[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Evidence for 1,4- and 1,6-Reductions of *cis* and *trans*-Phenyldibenzoylethylenes

BY ROBERT E. LUTZ AND CARL R. BAUER[1]

cis- and *trans*-phenyldibenzoylethylenes are reduced by zinc and acetic acid under comparable conditions to mixtures of the saturated 1,4-diketone and furan in widely differing ratios; the *cis*-isomer gives the smaller yield of furan. Taking into account the probable fine-structures of these compounds and the probable mechanism of reduction, involving free-radical transition states and enolate intermediates, it is concluded that *trans*-phenyldibenzoylethylene undergoes entirely 1,6-reduction and that the *cis* isomer resists this type of reduction and undergoes instead, or also to a very significant extent, 1,4-reduction of the benzalacetophenone system present.

This paper is based on an observation that under comparable conditions *cis*- and *trans*-phenyldibenzoylethylenes (I, II; R = H, R′ = C_6H_5) are reduced by zinc and concd. acetic acid to mixtures of the saturated 1,4-diketone (VII) and furan (IX) with the yield of furan very much higher from the *trans* isomer than from the *cis*. This difference in yield-ratios and especially its direction had at first seemed surprising in the light of the concept of conjugate reduction,[2] and in view of the greater ease of the acid-catalyzed addition–furanization of the *cis*-isomer by nucleophilic reagents such as the combination acetic anhydride and sulfuric acid.[3] It is in sharp contrast to the quantitative identity of the yield-ratios in the reduction under controlled conditions of the symmetrically substituted *cis* and *trans*-1,2-dimethyl-1,2-dimesitoylethylenes,[2e] $C_9H_{11}COC(CH_3){=}C(CH_3)COC_9H_{11}$. The evidence is considerable that unsaturated 1,4-diketones generally undergo conjugate reductions, but only a part of this evidence points unequivocally to 1,6-addition and the actual formation of the diene-diol of the type V; cyclic aldolization and furanization during reduction show only that reaction does not occur directly at the ethylene double bond and must involve the conjugated system, but it does not exclude the possibility of 1,4-reduction to a monoenol such as VI. It is logical to assume that the 1,6-reduction mechanism holds generally however because in analogy with the reduction of quinone one must suppose the reaction to be stepwise and to involve an unstable free radical transition state such as III which represents resonance forms contributing toward the structure and which is analogous to semiquinone. 1,4-Reduction to, and 1,4-oxidation of, monoenolates such as VI should occur far less readily than 1,6-reduction and 1,6-oxidation because of the necessarily higher energy of the free radical transition state in this case (XI *vs.* III) where there exists lesser possibilities for resonance.

Furanization, which can hardly occur by direct interaction of two dienediol hydroxyls under the mild conditions usually involved in the reductions, doubtless proceeds through the monoenolate (VI) followed by formation and dehydration of the cyclic hemiacetal [VI(b) → VIII → IX] and competing ketonization to the saturated 1,4-diketone [VI(a) → VII]. The configuration of the monoenolate must be as depicted, and only this configuration should permit furanization.

Recent ultraviolet spectral studies of the *cis* and *trans* unsaturated 1,4-diketones[4] indicate that in most cases both isomers have essentially comparable structures which approach planarity and are arranged as indicated in formulas I and II. It is logical to assume the maintenance during reduction of a significant degree of over-all planarity which would be necessary for effective resonance in the transition state (III). Consequently there is reason to suppose that the unstable diene-diol (V), the first intermediate product capable of appreciable life, would have the specific configuration indicated and postulated[2] as essential for furanization, but the original *cis–trans* configurational arrangements at the central double bond must now be lost and the identity of the ratios of the final products would be a necessary consequence.

Incidentally it should be noted that the formation of an enolate of the specific configuration depicted in the reductions above, is the same as has been postulated in 1,4-addition of the Grignard reagent to typical α,β-unsaturated ketones and required of a mechanism involving a cyclic transition state.[2k] It would therefore seem that the cyclic transition state in the 1,4-addition of the Grignard reagent is not necessary since the probable spatial alignment of the carbonyl group would be such as to give the specific postulated enolate in any case, and that if it is involved in favorable cases it probably is not of general importance since there exist cases of 1,4- and 1,6-additions of the Grignard reagent where this mechanism is impossible.[5]

We were led by the recent spectroscopic study of the fine structures of the unsaturated 1,4-diketones to be on the watch for differences in the yield-ratios of saturated diketone and furan in reductions of any pair of *cis* and *trans* isomers which showed significant differences in ultraviolet absorption characteristics, and we were not surprised to find the difference in the case of the *cis*- and *trans*-phenyldibenzoylethylenes. A logical explanation for *this specific case*, in contrast to others which might be regarded as normal and in which

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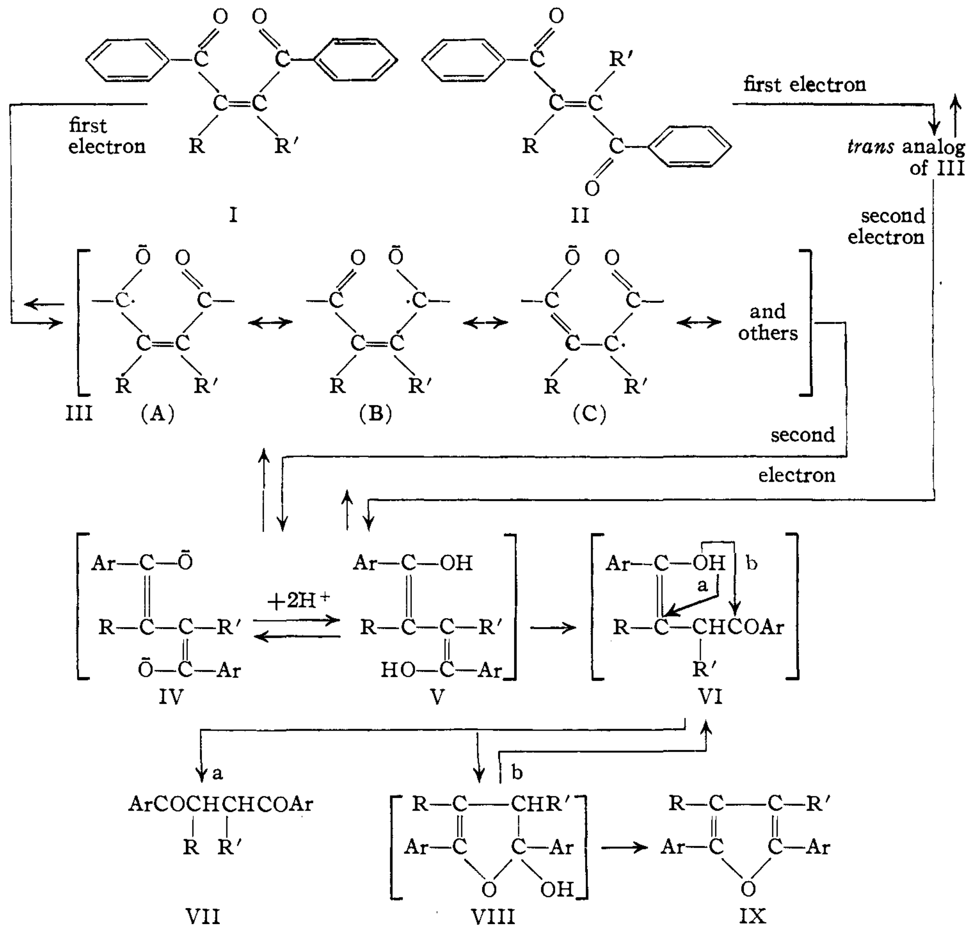
(1) Holder of a du Pont Co. Fellowship, 1949–1950.

(2) J. B. Conant and R. E. Lutz, THIS JOURNAL, (a) **45**, 1047 (1923). (b) **46**, 1254 (1924); (c) **49**, 1083 (1927); (d) R. E. Lutz, *ibid.*, **51**, 3008 (1929); (e) R. E. Lutz and R. J. Taylor, *ibid.*, **55**, 1593 (1939); R. E. Lutz and F. S. Palmer, *ibid.*, **57**, (f) 1947, (g) 1953, (h) 1957 (1935); (i) R. E. Lutz and J. L. Wood, *ibid.*, **60**, 7051 (1938); R. E. Lutz and W. G. Reveley, *ibid.*, (j) **61**, 1854 (1939); (k) **63**, 3180 (1941); (l) R. E. Lutz and C. J. Kibler, *ibid.*, **62**, 360 (1940).

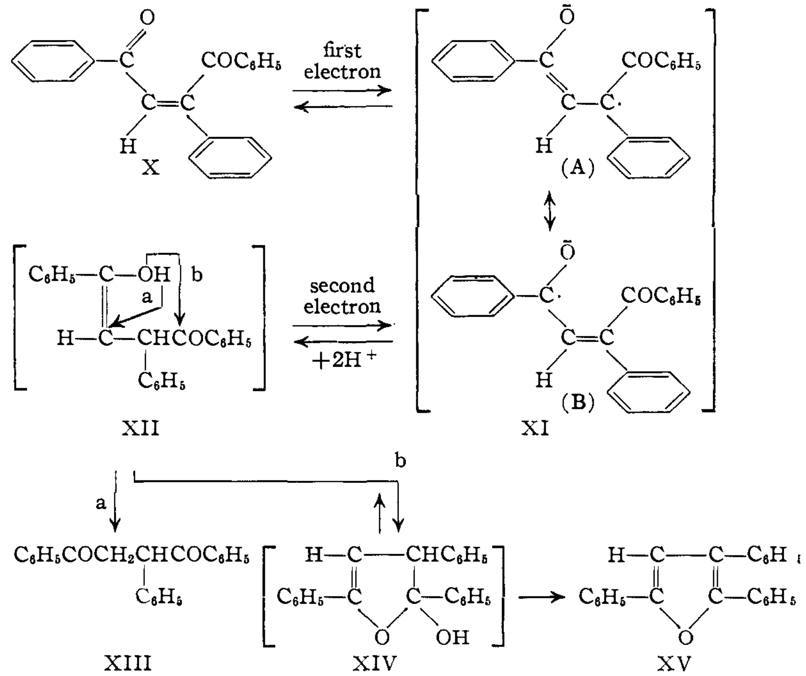
(3) (a) R. E. Lutz and C. E. McGinn, *ibid.*, **64**, 2585 (1942); (b) R. E. Lutz and P. S. Bailey, *ibid.*, **67**, 2229 (1945); (c) *cf.* also results to be published shortly [C. R. Bauer, Dissertation, University of Virginia (1950)].

(4) L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950).

(5) *Cf.* P. L. Julian and W. Cole, *ibid.*, **57**, 1607 (1935); P. L. Julian and W. J. Gist, *ibid.*, **57**, 2030 (1935); F. C. Whitmore and G. W. Pedlow, *ibid.*, **63**, 758 (1941).

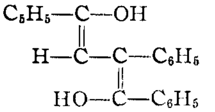


such differences should not appear, is derivable on theoretical grounds from a comparison of the ultraviolet absorption characteristics of these and the various other unsaturated 1,4-diketones.[4] Of the compounds studied so far of the type I–II, the molecules of all but one are clearly of one type and involve effective conjugation throughout the central aliphatic systems including both terminal oxygens. The one exception is *cis*-phenyldibenzoylethylene (X) where, in contrast with its *trans*-isomer which evidently has a normal unsaturated 1,4-diketone system, the *cis*-isomer appears to be non-planar with respect to this system and to consist of a planar *trans*-benzalacetophenone system with the remaining benzoyl group functioning simply as a substituent on this system and non-coplanar with it, as shown in formula X. A normal and planar resonance-stabilized semiquinone analog of the type III would either not be possible here or would be seriously impeded, and the normal and facile 1,6-reduction therefore would be either inhibited or suppressed to a significant extent. The benzalacetophenone system if it were to function completely independently of the non-coplanar benzoyl group, would be of a lower order of reducibility than the normal unsaturated 1,4-diketone system but it would be reduced (1,4-) much more readily



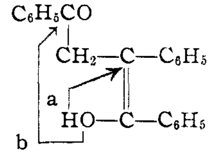
than the independent benzoyl group because here the free-radical transition state would involve an appreciable degree of resonance stabilization (*cf.* XI). The mono-enol (XII) would be the first product capable of free existence and it would necessarily have the configuration indicated. Here the cyclization to the furan would not be favored because this particular one of the two possible mono-enolates, in the absence of the stabilizing effect of the α-phenyl, would be quickly ketonized and of short life, whereas the carbonyl with which it must react in order for furanization to occur, would be relatively unreactive due to the phenyl group alpha to it.

The greater relative yield of the furan in the reduction of the *trans* compound is accounted for by the reasonable assumption that the dienediol first formed by unimpeded 1,6-reduction (XVI) would ketonize most rapidly at the enol carrying the lesser substitution, to give the isomeric mono-enol (XVII) which is then capable of competing ketonization (XVIIa) and furanization (XVIIb), but which would necessarily involve reaction between the longer-lived of the two possible mono-enolate groups and the remaining (and least-hindered) of the two possible carbonyl groups.



$$\begin{array}{l} C_6H_5\text{—}C\text{—}OH \\ \qquad \| \\ H\text{—}C\text{—}C\text{—}C_6H_5 \\ \qquad\quad \| \\ \quad HO\text{—}C\text{—}C_6H_5 \end{array}$$

XVI



XVII

It might be argued that the hindrance by the α-phenyl at the carbonyl remaining after 1,4-reduction (XII) should very seriously impede and perhaps almost entirely prohibit furanization under the circumstances; furthermore it may be unreasonable to assume that the postulated non-planarity between the benzalacetophenone and benzoyl systems in X is absolute here. A certain amount of 1,6-reduction might well occur also, although presumably under such interference as would significantly lower the reduction potential of the system and prevent the 1,6-reduction from outright dominance. The absence of dimolecular reduction here, which is prominent in the comparable reduction of *trans*-benzalacetophenone itself may be of some significance in this connection.

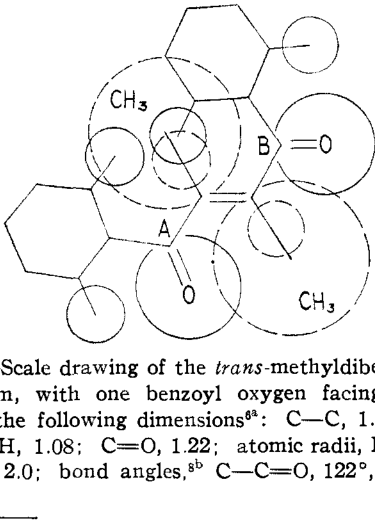


Fig. 1.—Scale drawing of the *trans*-methyldibenzoylethylene system, with one benzoyl oxygen facing outward, based on the following dimensions[6a]: C—C, 1.54; C=C, 1.33; C—H, 1.08; C=O, 1.22; atomic radii, H, 0.75; O 1.4; CH_3, 2.0; bond angles,[8b] C—C=O, 122°, C=C—C, 124.

In the above speculations both benzoyl oxygens of the *cis* and *trans* unsaturated 1,4-diketones are assumed to face inward toward the central double bond. Scale drawings based on van der Waals radii showing approximate relative interferences between groups indicate that this would undoubtedly be true in most cases including *cis*-phenyl-, methyl- and bromodibenzoylethylenes, but that it is less certain for the *trans*-isomers of these three compounds. A drawing for *trans*-methyldibenzoylethylene analogous to those in a preceding paper[4] but with one of the two benzoyl oxygens facing outward (Fig. 1) indicates that the benzoyl with the methyl beta to it will be least hindered when its oxygen faces inward (B) rather than outward (A), as has been assumed. However, the benzoyl with a methyl alpha to it would involve more nearly equal interferences with the two coplanar arrangements; when its oxygen is facing outward a modest overlap occurs in two directions whereas when this oxygen faces inward there is more serious overlap but in one direction only. In favor of the latter as the more stable arrangement in the analog with bromine or a non-coplanar phenyl as the alpha-substituent (groups which are not far different from the methyl in effective interference diameters), is the fact that electrostatic repulsions would be considerably less in this arrangement; furthermore the arrangement is analogous to that in the 3-substituted-2,5-diphenylfurans where the 3-methyl, phenyl or bromine appear to offer negligible interference with the effectiveness of the 1,4-diphenylbutadiene system.[7] This arrangement (A), but not the other is consistent with the fact that furanization occurs extensively during reduction of the *trans* isomer, and with the postulated mechanism outlined above.

Long standing and then seemingly anomalous data obtained in attempts to estimate the reduction potentials of unsaturated 1,4-diketones[2a,c,8] are now understandable in the light of the above discussion and lend support to the conclusions drawn. The "apparent reduction potentials," which are the arithmetical means of the oxidation–reduction potentials of two reducing combinations, the one of lowest potential capable of slowly reducing the compound in question and the other of nearest higher potential which is not, are on the order of +0.06 to 0.27 volt. In the case of one of the two really striking exceptions, namely, *cis*-phenyldibenzoylethylene ("dibenzoylstyrene") (X), the "apparent reduction potential" is below −0.4 volt and much too low for a true or normal unsaturated 1,4-diketone system, but it

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(6) (a) It should be recognized that the normal bond distances and angles given probably are affected in some slight degree by the conjugation of these groups. (b) These values were actually used for Fig. 1 of ref. 4 and should be substituted for the erroneous figures given under that diagram.

(7) S. M. King, C. R. Bauer and R. E. Lutz, THIS JOURNAL, **72**, 5058 (1950).

(8) (a) *Cf.* ref. 2c, page 1089; (b) J. B. Conant and H. B. Cutter, *J. Phys. Chem.*, **28**, 1096 (1924).

appears to be consistent with expectation based on present theory. The other exception is benzoyltrimethylacetylstyrene, $C_6H_5COC(C_6H_5)=CH-COC(CH_3)_3$, which is *cis*[9] and doubtless also is nonplanar with respect to the unsaturated 1,4-diketone system.

Further studies on *cis–trans* relationships in this field are in progress.

Experimental

The reductions of samples of the *cis-* and *trans*-phenyldibenzoylethylenes were run under conditions which were identical in all details.

A solution of 0.250 g. of the *cis*-unsaturated diketone in 10 ml. of concd. acetic acid was brought to 100° in a steam-bath. Half a gram of zinc dust was added and the mixture was stirred manually for 2 min. The mixture was filtered; the zinc residue was washed with 1 ml. of hot, and 1 ml. of cold solvent: 1.2 ml. of alcohol was added to the filtrate and water until turbidity developed; upon cooling to 0° 0.120 g. of 2,4,5-triphenylfuran was obtained; further addition of water and cooling gave an additional 0.025 g.; total yield 37.5% (61.2% from the *trans*-isomer); a third addition of water and cooling gave 0.026 g. of phenyldibenzoylethane and a fourth treatment gave an additional 0.030 g.; total yield 50.1% (22.3% from the *trans*-isomer). The products were practically pure and were identified by mixture melting points with authentic samples; total yield of products from *cis*, 87.6%, and from *trans*, 83.5%.

Charlottesville, Va.

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[9] R. C. Downing, Dissertation, University of Virginia (1941).

[Contribution from the Naugatuck Chemical Division, United States Rubber Company]

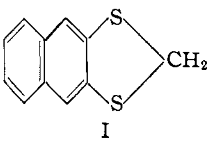
The Reaction of 2,3-Dichloro-1,4-naphthoquinone with Salts of Alkyl Substituted and Unsubstituted Dithiocarbamic Acids

By Norman K. Sundholm and Allen E. Smith

A study of the reaction of 2,3-dichloro-1,4-naphthoquinone with salts of dithiocarbamic acids was undertaken in order to prepare new fungicides. With amine salts of methyl- and ethyldithiocarbamic acids the metathetical products IIa and IIb cyclize during heating by elimination of hydrogen chloride to produce compounds for which the structure 2-alkyliminonaphtho-[2,3]-1,3-dithiole-4,9-dione (IIIa and IIIb) is in accord with the present experimental evidence. With dimethylammonium dimethyldithiocarbamate a quaternary salt is obtained. Since it gives the same hydrolysis product, believed to be naphtho-[2,3]-1,3-dithiole-2,4,9-trione (VII), as 2-methyliminonaphtho[2,3]-1,3-dithiole-4,9-dione affords, and gives the latter on pyrolysis, it should also have the naphtho[2,3]-1,3-dithiole ring system. This is the first time that compounds having this ring system are reported. With ammonium dithiocarbamate the only product isolated was dibenzo[b,i]thianthrene-5,7,12,14-tetrone; a likely route for its formation is presented.

With the hope of preparing compounds which would combine the high fungitoxic activities of 2,3-dichloro-1,4-naphthoquinone[1] and of salts of certain dithiocarbamic acids,[2] a study of the reaction of the dichloroquinone with equimolar amounts of amine salts of alkyl-substituted dithiocarbamic acids and ammonium dithiocarbamate was made.

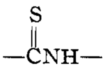
When amine salts of alkyl-substituted acids are employed, compounds which are believed to be derivatives of naphtho[2,3]-1,3-dithiole (I) are formed. This is the first time that compounds having this ring system are reported.



I

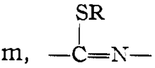
Treatment of 2,3-dichloro-1,4-naphthoquinone in aqueous suspension with an equimolar amount of methylammonium methyldithiocarbamate gives a crude product containing 9.12% chlorine. Very likely this product consists principally of IIa. When it is recrystallized from ethanol, a compound containing no chlorine and having an analysis consistent with IIIa or IV is obtained.

It has been well demonstrated that compounds containing the



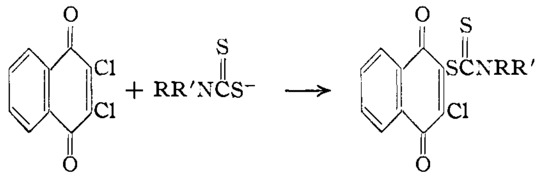
$\overset{\displaystyle S}{\overset{\|}{-\text{C}}}\text{NH}-$

group are alkylated on the sulfur atom,

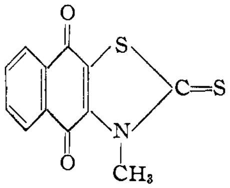


$\overset{\displaystyle \text{SR}}{\overset{|}{-\text{C}}}=\text{N}-$

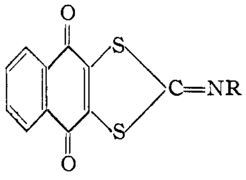
being formed. This has been observed with thioureas,[3] thioamides,[4] and, which concerns us more here, dithiocarbamic esters.[5]



IIa, R = CH_3, R′ = H
IIb, R = C_2H_5, R′ = H
IIc, R = R′ = CH_3



IV



IIIa, R = CH_3
IIIb, R = C_2H_5

By treating dithiocarbamic esters having at least one hydrogen atom attached to nitrogen with an alkyl iodide Delépine obtained the hydriodide (V) of an imidodithiocarbonic ester. Acid hydrolysis of the imido ester gave the ester (VI).

Compound IIa is such a dithiocarbamic ester; in addition it contains an alkylating center, the 3-carbon atom linked to a reactive chlorine atom. If

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[1] W. P. ter Horst and E. L. Felix, *Ind. Eng. Chem.*, **35**, 1255 (1943).

[2] M. C. Goldsworthy, E. L. Green and M. A. Smith, *J. Agr. Research*, **66**, 277 (1943).

[3] R. Connor, "Organic Sulfur Compounds," Chapt. 10 in H. Gilman's "Organic Chemistry," Sec. Ed., John Wiley and Sons. Inc., New York, N. Y., 1942, p. 841.

[4] S. Gabriel and Ph. Heymann, *Ber.*, **24**, 783 (1891).

[5] M. Delépine, *Bull. soc. chim. France*, [3] **27**, 57, 585 (1902); [3] **29**, 53, 59 (1903).