strong acid esterification catalyst as the temperature is raised above 65 to 75°.)

When acid hydrates such as oxalic acid dihydrate are to be esterified, no methanol is needed to initiate the reaction as the acetone dimethyl acetal is readily hydrolyzed by the water of hydration. To insure complete conversion of the acid, the amount of acetone dimethyl acetal used should be in slight mole excess (up to 10%) of the total water present and/or expected. The advantages of this method for preparing methyl esters are: (1) there is no need for a water azeotrope trap, (2) a high reaction rate is maintained during the entire esterification reaction, (3) acid hydrates can be readily esterified, and (4) the acid is completely converted to its methyl ester.

EXPERIMENTAL

Effect of acetone dimethyl acetal on the reaction rate during esterification. In Fig. 1 the results of four experiments on the esterification of propionic acid are plotted. The quantity of each reactant used is as given plus sufficient anhydrous dioxane to make the total volume in each experiment 100 ml. The unreacted propionic acid was determined periodically by titrating an aliquot with standard ethanolic sodium hydroxide solution.

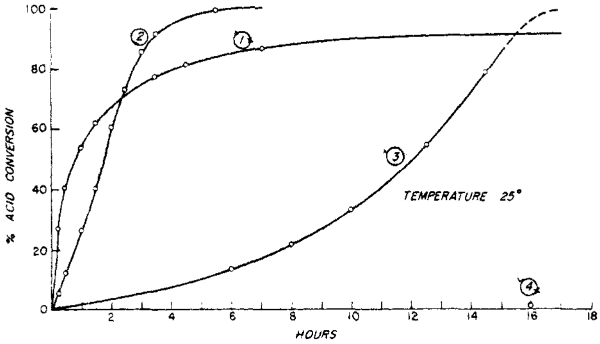

Fig. 1. Rate of esterification of propionic acid.

	1	2	3	4
MOLES OF				
Propionic acid	0.25	0.25	0.25	0.25
Methanol	0.75	0.25	0.075	0.00
Acetone dimethyl ketal	0.00	0.25	0.25	0.25
Hydrogen chloride	0.006	0.006	0.006	0.006

In experiment 1 the initial reaction rate was high but soon decreased and finally reached equilibrium where 94% of the propionic acid was converted. In experiment 2, two thirds of the methanol was present as a part of the acetone dimethyl acetal. The initial rate of this reaction was lower than in experiment 1; however, a high rate was maintained through almost all of the reaction period. In the early hours of experiment 3 the rate was low because the concentration of methanol was low. As the esterification proceeded, the concentration of the methanol increased as a result of the hydrolysis of the acetone dimethyl acetal and this effected a corresponding increase in the reaction rate. At 20 hr. all of the propionic acid in experiment 3 was converted and although no checks were made between 14 and 20 hr., the course of the reaction was probably as indicated. After 16 hr. there was no detectable conversion of the propionic acid in experiment 4. At 50 hr., 5% of the propionic acid was converted and from that point the reaction rate increased and all of the acid was converted. This experiment was repeated several times and each time there was essentially no reaction until 35 to 50 hr. and then there was a rapid conversion of the propionic acid. No special effort was made to exclude all atmospheric moisture or to use acetone dimethyl acetal that was absolutely free of methanol. Trace amounts of methanol and/or water would act as initiators for the reaction.

Esterification of dehydrated castor oil acids. A mixture of 200 ml. of dehydrated castor oils (1 ml. = 30.4 ml. $N/10$ NaOH), 0.60 mole of acetone dimethyl acetal, 0.3 mole of methanol and 0.012 mole of HCl was allowed to stand at room temperature. When checked 39 hr. later, more than 99% of the acids were esterified.

Preparation of dimethyl adipate. Four moles (585 g.) of adipic acid was added to a solution of 5 g. of *p*-toluenesulfonic acid dissolved in 5 moles (200 ml.) of methanol. This mixture was stirred in a 2 l. flask and maintained at 40° to 60°. As the reaction progressed, acetone dimethyl acetal was added in increments. By the end of 0.5 hr., 200 ml. had been added, by the end of 1 hr., 600 ml. total had been added (at this point all adipic acid was in solution), and by the end of 1.5 hr., a total of 1 l. (8 moles) of the acetone dimethyl acetal had been added. At the end of 2 hr. only 10% of the acid remained unreacted. After 4 hr. the reaction was 99% complete. One half of the crude solution was then distilled at a rate such that by the end of 3 hr. all of the acetone and methanol had been removed. This left a 98.8% yield of crude, straw colored dimethyl adipate, n_D^{25} 1.4275. On further distillation a 94% yield of pure dimethyl adipate (n_D^{25} 1.4263; b_{10}, 109°C.; lit.[3] n_D^{20} 1.4281; b_{20}, 122°C.) was recovered.

A similar experiment in which all of the reactants were mixed at one time and left overnight at room temperature (with stirring) resulted in 100% conversion of the adipic acid.

Preparation of dimethyl oxalate. One mole of oxalic acid dihydrate, 2 g. of *p*-toluenesulfonic acid and 2 moles of acetone dimethyl acetal were combined with stirring. Heat was applied so that a temperature of 50–55° was maintained. After 1.25 hr. another mole of acetone dimethyl acetal was added. After an elapsed reaction time of 2 hr. the final mole of acetone dimethyl acetal (4 mole total) was added. The reaction was 98% complete after 5 hr. at which time the methanol and acetone were distilled until only 175 ml. of the product–methanol solution remained. By cooling, filtering out the white crystalline product, and reworking the mother liquor, 107 g. of dimethyl oxalate (91% theory), m.p. 51–53° (lit.[1] m.p. 52.5–53.5°), was recovered.

Acknowledgment. The authors wish to thank Mr. Bernis Self for his aid in these experiments.

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Heterocyclic Vinyl Ethers XIV. Photochemical Dimerization of 2-Nitrobenzo-1,4-dithiadiene and Reactions of Benzo-1,4-dithiadiene with Mercuric Salts[1]

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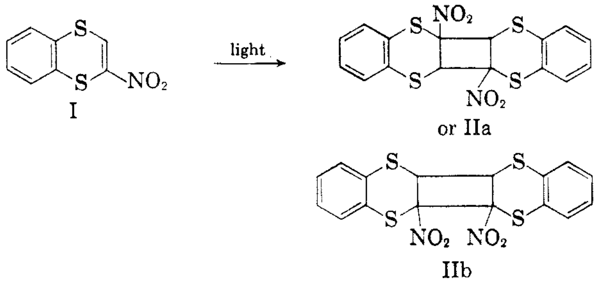
When 2-nitrobenzo-1,4-dithiadiene (m.p. 105–107°), which is red in color, is exposed to light, it is converted into a yellow solid (69% yield) which melts at 170.5–172°. This solid has been shown to be a dimer of I by elementary analysis and molecular weight determinations.



I

or IIa

IIb

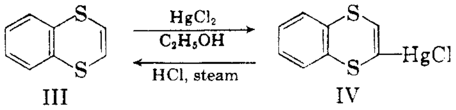
Oxidation of the dimer with potassium permanganate gave potassium benzene-*o*-disulfonate, characterized by its conversion into benzene-*o*-disulfonyl chloride, establishing that the nitro function remained attached to the more aliphatic carbon atoms during the dimerization.

Comparison of the infrared spectrum of I with that of the dimer showed that an increase in frequencies of the characteristic $-NO_2$ absorption accompanied dimerization (from 1515 to 1553 cm.$^{-1}$, and from 1320 to 1332 cm.$^{-1}$, respectively). These results suggested that the nitro group became less conjugated as a consequence of the dimerization,[3] since it has been previously observed that unconjugated nitro groups absorb at higher frequencies than do α,β-unsaturated nitro groups (compare nitrobenzene, 1535 and 1350 cm.$^{-1}$ with 1-nitropropane, 1553 and 1385 cm.$^{-1}$). The ultraviolet absorption spectra of I and that of the dimer also suggested that a decrease in conjugation of the nitro function accompanied dimerization. Thus, the monomer (I) showed two absorption maxima (235 mμ and 285 mμ), whereas the dimer showed only one at 239 mμ.

These data are consistent with the formulation of the dimer of I as the cyclobutane derivative IIa or IIb. Photochemical dimerizations of this type are well documented,[4] and cyclobutane structures have been established in several cases.[5] Structure IIa seems probable in view of the product reported for the photochemical dimerization of β-nitrosytrene.[5b]

Thiophene[6] and thianaphthene[7] are readily mercurated by reaction with mercuric chloride in ethanol or with mercuric acetate in ethanol and acetic acid. We have now examined the reaction of benzo-1,4-dithiadiene (III) with these reagents, employing conditions which give high yield of mercury derivatives with the thiophene analogs.

When benzo-1,4-dithiadiene (III) was treated with one equivalent of mercuric chloride in ethanol, there was obtained a 79% yield of a monomercurated derivative (m.p. 127–130°) which is thought to be 2-chloromercuribenzo-1,4-dithiadiene (IV).



III

IV

Although the position of the attached chloromercury derivative in IV was not established, it was assigned the two position by analogy with other electrophilic substitutions reported for benzo-1,4-dithiadiene.[8] That the product IV still retained the benzo-1,4-dithiadiene system intact was shown by recovery of III in 90% yield when IV was treated with hydrochloric acid and steam. The identity of recovered III was established by comparison of its ultraviolet spectrum with that of authentic III, and by conversion of the recovered product into 2-nitrobenzo-1,4-dithiadiene (I) by nitration.

The reaction of I with mercuric acetate in ethanol or in 50% aqueous acetic acid was more complex, no pure products were obtained. When I was treated with mercuric acetate in ethanol at room temperature, there was obtained an amorphous product which partially decomposed on attempted recrystallization from ethanol with the formation of free mercury. Elemental analysis of the high melting insoluble products, obtained using a variety of conditions, suggested that the expected products were not present in significant amounts.

EXPERIMENTAL

Photodimerization of 2-nitrobenzo-1,4-dithiadiene. 2-Nitrobenzo-1,4-dithiadiene (0.40 g., 1.89 m.moles, m.p. 105–107°) was exposed to sunlight for 15 days, during which time the color changed from red to light brown. The resulting brown solid was extracted with several portions of benzene, and the insoluble residue was discarded. The combined benzene extract was evaporated, and the resulting light tan solid was triturated with ethanol (two 1-ml. portions) to remove any unchanged starting material. The remaining tan product (0.358 g., 88%, m.p. 168–170° dec.) was recrystallized from ethanol giving 0.274 g. (69%) of pale yellow needles melting at 170.5–172°.

Anal. Calcd. for $C_{16}H_{10}O_4S_4N_4$: C, 45.48; H, 2.39; N, 6.63. Found: C, 45.44; H, 2.52; N, 6.48.

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(1) This work was supported by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022-Ord-2616.

(2) Presented in part at the 15th National Organic Symposium of the American Chemical Society, Rochester, N. Y., June 1957.

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The ultraviolet absorption spectrum of this product, determined in ethanol solution, showed 239 mμ max. (ϵ 25,300). The infrared spectrum showed characteristic[8] NO_2 absorption at 1332 and 1553 cm.$^{-1}$ These values compare with 235 mμ max. (ϵ 14,700), 285 mμ max. (ϵ 8030), and NO_2 absorption at 1320 and 1515 cm.$^{-1}$, for the monomer I.

The molecular weight of the dimer was determined by the freezing point depression method using benzene and nitrobenzene as the solvent. The product was relatively insoluble in benzene.

Calcd. M.W. 422. Found (average of three determinations each): in benzene, 448; in nitrobenzene, 406.

Oxidation of dimer with potassium permanganate. The oxidation of the dimer (129 mg.), with subsequent conversion of the resulting potassium benzene disulfonate to benzene-*o*-disulfonyl chloride, was carried out by a procedure previously described using 2-nitrobenzo-1,4-dithiadiene.[8] The yield of pure benzene-*o*-disulfonyl chloride (m.p. and mixture m.p. 145–146°) was 52 mg. (31%).

Chlomercuration of Benzo-1,4-dithiadiene. Mercuric chloride (1.80 g., 0.0076 mole) was added to a solution of benzo-1,4-dithiadiene[8] (1.10 g., 0.0066 mole) in 95% ethanol, and the resulting solution was heated at the reflux temperature for 1 hr. Water (35 ml.) was added to the cool reaction mixture, and the resulting pale yellow solid (m.p. 125–130° with previous softening at 100°) was recrystallized from ethanol-water. The light yellow needles that resulted (2.10 g., 79% yield) melted at 127–130°.

Anal. Calcd. for $C_6H_5S_2ClHg$: C, 23.94; H, 1.26. Found: 24.23; H, 1.74.

Hydrolysis of 2-chloromercuribenzo-1,4-dithiadiene. A mixture containing IV (0.919 g., 0.00229 mole), concentrated hydrochloric acid (5 ml.), and water (20 ml.) was distilled with steam. The yellow oil in the distillate was recovered by ether extraction, and was shown to be benzo-1,4-dithiadiene (0.341 g., 90% yield, n_D^{25} 1.6706) by comparison of its ultraviolet spectrum with authentic III,[8] and by its conversion into 2-nitrobenzo-1,4-dithiadiene (m.p. and mixture m.p. 105–107°).

Reaction of benzo-1,4-dithiadiene with mercuric acetate. (*A*) A solution of benzo-1,4-dithiadiene (1.00 g., 0.006 mole), mercuric acetate (4.80 g., 0.0151 mole), glacial acetic acid (5 drops), ethanol (30 ml.), and water (10 ml.) was heated at the reflux temperature for 5 hr. It was noted that considerable free mercury formed in the reaction. The mixture of yellow amorphous solid and free mercury (3.35 g.) was collected by filtration; the high melting (>300°) yellow solid was insoluble in all common solvents employed, and no method was found to remove all of the free mercury.

(*B*) A mixture identical to that described in A was heated for 30 min. No free mercury was noted, and there was obtained 1.78 g. of yellow solid. This material was insoluble in all solvents tested, and it did not melt at 300°; however, the material changed from orange to pink to brown during the attempted melting.

Anal. Found: C, 13.61; H, 1.15.

(*C*) A solution of III (1.00 g., 0.0060 mole), mercuric acetate (2.10 g., 0.0066 mole), glacial acetic acid (5 drops), ethanol (50 ml.), and water (15 ml.) was allowed to stand for 4 days at room temperature. The fine pale yellow solid (1.01 g.) was isolated by centrifugation. This material underwent a series of color changes, orange to pink to brown, when heated, and melted at 212–214°.

Anal. Found: C, 16.72; H, 1.57.

Attempts to purify this material by recrystallization from ethanol were unsuccessful because of its partial decomposition into free mercury.

(*D*) A mixture containing III (2.00 g., 0.0120 mole), mercuric acetate (4.03 g., 0.0126 mole), and 50% aqueous acetic acid (30 ml.) was stirred for 5 hr. at 45–50°. The resulting gummy solid which precipitated was soluble in acetic acid; however, when it was reprecipitated by the addition of water, the resulting product was insoluble in all solvents tried. A sample of this material was triturated with chloroform, benzene, and finally twice with hot glacial acetic acid. The light brown solid showed no change when heated to 300°.

Anal. Calcd. for $C_{12}H_{10}O_4S_2Hg_2$: C, 21.08; H, 1.47. Found: C, 21.90; H, 0.90.

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Synthesis of Cycloheptatriene

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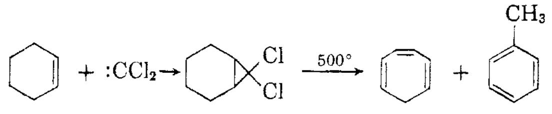
Several methods involving ring expansions are available for the synthesis of 1,3,5-cycloheptatriene (II). In the classical route,[1] the intermediate cycloheptanone is obtained by ring expansion of cyclohexanone. A more convenient preparation of cycloheptatriene is the irradiation by ultraviolet light of a solution of diazomethane in benzene.[2] In a third synthesis,[3] the solvolysis of the methanesulfonate of bicyclo[3.2.0]hept-2-en-6-ol was found to give a 50% yield of cycloheptatriene. More recently, II has been obtained by the thermal isomerization of bicyclo[2.2.1]heptadiene.[4]

A new two-step route to cycloheptatriene has now been discovered. It involves the preparation of 7,7-dichlorobicyclo[4.1.0]heptane (I), which can be obtained in 59% yield from dichlorocarbene and cyclohexene,[5] and its pyrolysis to a mixture of cycloheptatriene and toluene. At 500°, a 57% yield of a mixture of toluene (65%) and cycloheptatriene (35%) is obtained. The resulting solutions may be utilized to prepare derivatives of II, including tropylium bromide and Diels-Alder adducts.



I II

The effect of varying the temperature and residence time in the pyrolysis of I has not been ex-

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