EXPERIMENTAL

A well stirred and ground mixture of 0.2 mole of carboxylic acid and 0.1 mole of hydrazine hydrochloride was mixed with 8 to 10 times its weight of PPA. The resulting mixture was heated in an open flask with periodic stirring under the conditions given in the table. Then it was poured into a large volume of water and the product that separated out was filtered off, dried, and recrystallized from a suitable solvent. Diaminophenyl-1, 3, 4-oxadiazole was isolated from the aqueous acidic solution by making it alkaline.

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REACTION OF SULFOLENES WITH BENZOYL PEROXIDE AND IODINE

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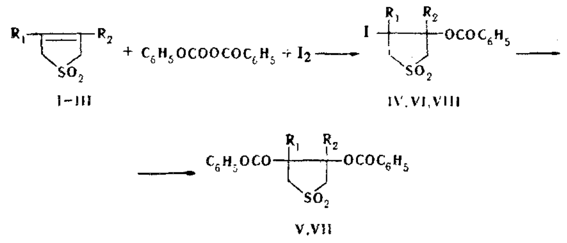
The reaction of 3-sulfolene with benzoyl peroxide and iodine has given 3-benzoyloxy-4-iodosulfolane and 3, 4-dibenzoyloxysulfolane. In the case of 3-methyl-3-sulfolene and 3, 4-dimethyl-3-sulfolene, the corresponding benzoylated iodohydrins have been isolated.

It has been reported previously [1] that 3-sulfolene I reacts with silver benzoate and iodine in a molar ratio of 1:2:1 with the formation of 3, 4-dibenzoyloxysulfolane and a small amount of 3-benzoyloxy-4-iodosulfolane, which can be regarded as the product of the reaction of I with the benzoyl hypoiodite formed by the reaction of silver benzoate with iodine [2]. According to Hammond and Soffer [3], the formation of benzoyl hypoiodite is also assumed in the thermal decomposition of benzoyl peroxide in carbon tetrachloride in the presence of iodine. Consequently, it appeared of interest to study the possibility of the benzoyloxylation of sulfolenes with benzoyl peroxide in the presence of iodine in accordance with the following scheme



I, IV, V $R_1=R_2=H$; II, VI, VII $R_1=H$, $R_2=CH_3$; III, VIII $R_1=R_2=CH_3$

The experiments were carried out in boiling carbon tetrachloride at a molar ratio of sulfolene to peroxide to iodine of 1:1.25:1. It was found that under these conditions the sulfolenes undergo practically no iodination. Decarboxylation of the benzoyl peroxide, accompanied by the formation of iodobenzene and phenyl benzoate takes place to a very small extent (3–5%), as can be judged from the amount of CO_2 formed and from the results of thin-layer chromatography. In the case of I, 35% of 3-benzoyloxy-4-iodosulfolane (IV) and 22% of 3, 4-dibenzoyloxysulfolane (V) were obtained. Since I does not react with benzoyl peroxide in the absence of iodine, the formation of V must be the result of a secondary reaction of the replacement of the iodine in IV by a benzoyloxy radical, the rate of which in this case is somewhat lower than in experiments with silver benzoate and iodine, this apparently being connected with the formation in the latter case of insoluble AgI.

Under similar conditions, 3-methyl-3-sulfolene (II) formed 3-benzoyloxy-4-iodo-3-methylsulfolane (VI) with a yield of 53%. It was impossible to isolate 3, 4-dibenzoyloxy-3-methylsulfolane (VII) although, from the results of thin-layer chromatography, a small amount of it was present in the reaction products. Since the conversion of II into VI was approximately equal to the total conversion of I into IV and V, it may be considered that a methyl group on the double bond has no appreciable influence on the addition of benzoyl hypoiodite but hinders the formation of VII.

In the case of 3, 4-dimethyl-3-sulfolene (III), 3-benzoyloxy-4-iodo-3, 4-dimethylsulfolane (VIII) was obtained in low yield (11%), which is apparently due to the steric blocking of the double bond by the two methyl groups in a similar manner to the way in which they influence hydrogenation or halogenation reactions [4].

Thus, under certain conditions the sulfolenes can react with benzoyl peroxide and iodine to form benzoylated sulfolane iodohydrins and benzoylated glycols, but the ratio of these two products is determined to a considerable extent by the presence of substituents on the double bond.

EXPERIMENTAL

a) Reaction of 3-sulfolene with benzoyl peroxide and iodine. A three-necked flask fitted with a nitrogen inlet, a chemical stirrer, and reflux condenser connected with a gasometer was charged with 5.9 g (50 mM) of **I**, 18.37 g (75 mM) of benzoyl peroxide, and 12.7 g (50 mM) of iodine in 100 ml of carbon tetrachloride. The mixture was boiled for 48 hr. The gas collected was analyzed for its CO_2 content. The iodine that had not reacted was determined by titration with 0.1 N sodium thiosulfate solution, and the benzoyl peroxide iodometrically. The consumption of iodine was 12.5 mM (25%) and that of benzoyl peroxide 27.6 mM (36.8%), 3.0 mM of this (4%) having been consumed in the formation of CO_2. In order to eliminate the unchanged iodine and benzoyl peroxide, the reaction mixture was washed successively with aqueous solutions of Na_2SO_3 and $NaHCO_3$ and then with water. The wash waters were extracted with chloroform. The carbon tetrachloride and chloroform were eliminated in vacuum. Recrystallization of the residues from ether and carbon tetrachloride yielded 4.0 g (22%) of **IV** and 6.4 g (35%) of **V**. After three crystallizations, **IV** was obtained with mp 179–180° C (literature data [1] mp 179–180° C) and **V** with mp 122–124° C (literature data: 124.5–125° C).

b) The reaction of 3.3 g (25 mM) of **II** with 9.0 g (37.5 mM) of benzoyl peroxide and 6.3 g (25 mM) of iodine in 50 ml of carbon tetrachloride under similar conditions gave 2.0 mM (3%) of CO_2 and 5.0 g (53%) of **VI**. After two crystallizations, the product melted at 129–130° C (literature data: 130–131° C). The presence of traces of **VII** in the reaction products was detected by thin-layer chromatography.

c) The reaction of 3.3 g (20.1 mM) of **III** with 7.3 g (30.2 mM) of benzoyl peroxide and 5.1 g (20.1 mM) of iodine in 45 ml of carbon tetrachloride gave 3.0 mM (5%) of CO_2 and 0.9 g (11%) of **VIII** with mp 150–153° C (literature data: 156–157° C). The presence of traces of **III** in the reaction product with **VIII** was established by thin-layer chromatography.

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REACTION OF DIMEDONE WITH ALDEHYDES AND β-AMINOVINYL CARBONYL COMPOUNDS

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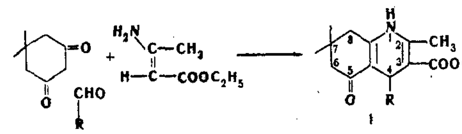
The unsymmetrical condensation of dimedone, an aldehyde, and various β-aminovinyl carbonyl compounds, and also bisacetonitrile, has given 3,4-disubstituted derivatives of 2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (**Va–f**). Compounds **Va, d, f** have been oxidized with H_2CrO_4 to the corresponding 3,4-disubstituted 2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines (**VIa–c**). The IR spectra of compounds **Va–c, f** and **VIa** and the UV spectra of compounds **Va, c, f,** and **VIa, c** have been recorded.

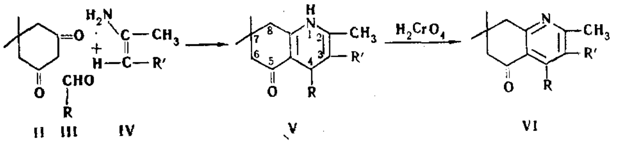
A preceding communication [1] described the unsymmetrical condensation of dimedone, an aromatic or aliphatic aldehyde, and an ester of β-aminocrotonic acid with the formation of a 4-substituted 3-ethoxycarbonyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (**Ia–c**).



I

a R=H **b** R=CH_3 **c** R=C_6H_5

Continuing our experiments, we tackled the problem of testing the possibility of a similar condensation with other β-aminovinyl carbonyl compounds. Condensation was carried out with acetylacetone imine, benzoylacetone imine, and bisacetonitrile, giving the corresponding 3,4-disubstituted derivatives of 2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline **Va–f**.



II III IV V VI

V: a R=C_6H_5; R′=$COCH_3$ d R=CH_3; R′=CN VI: a R=C_6H_5; R′=$COCH_3$
b R=H; R′=$COCH_3$ e R=H; R′=CN b R=CH_3; R′=CN
c R=C_6H_5; R′=CN f R=C_6H_5; R′=COC_6H_5 c R=C_6H_5; R′=COC_6H_5

The synthesis was carried out in ethanol with paraformaldehyde, acetaldehyde, and benzaldehyde. The synthesis with benzaldehyde gave good results. The