The Reaction of 5-Unsubstituted-1,2-Dithiole-3-thiones with some Activated Acetylenes

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5-Unsubstituted 1,2-dithiole-3-thiones undergo addition reactions with dimethyl acetylenedicarboxylate and dibenzoylacetylene to give amorphous 2-thioformylmethylene-1,3-dithioles. In certain cases these may undergo further addition of activated acetylene to give thiopyranspiro-1,3-dithioles, but may also lose sulfur to give bis-1,3-dithiolylidene-2-butenes, which are probably formed via initial dimerization of the thioformylmethylenedithioles. The stereochemistry of the products is discussed briefly.

Les dithiol-1,2 thiones-3 non substitués en -5 subissent des réactions d'addition avec l'acétylènedicarboxylate de diméthyle et le dibenzoylacétylène pour donner les thioformylméthylène-2 dithioles-1,3 amorphes. Dans certains cas, ceux-ci peuvent additionner de l'acétylène activé pour donner les bis-dithiolylidène-1,3 butènes-2; ces derniers sont probablement formés par une dimérisation initiale des thioformylméthylènedithioles. La stéréochimie des produits est discutée brièvement.

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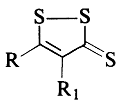
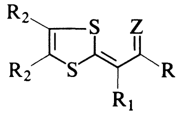
While the reaction of various activated acetylenes with 1,2-dithiole-3-thiones **1** has been studied extensively (1–5), most of these reactions have involved the use of 5-substituted 1,2-dithiole-3 thiones **1***a*. The initial products of the reaction are then 3-thioacylmethylene-1,3-dithioles **2***a*, formed by addition to the thione. Likewise, the reaction of 5-unsubstituted-1,2-dithiole-3-thiones **1***b*, would provide 3-thioformylmethylene-1,3-dithioles, **3**. These, being thials, would be expected to be much less stable than the thiones **2** (6). Little is reported on this type of reaction, but 4-phenyl-1,2-dithiole-3-thione (**1***c*) reacted with dibenzoylacetylene (5) to produce an unstable adduct which was demonstrated to be a thial, and **1***c* reacted with ethyl phenylpropiolate to give a product formed via a thial intermediate (7). It seemed desirable to investigate these reactions further to identify intermediates and products. It was also interesting to determine if the initial adducts reacted with more activated acetylene to form the spiran di-adducts **4** of the type reported for other 5-substituted-1,2-dithiole-3-thiones (3, 5). Most of our studies were performed on 1,2-dithiole-3-thione (**1***d*) and 4-phenyl-1,2-dithiole-3-thione (**1***c*). The activated acetylenes were dimethyl acetylenedicarboxylate and dibenzoylacetylene, and in one case, ethyl phenylpropiolate.

1,2-Dithiole-3-thione (**1***d*) reacted with 1 equiv of dimethyl acetylenedicarboxylate at room tem-



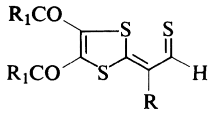
1

a $R' = H$
b $R = H$
c $R = H; R_1 = Ph$
d $R = R_1 = H$



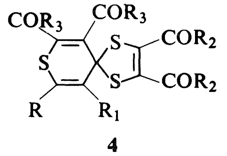
2

a $Z = S$
b $Z = O$



3

a $R = H; R_1 = OMe$
b $R = H; R_1 = Ph$
c $R = Ph; R_1 = OMe$
d $R = Ph; R_1 = Ph$

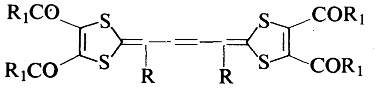


4

a $R = R_1 = H; R_2 = Ph; R_3 = OMe$
b $R = H; R_1 = Ph; R_2 = R_3 = OMe$
c $R = H; R_1 = R_2 = R_3 = Ph$

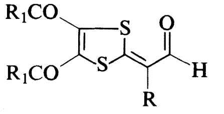
perature to provide two compounds, after only a short reaction time (3 h). The major component, which was not crystalline and was unstable, is probably the compound **3***a*, since its n.m.r. indicated the presence of a proton within the accepted range for thials (8).

A minor component was the only product identified when the reaction was allowed to proceed for 1 day, although then two other products were obtained as uncrystallizable glasses. This other component was probably the tetra-carboxylic ester **5***a* which could have been formed by extrusion of the thial sulfur atoms from two molecules of the thial **3***a*. Confirmation of this was achieved by heating **3***a* in benzene. From the solution **5***a* was obtained, although there were a number of other minor products. Treatment of the thione **1***d* with excess acetylenic ester gave rather similar results. Under no conditions were we able to obtain any diadduct of the type **4**.



5

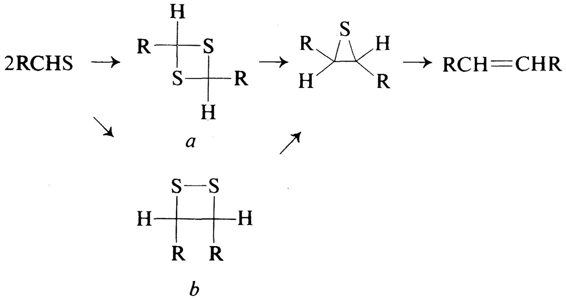
a R = H; R$_1$ = OMe
b R = H; R$_1$ = Ph
c R = Ph; R$_1$ = OMe
d R = R$_1$ = Ph



6

a R = Ph; R$_1$ = OMe
b R = R$_1$ = Ph

The compounds **5***a* could exist as two geometrical isomers with respect to the central double bond, but we are unable to distinguish what was actually formed, although the *trans* form seems more likely. This compound is probably formed by stepwise extrusion of two sulfur atoms from an initially formed dithiacyclobutane (Scheme 1). Presumably the formation of pyrylenes and dithiopyrylenes (9) from 4*H*-pyran-4-thiones and 4*H*-thiopyran-4-thiones proceeds via a similar scheme. Although the formulation "*b*" of the dimer cannot be excluded, the structure "*a*" appears more likely on the basis of results with other thiocarbonyl compounds. Such dimers are well known (10), although trimers may also be obtained. Thiaphosgene forms dimers (11, 12) and recently such intermediates have been proposed in the reaction of carbon disulfide with dimethyl acetylenedicarboxylate (13). No direct evidence appears to be available for the loss of sulfur from "*a*" to form the episulfide, but certain thiones under the influence of acetylides form both dithiacyclobutanes and episulfides (14). Possibly the former are precursors of the latter. Also, a dithiacyclobutanedioxide loses sulfur dioxide to form an episulfide (15). The last stage in the proposed scheme, the loss of sulfur from the episulfide to form the olefine, is a well-known reaction (16, 17). The geometry of the olefine would be determined by that of the initially formed dithiacyclobutane "*a*" or possibly "*b*". Although a *trans* geometry appears more likely, *cis* cannot be excluded. *Trans* products are common in many such cycloadditions (18).



SCHEME 1

The two other non-crystalline products obtained from the reaction of the acetylenic ester with **1***d* over 1 day were not identified. Spectroscopy (i.r. and n.m.r.) indicated that they were methyl esters of carboxylic acids, but lacking analytical data no satisfactory structure can be advanced.

Very similar results were obtained by treatment of the thione **1***d* with dibenzoylacetylene. Reaction over a short time provided the thial **3***b* as an amorphous brown solid. This was the major product. No tetraketone **5***b* was obtained, but it was the major product when the reaction was performed in boiling benzene for 1 day, and **3***b* gave **5***b* on further heating in benzene. Numerous other fractions were obtained by t.l.c. in these reactions, but in only trace amounts. As in the previous case, no assignment of the geometry of **5***b* was possible. No diadduct of the type **4** was isolated under any of the conditions tried with dibenzoylacetylenes, but when the thial **3***b* was heated with dimethyl acetylenedicarboxylate, the compound **5***b* was obtained, along with an orange oil. This could not be crystallized, but its spectroscopic properties indicated it might be the spiran **4***a*.

4-Phenyl-1,2-dithiole-3-thione (**1***c*) reacted with dimethyl acetylenedicarboxylate to give the thial mono-adduct **3***c* as a pasty brown solid. This was insufficiently stable to permit proper isolation, although evidence for the presence of a thial group was obtained. This was accompanied by a trace amount of the aldehyde **6***a* which was also obtained from the thial **3***c* by treatment with mercuric acetate. Further boiling of **3***c* in benzene or xylene gave the tetracarboxylic ester **5***c*, and treatment with more dimethyl acetylenedicarboxylate provided the spiran tetracarboxylic ester **4***b*. Compound **3***c* failed to react with ethylpropiolate. The aldehyde **6***a* was obtained in trace amounts in all these reactions, even when performed under nitrogen and in dry solvents. It appears that it is formed from unreacted thial by aerial oxidation or hydrolysis on the t.l.c. plates, prior to developing.

With dibenzoylacetylene, 4-phenyl-1,2-dithiole-3-thione (**1***c*) has been reported (5) to give an unstable thial. This reaction was further investigated to determine the products of further reaction. The thial **3***d* was obtained as a pasty solid which could not be purified satisfactorily. Refluxing it in benzene gave the tetraketone **5***d* in low yield, but better conversion was achieved in xylene. Small amounts of the spiran tetraketone **4***c* were also obtained from the reaction of the thione **1***c* with dibenzoylacetylene, and this was the major product when the thial **3***d* was treated with dibenzoylacetylene, although small amounts of the tetraketone **5***d* were also found. In all of these reactions, small amounts of the aldehyde **6***b* were obtained. As in the reaction of **1***c* with dimethyl acetylenedicarboxylate, this is probably formed by aerial oxidation of unreacted thial **3***d*.

From the above products, a sequence of reactions may be seen. Reaction of the initial 1,2-dithiole-3-thione **1***c* or *d* with the activated acetylene, first produces a thial mono-adduct, which may react in three ways. One reaction common to all studied is that producing the butendiylidenedithioles **5**. However, where the thial group is stabilized by conjugation to a phenyl group, as in **3***c* or *d*, it is possible that this reaction becomes slower, and other reactions may compete effectively with it, *i.e.* the thial may react with a suitably activated acetylene to form a di-adduct **4** or it may form the corresponding aldehyde **6** by hydrolysis or oxidation.

The n.m.r. spectra of the products derived from dimethyl acetylenedicarboxylate in deuterochloroform are interesting in that while the phenyl substituted compounds **3***c* and **5***c* demonstrate non-equivalence of the methyl groups on the ester function due to their different environments with respect to the exocyclic double bond, the methyl groups on the ester functions of **3***a* and **5***a* are equivalent. Related phenomena have been observed for the reaction products **2***a* of a variety of 1,2-dithiole-3-thiones with acetylenes (1, 4, 19–21). Where the acetylene is unsymmetrical, two geometrical isomeric products are obtained. The detection of non-equivalence or of isomers then seems to be related to the presence of a substituent α to the thiocarbonyl group in the thioacylmethylene-1,3-dithioles (originally a 4-substituent on the starting 1,2-dithiole-3-thione). However, the data for the analogous acylmethylene-1,3-dithioles **2***b* (22, 23) indicate that two isomers are present even where there is no α substituent. Interconversion of the two forms of the thioacyl compounds by isomerization about the exocyclic double bond has been suggested (21), and similar phenomena could render the ester functions equivalent in **3***a*, **5***a*, and other such derivatives of dimethyl acetylenedicarboxylate, but the magnetic equivalence of substituents seems to be merely co-incidental since the n.m.r. spectrum of **5***c* in hexadeuterobenzene, because of its solvent shift effects (24) indicated that the two ester groups had different shifts. The two isomers, however, may be interconvertible by a rate slower than the n.m.r. time scale. Unfortunately, **3***c* was insufficiently soluble in cold benzene to allow any conclusions to be made, and heating caused rapid formation of **5***c*. The aldehyde **6***a* also demonstrated non-equivalence of the ester functions.

Experimental

The i.r. spectra were performed on a Perkin–Elmer model 337 spectrophotometer, in liquid paraffin mulls except where otherwise stated. The n.m.r. spectra were obtained on a Varian Model 50/60A spectrometer, and unless otherwise stated in deuterochloroform solution using tetramethylsilane as an internal standard. Some of these were done in methylene chloride solution but peaks were not properly resolved in this. The t.l.c. was performed on 1 mm thick layers of silica gel type D.S.F. 5 supplied by Mondray Ltd. Development of plates was carried out using benzene with increasing proportions of chloroform. Where bands were not properly separated, the separate fractions were re-chromatographed. Melting points were obtained on a Fisher-Johns apparatus. Mass spectra were obtained on a Finnegan 1015 quadrupole mass spectrometer.

Reaction of 1,2-Dithiole-3-thione with Dimethyl Acetylenedicarboxylate

1,2-Dithiole-3-thione (25)(134 mg, 1 mmol) and dimethyl acetylenedicarboxylate (142 mg, 1 mmol) in benzene (30 ml) were stirred at room temperature for 3 h. The solvent was removed in the cold under reduced pressure, and t.l.c. of the crude material gave **3***a* as a brown paste (70%) which could not be purified further.

The n.m.r. of **3***a*, 5.78 (6H singlet, two equivalent CH_3 groups), 1.55 (1H doublet, $J = 7.5$ Hz, vinyl proton), -1.65 τ (1H doublet, $J = 7.5$ Hz, thial proton). The i.r. spectrum 1725 cm^{-1} (C=O str) broad peak in methylene chloride.

Traces of **5***a* (~10 mg) were also obtained as a purple solid. A repeat of the above reaction but for 24 h, and in boiling benzene gave **5***a* as purple matted needles from nitromethane, m.p. 195–197° (42%).

Anal. Calcd. for $C_{18}H_{16}S_4O_8$: C, 44.27; H, 3.28; S, 26.23. Found: C, 44.54; H, 3.06; S, 26.33.

The n.m.r. of **5***a*, 6.20 (12H singlet, four equivalent CH_3 groups), 4.15 τ (4H multiplet, methine protons). The i.r. spectrum, 1740, 1725, 1710 cm^{-1} (C=O str). In deuterobenzene, the methyl groups were evident at 6.77 and 6.75 τ.

Two other fractions were also isolated by t.l.c. (~30 mg each). These were obtained as uncrystallizable orange glasses. The n.m.r. indicated they were methyl esters.

Similar results were obtained when the thione **1***d* was allowed to react with excess acetylenic ester.

Conversion of Dimethyl 2-Thioformylmethylene-1,3-dithiole-4,5-dicarboxylate (3a) into Tetramethyl 1,4-Butenediylidene-2,2′-bis(1,3-dithiole-4,5-dicarboxylate) (5a)

The ester **3***a* (100 mg, 0.3 mmol) in benzene (25 ml) was refluxed for 24 h. Examination of the solution gave **5***a* (40%) along with six other fractions which gave only traces of material.

Reaction of 1,2-Dithiole-3-thione with Dibenzoylacetylene

The thione (134 mg, 1 mmol) and dibenzoylacetylene (26) (234 mg, 1 mmol) in benzene (25 ml) were stirred together at room temperature for 3 h. The solvent was removed in the cold under reduced pressure, and t.l.c. of the crude material gave **3***b* as a brown solid (74%). This could not be sufficiently purified for analysis.

The n.m.r. of **3***b*, 2.17 (1H doublet, $J = 7.5$ Hz, vinyl proton), 3.03 to 2.45 (10H bands, aromatic protons), 0.78 τ (1H doublet, $J = 7.5$ Hz, thial proton). The i.r. spectrum, 1660 cm^{-1}, broad, (C=O str) in methylene chloride.

A repeat of the above reaction for 18 h in boiling benzene gave **3***b* (4%) and the tetraketone **5***b* as dark green plates m.p. 203–205° from nitromethane (38%).

Anal. Calcd. for $C_{38}H_{24}S_4O_4$: C, 67.86; H, 3.57; S, 19.04. Found: C, 68.08; H, 3.67; S, 18.97.

The n.m.r. spectrum, 4.31 to 3.70 (4H multiplet, the methine protons), 2.90 to 2.40 τ (20H bands, aromatic protons). The i.r spectrum, 1630 and 1655 cm^{-1} (C=O str).

Ten other bands were also separated, but gave only traces of products. Similar results were obtained when the thione was treated with excess dibenzoylacetylene.

Reaction of 4,5-Dibenzoyl-2-thioformylmethylene-1,3-dithiole (3b) with Dimethyl Acetylenedicarboxylate to form 4a

The thial (20 mg, 0.055 mmol) and the ester (7.7 mg, 0.055 mmol) in benzene (3 ml) were refluxed for 3 h. From the mixture was isolated **5***b* (60%) and a small amount (~10 mg) of an orange glass which was possibly **4***a*.

Conversion of 4,5-Dibenzoyl-2-thioformylmethylene-1,3-dithiole-(3b) into 1,4-Butenediylidene-2,2′-bis(4,5-dibenzoyl-1,3-dithiole) (5b)

The diketone (150 mg, 0.24 mmol) in benzene (30 ml) was refluxed for 18 h. Work-up of the mixture gave **5***b* (43%) and ten other minor fractions.

Reaction of 4-Phenyl-1,2-dithiole-3-thione with Dimethyl Acetylenedicarboxylate

The thione (210 mg, 1 mmol) and the ester (142 mg, 1 mmol) in benzene (30 ml) were stirred at room temperature for 1.5 h. Work-up gave **3***c* as a brown pasty solid (85%) which could not be purified satisfactorily.

The n.m.r. spectrum of **3***c*, 6.25 and 6.17 (two 3H singlets, methyl groups), 2.73 (5H singlet, aromatic protons), 0.35 τ (1H singlet, thial proton). The i.r. spectrum, 1740 cm^{-1} (C=O) broad, methylene chloride solution.

Along with this compound was obtained a trace of **6***a*.

Conversion of Dimethyl α-Phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (3c) into Tetramethyl 1,4-Diphenyl-1,4-butenediylidene-2,2′-bis(1,3-dithiole-4,5-dicarboxylate) (5c)

The thial (230 mg, 0.65 mmol) in benzene (30 ml) was refluxed for 24 h. Work-up gave the tetracarboxylic ester as reddish-purple needles from nitromethane, m.p. 212–216° (43%).

Anal. Calcd. for $C_{30}H_{24}S_4O_8$: C, 56.25; H, 3.75; S, 20.00. Found: C, 56.17; H, 3.75; S, 19.82.

The n.m.r. spectrum of **5***c*, 6.22 and 6.27 (two 6H singlets, methyl protons), 4.23 (2H singlet, methine protons), 2.92 to 2.42 τ (10H bands, aromatic protons). The i.r. spectrum, 1725 and 1750 cm^{-1} (C=O str).

When the reaction was performed in boiling xylene, the yield was raised to 80%. A small amount (~5 mg) of **6***a* was also obtained in the reaction.

Preparation of Dimethyl-2-α-phenylformylmethylene-1,3-dithiole-4,5-dicarboxylate (6a)

The thial **3***c* (120 mg, 0.34 mmol) was added to a hot solution of excess mercuric acetate in acetic acid (10 ml). The dark color of the thial disappeared almost instantaneously. The solution was diluted with water and the benzene extract purified by t.l.c. The product was obtained as orange prisms, m.p. 127–129°, from ethanol:benzene 1:1 (80%).

Anal. Calcd. for $C_{15}H_{12}S_2O_5$: C, 53.53; H, 3.57; S, 19.04. Found: C, 53.61; H, 3.56; S, 19.21.

The n.m.r. of **6a** 6.23 and 6.18 (two 3H singlets, methyl groups), 2.73 (5H singlet, aromatic protons), 0.75 τ (1H singlet, thial proton). The i.r. spectrum, 1770 and 1750 (C=O str, from ester), 1630 cm^{-1} (C=O str, from aldehyde).

Reaction of Dimethyl-2-α-phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (3c) with Dimethyl Acetylenedicarboxylate

The thial (274 mg, 0.78 mmol) and the ester (122 mg, 0.78 mmol) in benzene (30 ml) were refluxed for 3 h. Work-up gave the diadduct **4b** as an uncrystallizable orange glass (40%). Mass spectrum showed a parent ion at *m/e* 494, calcd. 494, *m/e* 435 (M-CO_2CH_3)

The n.m.r. spectrum, 6.32 (6H singlet, two equivalent methyls on the dithiole ring), 6.18 and 6.13 (two 3H singlets, methyls on the thiopyran ring), 3.67 (1H singlet, vinyl proton), 2.78 to 2.50 τ (5H bands, aromatic protons). The i.r. spectrum 1720 cm^{-1} (C=O str) broad, in methylene chloride.

Attempted Reaction of Dimethyl α-Phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (3c) with Ethyl Phenylpropiolate

The thial (176 mg, 0.5 mmol) and the ester (87 mg, 0.5 mmol) in benzene (30 ml) were refluxed for 24 h. Only **5c** was isolated from the mixture. The n.m.r. examination of all fractions indicated none with an ethyl group.

Reaction of 4-Phenyl-1,2-dithiole-3-thione with Dibenzoylacetylene

The thione (420 mg, 2 mmol) and dibenzoylacetylene (464 mg, 2 mmol) in benzene (40 ml) were stirred at room temperature for 2½ h. Work-up of the mixture gave **3d** as a brown powder, which could not be purified sufficiently for analysis (71%).

The n.m.r. of **3d**, 2.99 to 2.50 (15H bands, the aromatic protons), −0.65 τ (1H singlet, the thial proton). The i.r. spectrum 1655 cm^{-1} (C=O str) broad, in methylene chloride.

Compound **4c** was also isolated as a yellow powder, m.p. 89–92° (14%).

Anal. Calcd. for $C_{41}H_{20}S_3O_4$: C, 72.57; H, 3.83; S, 14.22. Found: C, 72.47; H, 3.80; S, 14.06.

The n.m.r. spectrum of **4c**, 3.45 (1H singlet, vinyl proton), 3.10 to 2.11 τ (25H bands, the aromatic protons). The i.r. spectrum 1675 and 1640 cm^{-1} (C=O str).

Conversion of 2-α-Phenylthioformylmethylene-4,5-dibenzoyl-1,3-dithiole (3d) into 1,4-Diphenyl-1,4-butenediylidene-2,2′-bis(4,5-dibenzoyl-1,3-dithiole) (5d)

The thial (160 mg, 0.36 mmol) in xylene (26 ml) was refluxed for 24 h. Examination of the mixture gave **5d** as purple needles, m.p. 244–246° (51%).

Anal. Calcd. for $C_{50}H_{32}S_4O_4$: C, 72.94; H, 3.90; S, 15.54. Found: C, 72.72; H, 4.04; S, 15.39.

The n.m.r. spectrum of **5d**, 4.10 (2H singlet, methine protons), 3.00 to 2.35 τ (30H bands, the aromatic protons). The i.r. spectrum, 1675 cm^{-1} (C=O str) broad.

Also obtained was **6b** as an orange oil which could not be crystallized (16%). This compound was also prepared below.

The n.m.r. of **6b**, 3.07 to 2.33 (15H bands, the aromatic protons), 0.72 τ (1H singlet, the aldehydic proton). The i.r. spectrum, 1655 and 1625 cm^{-1} (C=O str). The mass spectrum *m/e* 428 (parent peak) calcd. 428.

Preparation of 2-α-Phenylformylmethylene-4,5-dibenzoyl-1,3-dithiole (6b)

The thial **3d** (200 mg, 0.45 mmol) in boiling acetic acid (10 ml) was treated with an excess of mercuric acetate. The solution turned yellow after 5 min and the mixture was poured into water and extracted with benzene. Evaporation gave **6b** as an uncrystallizable oil (85%). The mass spectrum, *m/e* 428 (parent peak), 234 (M-(PhCO·C)$_2$), 194; 105 (PhCO$^+$).

Reaction of 2-α-Phenylthioformylmethylene-4,5-dibenzoyl-1,3-dithiole (3b) with Dibenzoylacetylene

The thial (165 mg, 0.47 mmol) and dibenzoylacetylene (110 mg, 0.47 mmol) were refluxed in benzene (20 ml) for 18 h. Examination of the mixture gave **4c** (70%), **5d** (6%), and **6b** (6%). Also isolated was 49 mg of another orange solid, m.p. 190–193°. The mass spectrum *m/e* 573 (possibly metastable peak), 105 (PhCO$^+$).

Anal. Found: C, 73.08; H, 3.88; S, 13.98. This possibly corresponds to an isomer of **4c**.

Anal. Calcd. for $C_{41}H_{20}S_3O_4$: C, 72.57; H, 3.83; S, 14.22.

The n.m.r. spectrum of the compound, 3.05 to 2.15τ (25H bands, aromatic protons). The i.r. spectrum 1700, 1655, and 1645 cm^{-1} (probably C=O str).

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