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Organic Reactions of Sulfur Dioxide. II. Reaction with Ortho Esters

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Ortho esters react with an excess of sulfur dioxide to produce the corresponding esters and dialkyl sulfites. Thus, triethyl orthoacetate gave ethyl acetate and diethyl sulfite, triethyl orthopropionate, and triethyl orthobenzoate produced ethyl propionate, ethyl benzoate, and diethyl sulfite. On the other hand, triethyl orthoformate was less reactive and in addition to ethyl formate and diethyl sulfite also afforded diethyl carbonate. The reaction evidently involves formation of the corresponding dialkoxy carbonium ions and the alkyl sulfite anions, followed by a nucleophilic attack of the latter at the alkyl group of the dialkoxy carbonium ion to give the ester and the dialkyl sulfite.

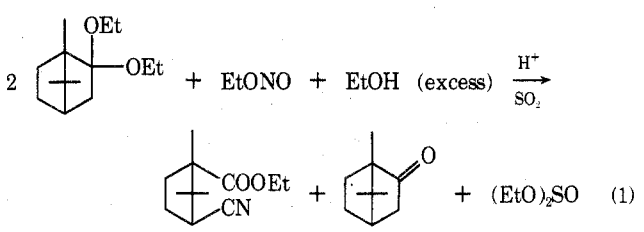
Recently we described the nitrosolysis reaction, a novel single step carbon–carbon bond cleavage of various ketones[1] and ketone acetals[2] effected through nitrosation. In the discussion of the mechanism of the nitrosolysis of cyclohexanone diethyl acetal, it was suggested that the initial cleavage affords the triethyl 6-oximinoorthohexanoate which in the presence of acid underwent dehydration to the ethyl 5-cyanopentanoate. The experimental evidence that this kind of dehydration of aldoximes with ortho esters to the corresponding nitrile is indeed a facile and general reaction was presented earlier.[3]

We wish now to describe a different transformation of an ortho ester intermediate in a particular nitrosolysis reaction, which led to a recognition of a novel and general reaction of ortho esters with sulfur dioxide.

Cyclohexanone enol ethers undergo facile reaction with sulfur dioxide,[4] and there is evidence that sulfur dioxide readily cleaves an alcohol from various ketone acetals.[5] It was recently reported that a reaction of photoexcited sulfur dioxide with trialkyl formates led to the formation of the corresponding "carbenium" ions,[6] but to our knowledge no reaction of ortho esters with unexcited sulfur dioxide was previously described.

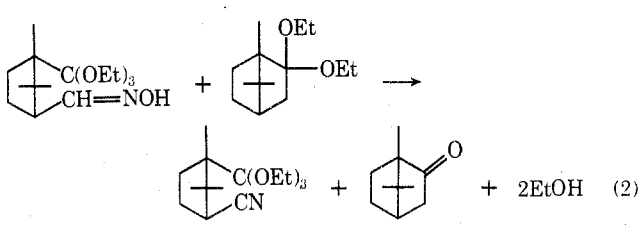
Results and Discussion

A reaction of camphor diethyl acetal with ethyl nitrite in sulfur dioxide solution containing excess ethanol and a catalytic amount of an acid gave about a 50% yield of the expected 1-carbethoxy-1,2,2-trimethyl-3-cyanocyclopentane. A preliminary experiment indicated that the reaction was unusually slow. Consequently, a Fisher pressure bottle, equipped with a pressure gauge and magnetic stirring bar, was charged with sulfur dioxide, camphor diethyl acetal, a solution of ethyl nitrite in ethanol, and ethanol containing a catalytic amount of dry hydrogen chloride. After the dry ice–acetone bath was removed, the reaction mixture was stirred at room temperature overnight. Unexpectedly, a GLC analysis of an aliquot revealed that in addition to approximately 50% of the expected 1-carbethoxy-1,2,2-trimethyl-3-cyanocyclopentane about 50% of camphor and diethyl sulfite were also present (eq 1).



(1)

While camphor diethyl acetal is extremely easily hydrolyzed by water,[7] it was demonstrated that the presence of camphor in the reaction mixture was not a consequence of the hydrolysis of unreacted camphor acetal during the analysis. Neither camphor diethyl acetal–ethanol in sulfur dioxide nor ethyl nitrite–ethanol solution in sulfur dioxide produced any diethyl sulfite. Consequently, it follows that both camphor and diethyl sulfite must be by-products in the nitrosolysis reaction of the camphor acetal itself. Hence, it was postulated that in the nitrosolysis of the acetal, the initially produced ortho ester oxime underwent a fast dehydration reaction with still unreacted camphor diethyl acetal to give the corresponding ortho ester nitrile (eq 2), which in turn reacted with sulfur dioxide to give the



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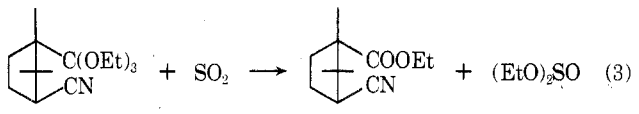


ester nitrile and diethyl sulfite (eq 3). Indeed, camphor diethyl acetal is a very efficient dehydrating reagent for conversion of aldoximes to nitriles[3] as indicated by almost instantaneous transformations of *n*-heptaldehyde oxime and *n*-butyraldehyde oxime to the corresponding nitriles in sulfur dioxide–ethanol solutions.

We have now established that trialkyl ortho esters do react with sulfur dioxide to give the esters and dialkyl sulfites (eq 4).

$$RC(OR')_3 + SO_2 \longrightarrow RCOOR' + (R'O)_2SO \quad (4)$$

Thus, NMR analysis of a solution of triethyl orthoacetate in liquid sulfur dioxide (sealed in an NMR tube at −70°), after 24 hr at room temperature, indicated practically complete conversion of the ortho ester to a mixture of ethyl acetate and diethyl sulfite. The GLC analysis confirmed this finding and showed that these were the only products in the reaction mixture.

The reaction appeared to be of a general nature as indicated by the similar transformation of triethyl orthopropionate, tri-*n*-propyl orthoacetate, triethyl orthobenzoate, and triethyl orthoformate. However, while the alkyl and aryl ortho esters reacted at room temperature, the triethyl orthoformate, under the same reaction conditions, appeared essentially unchanged. The relative reactivities of these ortho esters after 24 hr at 0° follow: triethyl orthoacetate, 1; triethyl orthopropionate, 1.16; triethyl orthobenzoate, 0.35; and triethyl orthoformate, ~0 (Table I).

The reaction of triethyl orthoformate with sulfur dioxide required more drastic conditions. After heating at 85–90° for *2 weeks*, a 60-MHz NMR analysis of a solution of triethyl orthoformate in an excess of sulfur dioxide indicated that only 45–50% of the orthoformate reacted. However, besides ethyl formate and diethyl sulfite, diethyl carbonate was also formed.[8]

When an equimolar mixture of tri-*n*-propyl orthoacetate and triethyl orthopropionate was treated with a catalytic amount of sulfur dioxide, a 60-MHz spectrum taken immediately after mixing suggested that a very fast alkoxy exchange had taken place. The GLC analysis indicated that in addition to the two starting ortho esters, tri-*n*-propyl orthopropionate, triethyl orthoacetate, *n*-propyldiethyl orthopropionate, di-*n*-propylethyl orthopropionate, *n*-propyldiethyl orthoacetate, and di-*n*-propylethyl orthoacetate were also present in the reaction mixture.[9] A reaction of the *trans*-4-*tert*-butylcyclohexyldiethyl orthoacetate with excess sulfur dioxide afforded a mixture of the *trans*-4-*tert*-butylcyclohexylethyl sulfite and *trans*-4-*tert*-butylcyclohexyl acetate with the configuration at the C_1 of the cyclohexane ring unchanged.

The following known facts are pertinent to the mechanism of reaction of sulfur dioxide with ortho esters. It is well established that sulfur dioxide readily enters in an equilibrium with alcohols[10] (eq 5), and causes racemization

$$ROH + SO_2 \rightleftharpoons ROSO_2H \quad (5)$$

of optically active α-phenylethyl alcohol[11] and 1-phenylethyl chloride.[12] The latter reaction apparently does not involve intermediate formation of styrene.[13] On the other hand, sulfur dioxide readily eliminates an alcohol from certain ketone acetals.[5] From the racemization studies with α-phenylethyl alcohol, Tokura and Akigama concluded that the reaction with sulfur dioxide probably involved slow, rate-determining formation of an intermediate (probably as an ion pair) which then underwent fast dissociative racemization.[11]

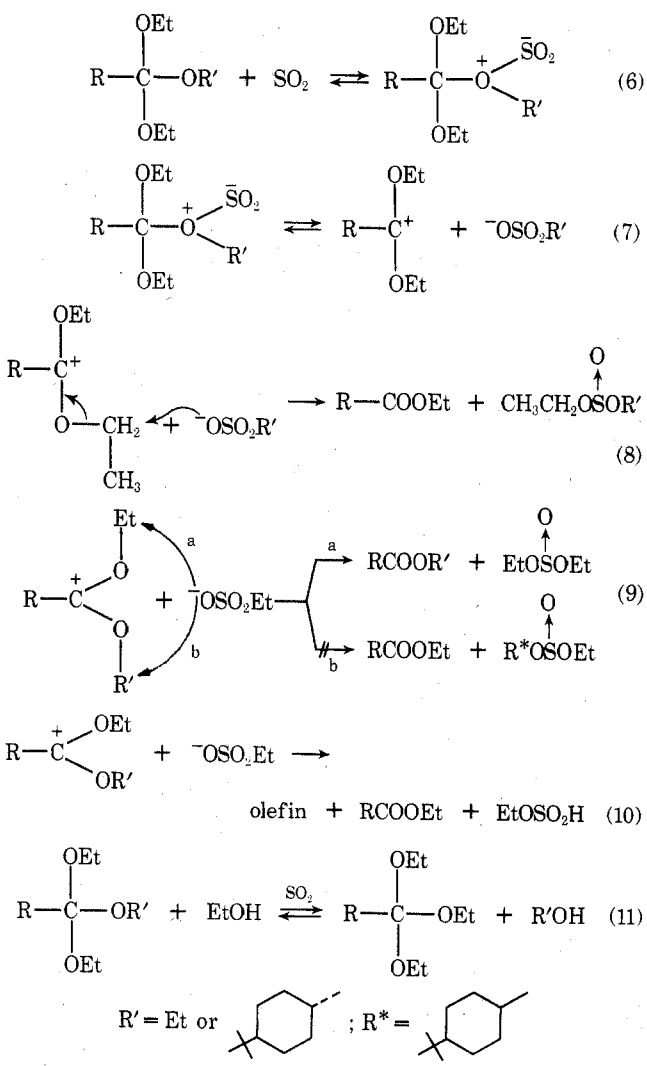
Table I
Reaction of Various Ortho Esters with Sulfur Dioxide[a]

Ortho ester	Products[b]	Relative reactivity[c]
$CH_3C(OEt)_3$	CH_3COOEt, $(EtO)_2SO$	1.0[d]
$CH_3CH_2C(OEt)_3$	CH_3CH_2COOEt, $(EtO)_2SO$	1.3
$C_6H_5C(OEt)_3$	C_6H_5COOEt, $(EtO)_2SO$	0.36
$HC(OEt)_3$	$HCOOEt$, $OC(OEt)_2$, $(EtO)_2SO$	~0[e]

[a] Reaction carried out in an NMR tube at an appropriate temperature using approximately 20% (by volume) solutions in sulfur dioxide; see Experimental Section for details. [b] The extent of the reaction was followed by NMR and when starting ortho ester disappeared, the NMR tube was cooled, opened, and analyzed by GLC. [c] From incomplete conversions at 0° for 24 hr. [d] Approximately 35% conversion. [e] The reaction was very slow and no attempt was made to determine time required to achieve complete conversion; see Experimental Section.

The mechanism of the reaction of ortho esters with sulfur dioxide very likely involves the following transformation (Scheme I). Initially, sulfur dioxide forms an interme-

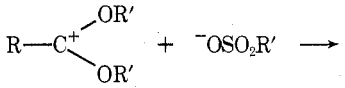
Scheme I



diate via a fast and reversible coordination with a free electron pair at the oxygen (eq 6), which undergoes the oxygen-acyl bond cleavage (eq 7) followed either by the recombination to provide the exchanged ortho ester, or by a nucleophilic substitution by the just generated sulfite anion on the primary center of the dialkoxy carbonium ion,[14] to produce the ester and the dialkyl sulfite (eq 8). Since a nucleophilic substitution with sulfinate ions RSO_2^- at the positive oxygen provides sulfinic esters rather than sulfones,[15] it is perhaps not surprising that the sulfite anions generated in eq 7 also act as an oxygen rather than a sulfur nucleophile in eq 8.

In the above discussed experiment with the *trans*-4-*tert*-butylcyclohexyldiethyl orthoacetate, in addition to the *trans*-4-*tert*-butylcyclohexyl acetate and the *trans*-4-*tert*-butylcyclohexylethyl sulfite, a substantial quantity of 4-*tert*-butylcyclohexene (about 20–30% of maximum possible) and *trans*-4-*tert*-butylcyclohexanol were also formed.[16] The formation of the *trans*-4-*tert*-butylcyclohexylethyl sulfite can be viewed as a consequence of nucleophilic substitution with *trans*-4-*tert*-butylcyclohexyl sulfite anion (R′ = *trans*-4-*tert*-butylcyclohexyl) at the primary center (eq 8), while the formation of the *trans*-4-*tert*-butylcyclohexyl acetate is probably a result of the nucleophilic substitution with the ethyl sulfite anion at the primary (eq 9a) rather than at the secondary center (eq 9b) of the dialkoxy carbonium ion (R′ = *trans*-4-*tert*-butylcyclohexyl, R* = *cis*-4-*tert*-butylcyclohexyl). The absence of the *cis*-4-*tert*-butylcyclohexylethyl sulfite, which might be expected from the nucleophilic attack by the ethyl sulfite anion at the C_1 carbon of the *trans*-4-*tert*-butylcyclohexyl group in the corresponding dialkoxy carbonium ion (eq 9b, R* = *cis*-4-*tert*-butylcyclohexyl), is not surprising in view of the propensity of secondary systems to undergo the elimination rather than substitution reactions.[17,18] Indeed, a substantial quantity of the olefin (4-*tert*-butylcyclohexene) formed in this reaction (eq 10) further supports this view. Since the half ester of sulfurous acid formed in eq 10 exists in an equilibrium with the alcohol[10] (eq 5), it also follows that the ethanol should replace *trans*-4-*tert*-butylcyclohexanol from the "mixed" ortho ester to provide the thermodynamically more stable triethyl orthoacetate (eq 11), as indeed has been observed.[19]

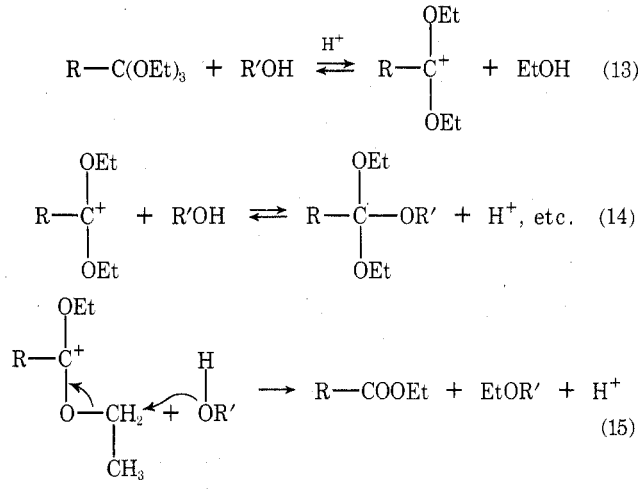
In the reaction of an all-secondary trialkyl orthoformate with sulfur dioxide, nucleophilic substitution by the secondary alkyl sulfite anion on the secondary carbon atom of the corresponding dialkoxy carbonium ion should be very ineffective. Instead, formation of the corresponding olefin, secondary alkyl formate, and the alcohol in equimolar quantities should be expected (eq 12). A reaction of the tri-



olefin + HCOOR′ + R′OSO₂H (12)

trans-4-*tert*-butylcyclohexyl orthoformate (eq 12, R′ = *trans*-4-*tert*-butylcyclohexyl) with excess of sulfur dioxide at room temperature was complete in less than 1 hr. The fact that 4-*tert*-butylcyclohexene, *trans*-4-*tert*-butylcyclohexanol, and *trans*-4-*tert*-butylcyclohexyl formate were formed in equimolar amounts, and that di-4-*tert*-butylcyclohexyl sulfite was not found among the reaction products, further supports the above mechanism.

It is of interest to recall that the accepted mechanism for acid-catalyzed hydrolysis of ortho esters calls for a fast and reversible protonation of the ortho ester, followed by a slow, rate-determining formation of the corresponding dialkoxy carbonium ion, and the fast and irreversible reaction of the latter with water to produce the ester and the alcohol.[20] If, however, an ortho ester is subjected to a reaction with an alcohol in the presence of an acid catalyst, it may be expected that the alkoxy exchange would also proceed through a slow, rate-determining formation of the dialkoxy carbonium ion (eq 13), followed by reaction of the latter with the alcohol to regenerate the original or the exchanged ortho ester (eq 14). Contrary to the hydrolysis mechanism,



in which the dialkoxy carbonium ion reacts irreversibly with water as the nucleophile,[20] the reaction of the dialkoxy carbonium ion with the available alcohol nucleophile is a reversible one. Hence, it is conceivable that under these reaction conditions a competing, higher energy but irreversible reaction path, a nucleophilic attack of the alcohol at the alkoxy carbon atom of the dialkoxy carbonium ion to produce the corresponding ester and ether (eq 15), may become operational. Alternatively, in the case of an ortho ester containing a secondary alkoxy group, by analogy with the reaction with sulfur dioxide, elimination rather than substitution may be expected. Indeed, both of these reactions were observed. Thus, when triethyl orthopropionate was heated under reflux with an excess of ethanol, the ortho ester gradually disappeared and the reaction solution contained the ethyl propionate and diethyl ether. On the other hand, heating the tri-*trans*-4-*tert*-butylcyclohexyl orthoformate with a catalytic amount of methanesulfonic acid led to the formation of the *trans*-4-*tert*-butylcyclohexyl formate, 4-*tert*-butylcyclohexene, and *trans*-4-*tert*-butylcyclohexanol, as expected.

Experimental Section

Most of the ortho esters used in this work were commercial products purified when necessary by distillation. The sulfur dioxide was MCB anhydrous grade and was passed through Linde AW-300 molecular sieves prior to use. *trans*-4-*tert*-Butylcyclohexanol was prepared by a reduction of the ketone with "mixed hydride", according to Eliel's procedure.[21] Boiling and melting points reported are uncorrected. GLC analyses were carried out generally on Hewlett-Packard 5700A instrument 3- or 6-ft columns of either 10% SE-30 on Chromosorb W or the corresponding 10% Carbowax 20M columns. Proton NMR spectra were recorded on either Varian A-60 MHz or HA-100 MHz instruments.

Camphor Diethyl Acetal. Camphor diethyl acetal was prepared from camphor, triethyl orthoformate, and ethanol, according to the published procedure.[21]

Reaction of Camphor Diethyl Acetal with Ethyl Nitrite–Ethanol in Sulfur Dioxide. A 100-ml Fisher pressure bottle, equipped with a magnetic stirring bar and a pressure gauge, protected with a nitrogen bubbler, was placed in a dry ice–acetone bath and charged with sulfur dioxide (25 ml), camphor diethyl acetal (3.61 g, 16 mmol) in 5 ml of ethanol, a solution of ethyl nitrite in ethanol (3.5 ml, 20 mmol), and 0.5 ml of 1*N* solution of dry hydrogen chloride in absolute ethanol. The dry ice–acetone bath was removed and the reaction solution stirred overnight at room tem-

perature. The reaction vessel was cooled in a dry ice–acetone bath, opened, and the contents poured into an excess of precooled chloroform containing an internal standard. The excess of sulfur dioxide was allowed to evaporate and GLC analysis of the residue indicated about 40–50% yield of diethyl sulfite, 40–50% yield of camphor, and 40–50% yield of 1-carbethoxy-1,2,2-trimethyl-3-cyanocyclopentane. A distillation afforded 1.16 g of the cyano ester, bp 80–84° (0.4 mm). Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69. Found: C, 68.78; H, 9.02; N, 7.0. Ir 2252, 1738 cm^{-1}; NMR ($CDCl_3$) δ 4.15 (q, 2 H), 3.0–1.5 (m, 5 H), 1.3–1.05 (1 t + 3 S, 12 H).

Dehydration of *n*-Heptaldehyde Oxime and *n*-Butylaldehyde Oxime with Camphor Diethyl Acetal. To a solution of the oxime (10 mmol) in sulfur dioxide–ethanol (7 + 3 ml), a few drops of a 1 *N* solution of dry hydrogen chloride in ethanol were added. An exothermic reaction occurred and GLC analysis indicated that the oxime was essentially quantitatively converted to the corresponding nitrile, while the camphor diethyl acetal was converted into camphor.

***trans*-4-*tert*-Butylcyclohexyldiethyl Orthoacetate.** A mixture of *trans*-4-*tert*-butylcyclohexanol (15.6 g, 100 mmol) and triethyl orthoacetate (32.5 g, 200 mmol) was placed in a distilling flask attached to a short distilling column and a few drops of methanesulfonic acid were added. The flask was slowly heated until approximately 100 mmol of ethanol distilled off. The acid was neutralized with a slight excess of sodium methoxide and the residue distilled in vacuo. There was obtained 20.3 g of *trans*-4-*tert*-butylcyclohexyldiethyl orthoacetate, bp 100–104° (0.5–0.6 mm). Anal. Calcd for $C_{16}H_{32}O_3$: C, 71.28; H, 11.54. Found: C, 71.35; H, 11.42. NMR ($CDCl_3$) δ 3.6 (q + broad s, 5 H), 1.48 (s, 3 H), 1.19 (t, 6 H), 0.88 (s, 9 H), and remaining cyclohexyl hydrogens appearing as several broad signals between δ 2.2 and 0.8.

Tri-*trans*-4-*tert*-butylcyclohexyl Orthoformate. A mixture of *trans*-4-*tert*-butylcyclohexanol (15.6 g, 100 mmol), triethyl orthoformate (3.3 ml, 20 mmol), and a drop of methanesulfonic acid was placed in a distilling flask and heated at 50° under slight vacuum until approximately 60 mmol of alcohol distilled off. The reaction mixture was made alkaline with sodium methoxide and the residue distilled in vacuo to give tri-*trans*-4-butylcyclohexyl orthoformate, bp 132–136° (0.1 mm), 5.3 g. Anal. Calcd for $C_{31}H_{58}O_3$: C, 77.77; H, 12, 21. Found: C, 78.01; H, 12.18. NMR ($CDCl_3$) δ 5.4 (s, 1 H), 3.6 (broad s, 3 H), 2.2–0.8 (broad multiplet, 27 H), 0.8 (s, 27 H).

Typical Procedure for a Reaction of Ortho Esters with Sulfur Dioxide. A heavy-wall glass NMR tube containing triethyl orthoacetate and a drop of tetramethylsilane was attached via convenient adapter to a small dry ice condenser and flushed with dry nitrogen. The condenser was filled with dry ice–acetone and the NMR tube placed in a small dry ice–acetone bath. Sulfur dioxide was passed through a Linde AW-300 molecular sieve column and condensed directly into the NMR tube to obtain a solution approximately 20% by volume. The sulfur dioxide line was closed, the NMR tube sealed under slight vacuum at −70°, and brought to the desired temperature,[24] and the reaction progress followed up by NMR analysis. After 24 hr at room temperature a 60-MHz NMR spectrum revealed that about 80% of the ortho ester was converted to a mixture of equal amounts of ethyl acetate and diethyl sulfite: δ 4.1 (2 q, 6 H), 2.0 (s, 3 H), 1.2 (t, 9 H). The gas chromatographic analysis after complete reaction confirmed the above finding and, in addition, showed that these were the only reaction products. The results are summarized in Table I.

Reaction of Triethyl Orthoformate with Sulfur Dioxide. A mixture of triethyl orthoformate with excess sulfur dioxide was sealed in a NMR tube as above.[24] After 24 hr at 0°, NMR analysis indicated that no appreciable reaction took place. The NMR tube was placed in a bath and heated at 85–90° and periodically analyzed by NMR. After heating for 2 weeks, only 45–50% of the orthoformate was consumed. In addition to ethyl formate and diethyl sulfite, diethyl carbonate was also formed: δ 8.1 (s, HCOO–), 4.1–4.2 (3 q, CH_3CH_2O). GLC analysis confirmed the above finding and also showed that several other unidentified compounds were present in small quantities. While the ratio of the ethyl formate to diethyl sulfite was approximately the same, the ratio of the ester to the diethyl carbonate was approximately 4:1.

Reaction of a Mixture of Tri-*n*-propyl Orthoacetate and Triethyl Orthopropionate with Excess Sulfur Dioxide. A mixture of equal parts of tri-*n*-propyl orthoacetate and triethyl orthopropionate with 4–5 parts of sulfur dioxide was sealed in a NMR tube as above.[24] After 3 days at room temperature the NMR tube was cooled and opened, and the contents were poured into a precooled chloroform. A GLC analysis indicated the presence of ethyl acetate, ethyl propionate, *n*-propyl acetate, *n*-propyl propionate, diethyl sulfite, di-*n*-propyl sulfite, and *n*-propylethyl sulfite. A control experiment showed that neither dialkyl and di-*n*-propyl sulfite nor the corresponding acetates and propionates exchanged under the reaction conditions.

Reaction of a Mixture of Tri-*n*-propyl Orthoacetate and Triethyl Orthopropionate with an Insufficient Amount of Sulfur Dioxide. A mixture of equal parts of tri-*n*-propyl orthoacetate and triethyl orthopropionate was mixed with sulfur dioxide (about 5% by volume) in a NMR tube and sealed at −70° as above.[24] The NMR tube was warmed up to room temperature and immediately analyzed by NMR. A complex NMR spectrum suggested that a fast alkoxy exchange had taken place. GLC analysis (as above) showed eight peaks. No appreciable quantity of the products observed in the preceding experiment were present in the reaction mixture. Tri-*n*-propyl orthoacetate, tri-*n*-propyl orthopropionate, triethyl orthopropionate, and triethyl orthoacetate were identified by peak enhancement with the authentic samples, and the remaining four peaks were assumed to be *n*-propyldiethyl orthopropionate, di-*n*-propylethyl orthopropionate, *n*-propyldiethyl orthoacetate, and di-*n*-propylethyl orthoacetate.[25]

Reaction of *trans*-4-*tert*-Butylcyclohexyldiethyl Orthoacetate with Sulfur Dioxide. A solution of *trans*-4-*tert*-butylcyclohexyldiethyl orthoacetate containing a drop of tetramethylsilane in liquid sulfur dioxide (about 20% by volume) was sealed in a NMR tube.[24] After standing at room temperature for 3 days, NMR analysis suggested the presence of 4-*tert*-butylcyclohexene, ethyl acetate, diethyl sulfite, ethanol, etc. After removal of excess sulfur dioxide, GLC analysis showed the presence of ethyl acetate (65–70%), 4-*tert*-butylcyclohexene (~25–30%), diethyl sulfite (~50–55%), *trans*-4-*tert*-butylcyclohexanol (~20%), *trans*-4-*tert*-butylcyclohexyl acetate (30–35%), and *trans*-4-*tert*-butylcyclohexylethyl sulfite (~20%). All compounds, except the mixed sulfite, were identified by peak enhancement with the authentic samples. Upon hydrolysis the mixed sulfite afforded *trans*-4-*tert*-butylcyclohexanol, thus showing that the stereochemistry of the C_1 cyclohexane carbon was not changed in the course of the reaction.

Reaction of Tri-*trans*-4-*tert*-butylcyclohexyl Orthoformate with Sulfur Dioxide. A solution of tri-*trans*-4-*tert*-butylcyclohexyl orthoformate containing a drop of tetramethylsilane in liquid sulfur dioxide (about 20% by volume) was sealed in a NMR tube.[24] After standing at room temperature for 1 hr, NMR analysis suggested complete reaction. GLC analysis of the solution showed that 4-*tert*-butylcyclohexene, *trans*-4-*tert*-butylcyclohexanol, and *trans*-4-*tert*-butylcyclohexyl formate were formed in approximately the same quantities.

Acid-Catalyzed Reaction of Triethyl Orthopropionate and Ethanol. A solution of triethyl orthopropionate (8.8 g, 50 mmol) and ethanol (46 g, 1 mol) containing a few drops of methanesulfonic acid was heated under reflux and periodically analyzed by GLC. The ortho ester gradually disappeared and diethyl ether and ethyl propionate were formed.

Acid-Catalyzed Reaction of Tri-*trans*-4-*tert*-Butylcyclohexyl Orthoformate. The tri-*trans*-4-*tert*-butylcyclohexyl orthoformate (5 g), in the presence of a few drops of methanesulfonic acid, was heated at 100° under vacuum and the decomposition products collected in a trap cooled with liquid nitrogen. A GLC analysis indicated the presence of *tert*-butylcyclohexene, *trans*-4-*tert*-butylcyclohexyl formate, and *trans*-4-*tert*-butylcyclohexanol in equal amounts.

Registry No.—Camphor diethyl acetal, 52162-25-1; ethyl nitrite, 109-95-5; ethanol, 64-17-5; 1-carbethoxy-1,2,2-trimethyl-3-cyanocyclopentane, 57346-54-0; *n*-heptaldehyde oxime, 5314-31-8; *n*-butyraldehyde oxime, 110-69-0; *trans*-4-*tert*-butylcyclohexyldiethyl orthoacetate, 57346-55-1; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; triethyl orthoacetate, 78-39-7; tri-*trans*-4-*tert*-butylcyclohexyl orthoformate, 57346-56-2; triethyl orthoformate, 122-51-0; tri-*n*-propyl orthoacetate, 55844-54-7; triethyl orthopropionate, 115-80-0; triethyl orthobenzoate, 1663-61-2; sulfur dioxide, 7446-09-5.

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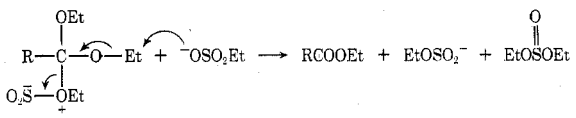
(5) Reference 4 and unpublished observations.
(6) J. R. Nooi, P. C. Van der Hoeven, and W. P. Haslinghuis, *Recl. Trav. Chim. Pays-Bas*, **91**, 161 (1972).
(7) The formation of camphor diethyl acetal under usual reaction condi-

tions[22] is a slow process. This is very likely a consequence of the pronounced steric hindrance imposed by the geminal methyl group. For the same reasons one would expect the acetal to be very reactive. Indeed, camphor diethyl acetal is hydrolyzed in the presence of a catalytic amount of acid, or sulfur dioxide, to camphor and ethanol with extreme ease.

(8) We did not investigate this particular reaction in any detail.
(9) A similar mixture of these eight ortho esters was also found when a drop of methanesulfonic acid was added to a mixture of the same two ortho esters.
(10) G. Hesse and S. Majmudar, *Chem. Ber.*, **93**, 1129 (1960).
(11) N. Tokura and F. Akigama, *Bull. Chem. Soc. Jpn.*, **39**, 838 (1966).
(12) E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1271 (1937).
(13) H. Hart and G. Levitt, *J. Org. Chem.*, **21**, 921 (1956).
(14) This may be an oversimplification and certainly there are alternative possibilities. For example, the reaction between the ethyl sulfite anion and the ortho ester coordinated with sulfur dioxide may provide the same products.



(15) M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **39**, 1296 (1966).
(16) The relative amounts varied from experiment to experiment.
(17) See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 227.
(18) For the same reason one would not expect that the corresponding dicyclohexyl sulfite would be formed in the reaction, and indeed it was not observed among the reaction products.
(19) Clearly, the extent of the exchange reaction, i.e., the formation of the *trans*-4-*tert*-butylcyclohexanol (eq 11), will be a function of the relative rates of the respective processes. The relative amounts of the products varied from experiment to experiment and the ratio of ethanol/*trans*-4-*tert*-butylcyclohexanol was not constant.
(20) See, for example, E. H. Cordes in "The Chemistry of Carboxylic Acids and Esters", S. Patal, Ed., Interscience, New York, N.Y., 1967, pp 632–656.
(21) E. L. Eliel, R. J. L. Martin, and D. Nasipuri, *Org. Synth.*, **47**, 16 (1967).
(22) A. Arbuzow, *Chem. Zentralbl.*, **79**, 1340 (1908).
(23) Ethyl nitrite was prepared from sodium nitrite and ethanol according to the procedure of W. L. Semon and V. R. Damerell, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 204.
(24) *Caution:* excessive pressure!
(25) The same eight peaks were also present in the reaction mixture of the same two ortho esters a short time after a catalytic amount of methanesulfonic acid was added.

Cyclobutylcarbinyl *p*-Bromobenzenesulfonate Solvolysis. 1-Aryl Substituent Effect upon Product Distribution

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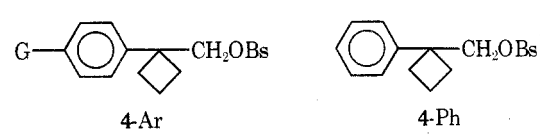
The acetolysis products of 1-phenylcyclobutylcarbinyl (4-Ph), 1-*p*-nitrophenylcyclobutylcarbinyl (4-NPh), and 1-*p*-methoxyphenylcyclobutylcarbinyl (4-MPh) brosylates have been determined in the presence of urea. All of the substrates give 1,2-phenyl rearranged products. The products of the reactions along with previously determined kinetic data[1] suggest that ionization occurs prior to rearrangement. In turn, the phenonium ion intermediate (II) partitions itself among the various product pathways. The mechanistic details are discussed in terms of the Winstein solvolysis scheme.

In a previous[1] solvolytic investigation, it was reported that the transition state for the acetolysis of 4-Ar has little phenonium ion character. Support for this postulate was afforded by the Hammett behavior of 4-Ar ($\rho = -1$), which reveals little direct conjugation between the para substituent and the developing cationic center. For example, the Hammett behavior of a series[2] of para-substituted neophyl tosylates and related systems, solvolyzing with aryl participation, is characterized by ρ values of about -3; while other related systems, solvolyzing without aryl participation, are characterized[2] by ρ values of about -1.



4-Ar 4-Ph

On the other hand, the fact that only 1,2-phenyl rearranged products were isolated[1a] from the acetolysis of 4-Ph provides strong evidence for phenyl bridging in the transition state leading to the intermediate which reacts with solvent.

These findings were rationalized[1b] in terms of Scheme I,

Scheme I