenol and since the color of XXXI in water was *p*H-variable, XXXI presumably contained an azo coupling product along with 2,6-dimethylphenol. In this same experiment, only a trace of solid resulted when the usual acid wash was made basic.

Removal of ether from Extract XXX gave "red oil" which partially crystallized in 3 hr. at 5°; solid IV, removed and washed with cold hexane, amounted to 6.42 g. (43%), m.p. 100–103°.

The remaining oil (and hexane wash) was cautiously distilled through an 8 × 250 mm. tube until low boiling material was removed; 3.28 g. (44%) of ethyl ethylxanthate (VIII) distilled, b.p. 80–82° (9 mm.), n_D^{25} 1.5353–1.5354; reported, b.p. 78° (18 mm.),[19] n_D^{19} 1.5375.[31] The identity of VIII first was suggested by analysis of material from an earlier experiment, n_D^{25} 1.5349.

Anal. Calcd. for $C_5H_{10}OS_2$: C, 39.97; H, 6.71; S, 42.68. Found: C, 40.65; H, 6.92; S, 43.13.

For evidence that the VIII was not formed simply by decomposition of I, 9.9 g. of I in 50 ml. of water was heated at 50–55° for 1 hr; the *p*H rose from 7 to 8 but no insoluble oil (*i.e.* VIII) was observed at any time.

Undistilled residue (10.17 g.) from the distillation was dissolved in enough hexane to give 50 ml. of solution, which was chromatographed. Fractions were discerned by evaporating occasional small amounts of effluent in a bath at 50° (VII melted, IV did not). Elution with hexane removed 5.12 g. of VII (23%, m.p. 45–49°), which was followed by oil (1.51 g., probably a mixture of VII and IV). Benzene then eluted greasy IV in three fractions (2.91 g.; 19%). Ether and ethyl acetate subsequently removed 0.34 g. of gum (similar gum previously had nitrogen but no sulfur). All weights were obtained after drying to constant values.

The combined fractions of crude VII, recrystallized from hexane, had a melting point and mixture melting point with authentic VII [see 1(e)] of 48.5–49.5°. The combined fractions of crude IV, recrystallized (hexane), had a melting point and mixture melting point with authentic IV [see 1(e)] of 99–102°.

(d) *Modified conditions in the formation of* IV. The procedures of 1(a) were followed in preparing and neutralizing the diazonium salt VI and in isolating IV (m.p. in the range of 101–103.5°). Solutions of VI from one molar proportion of amine XXIX were added dropwise to solutions at 50–60° containing 0.52 (Expt. 1) and 3.00 molar proportions of the xanthate I; the yields of IV were 40% and 54%, respectively; since repetition of Expt. 1 with rapid addition of the VI gave IV in 42% yield, reasonable variations in the mode of addition probably are unimportant.

In experiments with the solid presumed diazoxanthate, solutions containing 2.1 (Expt. 2) and 0.52 (Expt. 3) molar proportions of the xanthate I were added rapidly at −5° to a solution of VI, and the mixtures then were warmed slowly to 60°; the yields of IV were 1% and 25% respectively. The same result (25% of IV) ensued as in Expt. 3 when the mixture of VI and I, prepared at −5°, was added quickly to water at 60°. It is worth adding that nearly half of the chromatographed product from Expt. 2 contained no sulfur, nitrogen, or halogen; since this material was soluble in concd. sulfuric acid, it evidently contained oxygen.

In the studies of VI and VII in methanol, a control experiment first established that I itself would react reasonably well: Sodium nitrite (1.4 g.) in water (2 ml.) was added at *ca.* −5° to 2.4 g. of the amine XXIX in methanol (20 ml.) containing concd. hydrochloric acid (5 ml.). The mixture was neutralized with saturated methanolic sodium hydroxide and decanted from salt into a boiling solution of 4.5 g. of I in methanol (30 ml.). After rapid evolution of gas was complete, methanol was distilled (reduced pressure), the residue was dissolved in ether, and IV was isolated as in 1(a); yield 0.75 g. (25%), m.p. 101–103.5°. Replacement of I by 3.8 g. of VII resulted in no isolable IV and in recovery of 3.2 g. (84%) of VII, m.p. 48–49°.

When a neutralized solution of the diazonium salt VI was added to an equimolar amount of the xanthate VII in a vigorously stirred water suspension at 55°, VII was recovered in 88% yield.

In the search for free radicals in the usual Leuckart reaction, 0.1 mole of the diazonium salt VI in neutralized solution was added to an aqueous solution of 0.12 mole of I and 71.1 g. of acrylamide, all essentially according to 1(a); the first few drops caused a vigorous reaction—the temperature rose to *ca.* 90° and the solution became quite viscous. After completion of addition and separation of oil, addition of the aqueous layer to acetone or ethanol gave a dough presumed to be polyacrylamide, which eventually hardened (Acrylamide itself is quite soluble in ethanol and acetone; further evidence that the dough was polyacrylamide was afforded by its failure to diffuse through a cellophane membrane). In a similar experiment, 0.2 mole of acrylamide was added to

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(27) R. M. Pierson, A. J. Costanza, and A. H. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

(28) H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955).

(29) E. Campaigne and S. W. Osborn, *J. Org. Chem.*, **22**, 561 (1957).

(30) L. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946 (1951).

(31) H. Reihlen, E. Elben, and J. Everet, *Ann.*, **485**, 43 (1931).

the solution of VI which then was added to the I; chromatography of the resulting "red oil" gave crude IV and VII in yields of *ca.* 48% and 27% respectively (a control experiment gave IV in 53% yield and VII in *ca.* 23% yield); the water layer contained solid which was apparently polyacrylamide. That free radicals could form from diazonium salts under the conditions of the Leuckart reaction was suggested by diazotizing aniline and XXIX (0.1 molar solutions in 0.3*N* hydrochloric and sulfuric acid respectively), destroying excess nitrous acid (urea), and adding tetramethyl-*p*-phenylenediamine; with either solution, neutralization at 0° (sodium carbonate) resulted in the deep blue color of the Wurster salt. Similar unneutralized solutions were not colored at 0° but that from XXIX reacted vigorously and quickly became blue at 15–20°, unlike that from aniline which reacted vigorously only at 40–50° and became blue only near the end of reaction.

(e) *Independent synthesis of reaction products.* In the synthesis of IV, 2.77 g. of the presumed thiol III, prepared as described in 1(b), in benzene (10 ml.) was added to 0.99 g. of phosgene[32] in benzene (15 ml.). Dry pyridine (2.27 g.) was added. After the exothermic reaction, the mixture was heated 0.5 hr. under reflux and then was washed with 5% hydrochloric acid and water. Drying and removal of solvent left bis(2,6-dimethylphenyl) dithiolcarbonate (IV), m.p. 102–103.5°. After recrystallization, the melting point and mixture melting point with IV prepared as described in 1(a) were 103–104.5° (infrared spectra identical). A pungent chlorine-containing oil resulted when phosgene was bubbled through an alkaline solution of III; since it gave IV with more III and pyridine, it probably was the chlorothiolformate, 2,6-$(CH_3)_2C_6H_3S{\cdot}CO{\cdot}Cl$.

In the synthesis of VII, 4.00 g. of ethyl chlorothionoformate[33] (50% yield, but in carbon tetrachloride) was added to 4.5 g. of III in benzene (15 ml.) at 5°. Dry pyridine (5 g.) in benzene (15 ml.) then was added dropwise below 10°. The mixture was stirred overnight and allowed to warm to room temperature. The benzene solution was decanted from pyridine hydrochloride, washed with water, 5% hydrochloric acid, 5% aqueous sodium hydroxide, and dried. Removal of benzene left 4.2 g. of oil which was distilled in a short-path apparatus. The distillate (b.p. *ca.* 110–114°, 0.4 mm.), recrystallized from ethanol, gave 2.36 g. (32%) of 2,6-dimethylphenyl ethylxanthate (VII), m.p. 48–49°. Further recrystallization (ether) gave VII with a constant melting point, 48.5–49.5°.

Anal. Calcd. for $C_{11}H_{14}OS_2$: C, 58.37; H, 6.23; S, 28.33. Found: C, 58.56; H, 6.41; S, 28.33.

The *p*H of a solution of 0.11 g. of VII in ethanol (25 ml.)-water (6 ml.) containing 14 ml. of 0.11*N* aqueous sodium hydroxide remained that of a control (VII omitted) during 2 hr. at 25°. Heating at 50° caused a gradual decrease in *p*H from 10.7 to 10.1 in 2 hr.; after 24 hr. the *p*H was 10.6 and V had separated. When VII was heated at 133–139° (0.3 mm.) for 1.3 hr., 95% was recovered, m.p. and mixture m.p. 48–50°.

Authentic VIII was obtained[19,34] by heating 40.1 g. of I, 32.7 g. of ethyl bromide and 30 ml. of ethanol at 50° for 4.5 hr.; removal of solid, then of solvent, drying over sodium sulfate, and distillation gave 30.8 g. (82%); b.p. 85–87° (15 mm.), n_D^{25} 1.5350; phenylhydrazide m.p. 71–73.5° (reported,[19] m.p. 72–24°(*sic*); Chloramine-T derivative, m.p. 185–186° (reported,[19] m.p. 186–187.5°).[35]

Stability of VIII to conditions used in its washing after Leuckart reactions was demonstrated by shaking 10 drops with 1 ml. of 5% acid or base for 1 min. and allowing the mixture to stand for 2 hr.; there was negligible change in the volume of VIII (similar result after 2 hr. at 80°). In assessing stability under conditions of the Leuckart reaction itself (and the subsequent distillation), the reaction was performed exactly as in 1(c) but with addition of 6.91 g. of VIII along with the solution of VI to 19.9 g. of I in 100 ml. of water. Of the 8.86 g. of VIII isolated (n_D^{25} 1.5340–1.5354), the result of 1(c) had indicated that *ca.* 3.28 g. was formed in the reaction proper; hence the difference (5.58 g.) represented VIII which had survived from that added, indicating that only *ca.* 81% (5.58 × 100/6.91) of VIII formed in the Leuckart reaction can be expected to survive. Accordingly, to convert the % yield of VIII actually isolated to the yield probably formed in Leuckart reactions (the correction referred to in footnote c of Table I), it was multiplied by 1.24 (i.e., 6.91/5.58).

2. *Reactions of the 2,6-diethylbenzenediazonium salt* X. (a) *With* I. The diazonium salt X, prepared from 29.8 g. of 2,6-diethylaniline at −4 to −2° was poured during *ca.* 2 min. into 200 ml. of a hot solution of I as usual. The "red oil", subjected to careful partial distillation through a 6 × 260-mm. tube with a heated jacket, gave 3.98 g. (27%) of VIII, b.p. 47–48°, n_D^{25} 1.5290–1.5350. Of the 39.41 g. of undistilled residue, 9.65 g. was chromatographed. Elution with hexane gave 3.61 g. (29%) of 2,6-diethylphenyl ethylxanthate (XII), m.p. 40–43°, which was recrystallized from alcohol to a constant melting point, 43–44°.

Anal. Calcd. for $C\,_{3}H_{18}OS_2$: C, 61.37; H, 7.13; S, 25.20. Found: C, 61.44; H, 7.13; S, 24.87.

Thermal stability of the XII was demonstrated by recovery of 99% (m.p. and mixture m.p. 43–44°) after keeping under nitrogen for 6 hr. at 133–135°.

Further elution with hexane gave 1.10 g. of oil, probably XII mixed with bis(2,6-diethylphenyl) dithiolcarbonate (XI). Benzene elution then gave 3.51 g. (40%) of XI, m.p. 49–54°, which was recrystallized from ethanol to a constant melting point, 56.5–57.0°.

Anal. Calcd. for $C_{21}H_{26}OS_2$: C, 70.34; H, 7.31; S, 17.89. Found: C, 70.63; H, 7.36; S, 17.92.

More benzene gave 0.61 g. of unidentified solid, m.p. 32.5–36° (depressed by XI), after which benzene, ether, and ethyl acetate eluted 0.6 g. of gum.

(b) *With potassium benzylxanthate.* The salt X, prepared as in (a), was added rapidly to 55.14 g. of potassium benzylxanthate in 200 ml. of water at 50–60°. The "red oil" (61.57 g.) was isolated as usual. With no attempt to distil, 12.37 g. was chromatographed on alumina containing 1% by weight of "Luminescent Chemical 2 Yl."[36] Hexane eluted 5.41 g. (43%) of colorless 2,6-diethylphenyl benzylxanthate, m.p. 57–64.5°; recrystallization from alcohol gave material with a constant melting point, 65.5–66.0°.

Anal. Calcd. for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37; S, 20.26. Found: C, 68.07; H, 6.35; S, 20.26.

Further elution (hexane) gave 0.9 g. of oil and then 3.61 g. (50%) of oily XI. Three recrystallizations from ethanol gave XI, m.p. and mixture m.p. 53–57°, (1.32 g., 18%; the apparently low recovery probably resulted actually because of the presence of considerable benzyl benzylxanthate in the 3.61 g. of crude XI). Elution with more hexane, then benzene, gave 0.84 g. of oil.

(c) *With potassium isopropylxanthate.* The salt X, prepared as in (a), was added rapidly to 42.9 g. of potassium isopropylxanthate in 200 ml. of water at 50–60°. The "red oil" (50.99 g.) was isolated as usual, but as in 2(b) without distillation, and 10.06 g. was chromatographed. Hexane eluted 3.08 g. (29%) of presumed crude 2,6-diethylphenyl isopropylxanthate as oil, n_D^{25} 1.5452–1.5730. Benzene eluted 2.64 g. (37%) of crude XI, m.p. 51–56°, which after recrys-

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[32] H. Erdmann, *Ber.*, **26**, 1993 (1893).

[33] H. Rivier and P. Richard, *Helv. Chim. Acta*, **8**, 496 (1925).

[34] A. I. Vogel, *J. Chem. Soc.*, 1848 (1948).

[35] In our experience, this derivative should be purified immediately; delay may result in a compound melting at 121–122°.

[36] Photo Products Dept., Du Pont Co., Wilmington, Del. This mixture, which fluoresced under ultraviolet light except in regions containing fairly large amounts of adsorbed product, is similar to one used by J. F. Carson and F. F. Wong, *J. Org. Chem.*, **22**, 1725 (1957).

tallization (ethanol) amounted to 2.00 g. (28%), m.p. and mixture m.p. 54–56.5°.

3. *Reaction of the o-toluenediazonium salt* XIII. The procedures of 1(c) were duplicated with 10.7 g. of *o*-toluidine in lieu of XXIX. The "red oil" left after removal of ether was partially distilled as in 2(a); yield of VIII, 2.72 g. (36%), b.p. 44–70° (1–5 mm.) n_{D}^{25} 1.5354–1.5356. A portion (15.58 g.) of the undistilled residue (16.24 g.) was chromatographed. Hexane eluted 8.52 g. (42%) of *o*-tolyl ethylxanthate (XV), n_{D}^{25} 1.6050–1.6139, intermediate fractions of which after two distillations gave XV, b.p. 89° (0.5 mm.), n_{D}^{25} 1.6001.

Anal. Calcd. for $C_{10}H_{12}OS_2$: C, 56.56; H, 5.70; S, 30.20. Found: C, 56.31; H, 5.77; S, 30.77.

Elution with hexane and then benzene gave 6.57 g. (50%) of crude bis(*o*-tolyl) dithiolcarbonate (XIV; m.p. 40–47°) which, recrystallized from ethanol, gave 5.92 g. (45%) of XIV, m.p. 46–48°; after further recrystallization, the melting point was constant, 49–49.5°.

Anal. Calcd. for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14; S, 23.37. Found: C, 65.73; H, 5.12; S, 23.45.

Continued elution gave only 0.21 g. of gum.

4. *Reaction of the benzenediazonium salt* XVI. The usual procedure was followed, as in 1(c), with 18.6 g. of aniline, but with 21.8 ml. of sulfuric acid and with diazotization and neutralization at −4°. Partial distillation of the "red oil" as in 2(a) gave 2.67 g. (18%) of VIII, b.p. 55–72° (3 mm.), n_{D}^{25} 1.5353–1.5358. Of 30.61 g. of undistilled residue, 11.54 g. was chromatographed. Hexane eluted 7.4 g. (50%) of oily phenyl ethylxanthate (XVIII), n_{D}^{25} 1.6043–1.6267, which upon distillation gave 5.30 g. (36%) of XVIII, b.p. 92–120° (0.4–0.6 mm.), n_{D}^{25} 1.6064–1.6156; recrystallization of the less volatile pot residue (1.3 g.) gave 0.3 g. of phenyl disulfide, m.p. and mixture m.p. 59.5–61° (9% of phenyl disulfide was obtained in another experiment in which an attempt was made to separate the products in the "red oil" by distillation). Fractional distillation of the crude XVIII gave material boiling at 110–111° (1.3 mm.), n_{D}^{25} 1.6078; reported,[37] b.p. 155° (16 mm.).

Anal. Calcd. for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 54.82; H, 4.85; S, 31.83.

Elution with benzene then gave 2.8 g. (30%) of crude phenyl dithiolcarbonate (XVII). Recrystallization from ethanol left 1.00 g. (11%), m.p. 40–42°; further recrystallization gave XVII, m.p. and mixture m.p. 41–43° (authentic XVII was prepared in 73% yield using phosgene as described for IV, m.p. 41–43°).[38] Elution finally with ethyl acetate gave only gum (0.6 g.).

In determining the thermal stability of XVII, it was heated at 160–170° for 6 hr. with 100% recovery (m.p. and mixture m.p. 42–43°), and at 304° for 0.5 hr. with 35% conversion to phenyl disulfide (m.p. and mixture m.p. 58–60°); 85% was recovered (m.p. and mixture m.p. 42.5–44°) after distillation at 164–170° (0.6–1 mm.).

5. *Reactions of the p-methoxybenzenediazonium salt* XIX. So that the reactions of XIX and XXII would be comparable, the diazotization of 12.3 g. of *p*-anisidine was performed much like that in 6, by dissolving it in water (120 ml.) containing sulfuric acid (10 ml.), cooling rapidly in ice-salt and adding, in one portion, 35 ml. of a cold solution of sodium nitrite (6.9 g.) in water (40 ml.); 7 ml. more was required for a positive starch-iodide test. The neutralized solution was added to I and the "red oil" was partially distilled as in 1(c). The yield of VIII was 1.51 g. (20%); b.p. 34–38° (1.3 mm.), n_{D}^{25} 1.5355–1.5367.

Chromatography of 7.14 g. of the 18.66 g. of undistilled residue and elution with hexane gave 3.12 g. (36%)[39] of crude *p*-methoxyphenyl ethylxanthate (XXI), n_{D}^{25} 1.6082–1.6272. Two distillations gave XXI, b.p. 82–84° (0.05 mm.), n_{D}^{25} 1.6073.

Anal. Calcd. for $C_{10}H_{12}O_2S_2$: C, 52.60; H, 5.30; S, 28.08. Found: C, 52.12; H, 5.46; S, 28.86.

Further elution gave 1.19 g. (20%) of crude bis(*p*-methoxyphenyl) dithiolcarbonate (XX), m.p. 94–109°; recrystallization (ethanol-benzene) gave 0.72 g. (12%), m.p. 107–110°, and ultimately XX with a constant m.p. of 110–111°.

Anal. Calcd. for $C_{15}H_{14}O_3S_2$: C, 58.80; H, 4.60. Found: C, 59.03; H, 4.65.

Benzene and ethyl acetate eluted only gum (0.5 g.).

To ascertain whether 4,4′-dimethoxybiphenyl might have been formed, part of the "red oil" was saponified and the mixture then steam distilled. No biaryl was isolated, although biphenyl easily steam-distilled when a sample was added to the saponification mixture.

6. *Reaction of the p-nitrobenzenediazonium salt* XXII. *p*-Nitroaniline was diazotized[40] by dissolving 13.8 g. in water (60 ml.) and concd. sulfuric acid (15 ml.), adding ice (100 g.), chilling to −3°, and adding in one portion a cold solution of 7.68 g. of sodium nitrite in water (40 ml.). The mixture was stirred for 15 min., neutralized, and added to I (2 min.). Instead of immediate evolution of nitrogen and formation of oil, a bright red solid formed; it persisted for several seconds and then decomposed with a loud hiss to a dark oil. Heat was removed and the mixture was stirred for 15 min. (once, the red solid decomposed only during this period). The ether (and 100 ml. of benzene) extract of the crude reaction product was washed and dried as usual. Upon removal of most of the ether and some benzene, 1.17 g. (7%) of bis(*p*-nitrophenyl) dithiolcarbonate (XXIII) crystallized, m.p. 179.5–184°.

Attempted distillation of a similar reaction mixture at bath temperatures up to 120°, at which VIII usually distilled (1 mm.), had given no appreciable distillate. In the present experiment, distillation of 8.99 g. of the "red oil" (21.12 g.; obtained as usual after removal of the XXIII and concentration) did yield 0.70 g. (22%) of VIII, b.p. 44–151° (2–3 mm.), n_{D}^{25} 1.5363; however, the bath temperature required was 155–197° rather than the usual 125°.

Since this VIII might have been produced by thermal decomposition, another portion (5.04 g.) of the "red oil" was chromatographed directly. Hexane eluted 0.36 g. of oil; this, distilled, yielded material with an infrared spectrum much like that of VIII but this distillate probably contained little VIII since it lacked three infrared absorption bands of the VIII and had n_{D}^{25} 1.6250–1.6270.[41] Benzene (150 ml.) then eluted 2.44 g. (42%) of *p*-nitrophenyl ethylxanthate (XXIV), m.p. 34–56°; recrystallization (ethanol) gave 1.92 g. (33%), m.p. 47–51° and finally white XXIV with a constant m.p. 49.5–50°.

Anal. Calcd. for $C_9H_9NO_3S_2$: C, 44.43; H, 3.73. Found: C, 44.39; H, 3.80.

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(37) H. Rivier, *Bull. soc. chim. France*, (4) **1**, 738 (1907).

(38) Reported melting points usually have been in the range of 41–44° (*e.g.*, D. G. Crosby and C. Niemann, *J. Am. Chem. Soc.*, **76**, 4463 (1954), but 63° has been reported (G. Daccomo; *cf. Beilstein's Handbuch*, **6**, 312).

(39) Includes XXI from a second chromatogram of a large end fraction; the second chromatogram also gave 0.97 g. of oil (n_{D}^{25} 1.6483–1.6495), which solidified, and 0.73 g. of a solid, neither of which were studied further.

(40) Ref. 3, p. 6.

(41) If VIII were formed in this Leuckart reaction, it should have been present in this fraction. Since its failure to form would be exceptional, this part of the experiment was repeated, but still with inconclusive results. Although distillation of the hexane effluent from the second reaction unquestionably gave VIII (17%; b.p. 47–60° (5–6 mm.), n_{D}^{25} 1.5348–1.5352) again high bath temperatures were required (152–225°). Accordingly, while VIII *seems* to be a genuine product of reaction, there is a definite possibility that it is produced instead by thermal decomposition. *p*-Nitrophenyl ethylxanthate (XXIV) was shown to be thermally stable: after 6 hr. under nitrogen at 133–135°, 96% was recovered, m.p. and mixture m.p. 46.5–48°.

Further elution with benzene gave an intermediate fraction (0.6 g.) and then 0.80 g. (20%) of presumed XXIII, m.p. *ca.* 150–178°, which upon recrystallization from benzene gave 0.68 g. (17%; m.p. 178.5–184°) and finally colorless XXIII with a constant m.p. 183.5–184.5°; reported,[42] 174.5°.

Anal. Calcd. for $C_{13}H_8N_2O_5S_2$: C, 46.42; H, 2.40; S, 19.07. Found: C, 46.79; H, 2.69; S, 19.00.

Elution with ethyl acetate gave only gum (0.7 g.) and 0.13 g. of a solid (m.p. 160–173°, different from XXIII).

Acknowledgment. The authors are indebted to the Office of Ordnance Research, U. S. Army, for generous financial support of this investigation.

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[42] W. R. Waldron and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 2403 (1923).

[CONTRIBUTION FROM THE RADIUM INSTITUTE OF THE UNIVERSITY OF PARIS]

Orientation in Friedel-Crafts Acylations of 6-Substituted Chrysenes

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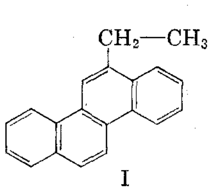
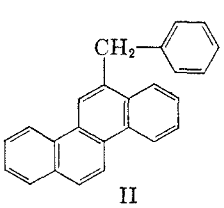
The Friedel-Crafts acylations of 6-ethyl- and 6-benzylchrysene are shown to take place in position 12; in the case of 6-benzylchrysene and acetyl chloride some disubstitution occurs, to give a diketone whose constitution is shown to be 6-(4′-acetylbenzyl)-12-acetylchrysene.

Whereas there is abundant proof[1] that Friedel-Crafts reactions with chrysene occur preferentially in position 6, the orientation in similar substitution reactions with 6-alkylchrysenes has hitherto not been investigated. In theory, such reactions should lead to 12-substituted derivatives, the positions 6 and 12 in the molecule of chrysene being the most reactive sites in view of their high free valence index.[2] Furthermore, we recently established that 6-ethylchrysene undergoes nitration to give 6-ethyl-12-nitrochrysene.[3]

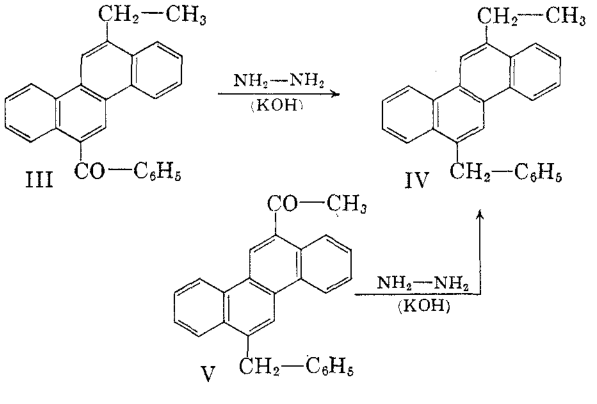
The present work records the results of Friedel-Crafts acylations of 6-ethylchrysene (I) and 6-benzylchrysene (II). The aluminum chloride-catalyzed reaction of benzoyl chloride with (I), using carbon disulfide as the solvent, had been studied by Funke and Ristic,[4] who obtained a monoketone whose structure they did not investigate. We now found that this ketone readily underwent Wolff-Kishner reduction to give a 6-ethyl-x-benzylchrysene. The same hydrocarbon was obtained when 6-benzylchrysene was submitted to acetylation with acetyl chloride and aluminum chloride and the resulting ketone reduced by the Wolff-Kishner method. The fact that the same hydrocarbon was obtained in these two sets of reactions shows that it was 6-ethyl-12-benzylchrysene (IV), the starting ketones therefore being, respectively, 6-ethyl-12-benzoylchrysene (III) and 6-benzyl-12-acetylchrysene (V). These experimental results confirm those obtained by π-electron density computations as regards the pronounced reactivity of both positions 6 and 12 in the molecule of chrysene.



I



II



It is of interest to note that in the Friedel-Crafts acetylation of 6-benzylchrysene, small amounts of a diketone were obtained along with the monoketone (V). This by-product was found to be 6-(4′-acetylbenzyl)-12-acetylchrysene (VI), as it underwent Wolff-Kishner reduction to a hydrocarbon, which could also be prepared in a different way, *viz.* Friedel-Crafts acylation of 6-ethylchrysene with *p*-ethylbenzoyl chloride followed by reduction of the ensuing ketone, which therefore must have been 6-ethyl-12-(4′-ethylbenzoyl) chrysene (VII). Hence, the hydrocarbon in ques-

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[1] See, for instance, F. Bergmann and H. E. Eschinazi, *J. Am. Chem. Soc.*, **65**, 1413 (1943); N.P. Buu-Hoï, *J. Org. Chem.*, **19**, 721 (1954).

[2] *Dictionary of Values of Molecular Constants (calculated theoretically by Wave Mechanical Methods)*, Vol. II, p. 29 (C. A. Coulson and R. Daudel, eds., Oxford and Paris).

[3] P. Mabille and N. P. Buu-Hoï, *J. Org. Chem.*, **25**, 216 (1960).

[4] K. Funke and J. Ristic, *J. prakt. Chem.*, [2] **146**, 151 (1936).