B.—To a solution of 18 g of **1** in 60 ml of chloroform, a crystal of iodine (0.2 g) was added and the solution was irradiated for 48 hr. Work-up as described above gave 4.0 g (22%) of product, mp 127–128.5°.

trans,trans,trans-**1,2-Dibenzoyl-3,4-di-2-thenoylcyclobutane** (**6**).—A solution of 8 g of **2** in 20 ml of chloroform was irradiated for 20 hr. The same procedure as in the previous experiments furnished 0.45 g (6%) of the product **6**, mp 132–134° (from ethanol). In a second run the irradiation time was prolonged to 48 hr. The product was obtained in 10% yield, mp 130–132°. The mass spectrum showed peaks at *m/e* 428, 410, 323, 214, and 192.

Anal. Calcd for $C_{26}H_{20}O_2S_2$: C, 72.87; H, 4.71; S, 14.96; mol wt, 428.6. Found: C, 72.80, 72.90; H, 4.82, 4.79; S, 14.82, 14.95; mol wt (osm), 416.9, 424.1.

trans,tarns,trans-**1,2-Di-2-thienyl-3,4-di-2-thenoylcyclobutane** (**7**) and *trans,cis,trans*-**1,3-Di-2-thienyl-2,4-di-2-thenoylcyclobutane** (**8**).—A solution of 8 g of **3** in 25 ml of chloroform upon irradiation for 20 hr furnished 0.3 g (4%) of a mixture of **7** and **8**, mp 124–134°. No attempts were made to separate the mixture. The mass spectrum showed only peaks with *m/e* of 220.

Anal. Calcd for $C_{22}H_{16}O_2S_4$: C, 59.97; H, 3.67; S, 29.11; mol wt, 440.6. Found: C, 60.14, 59.99; H, 3.57, 3.70; S, 29.04, 28.90; mol wt (osm), 437.4, 431.7.

trans,trans,trans-**1,2-Dibenzoyl-3,4-diphenylcyclobutane** (**9**).—A solution of 17 g of **4** in 50 ml of chloroform was irradiated in small quartz tubes for 20 hr. Work-up in the usual way afforded 1.0 g (6%) of product, mp 125–126.5° (lit.[2] 124–125°). By prolonging the irradiation time and adding a crystal of iodine, the yield of **9** could be improved to 28%.

trans,cis,trans-**1,3-Dibenzoyl-2,4-diphenylcyclobutane** (**10**).—A solution of 7 g of **4** in 20 ml of chloroform was irradiated in ordinary micro test tubes for 20 hr. After evaporation of the solvent, a yellow oil was obtained consisting mainly of starting material (*cis–trans* mixture). Ethanol was added and, on standing, starting material crystallized. It was removed by filtration. From the mother liquor 10 mg (0.15%) of **10** crystallized eventually, mp 234–236° (lit.[2] 225–226°).

Registry No.—**5**, 24825-03-4; **6**, 24825-04-5; **7**, 24825-05-6; **8**, 24825-06-7; **9**, 24825-07-8; **10**, 24825-08-9.

1,5-Hydrogen Migrations in Bicyclic Carboxaldehydes

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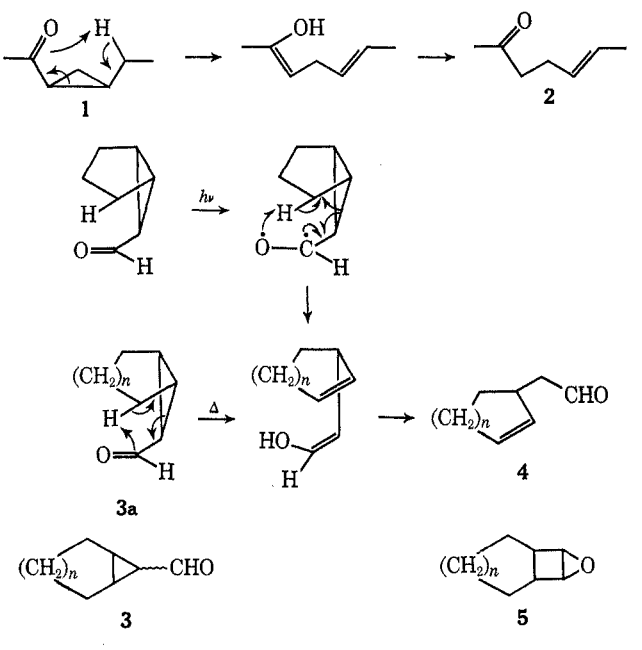
Cyclopropyl ketones have been reported to undergo thermal and photochemical rearrangements to homoallylic ketones (**1** → **2**).[1,2] We have observed that analogous reactions occur in bicyclic carboxaldehydes, **3** (n = 1, 2), where 1,5-hydrogen migration is possible, leading to δ^2-cycloalkenyl acetaldehydes, **4** (n = 1, 2).

Injection of the *endo* isomers of **3** (n = 1, 2) into a vapor phase chromatograph (vpc) at 190° with the injection port heated to 230° produces a single volatile compound identified as the corresponding cycloalkenyl acetaldehyde, **4** (n = 1, 2).[3] The *exo* isomers are inert under these conditions.

The dropwise addition of the *endo* isomer of **3** (n = 1) onto a column of glass beads at 300° under helium gas flow gives a crude pyrolysate whose nmr spectrum is identical with that of **4** (n = 1). The *exo* isomer of **3** (n = 1) remains unchanged at temperatures as high as 400° suggesting that the reaction is not proceeding in a stepwise fashion involving the initial cleavage of the cyclopropyl bond. The necessity for the proximity of the carbonyl group and a γ hydrogen has been demonstrated in a similar bicyclic system where initial thermal rearrangement to a cycloalkenyl acetaldehyde is postulated.[4] The thermal instability of *endo*-**3** (n = 1, 2) may account for its absence and the presence of **4** (n = 1, 2) among the products of the thermal rearrangement of the cyclobutene epoxides, **5** (n = 1, 2).[3]

The irradiation of a 1% ethereal solution of **3a** (n = 1) with 3000 Å light gives **4** (n = 1) in *ca.* 30% yield. Similar irradiation of *exo*-**3** (n = 1) gives a complex mixture of products which does not contain significant amounts of **4** (n = 1). Initial rupture of the cyclopropyl bond would give a common intermediate. An intramolecular γ hydrogen abstraction (Norrish "type II"), leading to the formation of **4**, can only occur in the *endo* isomer. It appears that this pathway is favored when possible.[2]



Experimental Section[5]

Bicyclic Carboxaldehydes (**III**).—The *endo* isomers of **3** (n = 1, 2) were synthesized by known procedures.[6,7] The *exo* isomers of **3** (n = 1, 2) were synthesized by epimerization of the *endo* isomers.[7] The aldehydic protons of the *exo* and *endo* isomers have different chemical shifts in their nmr spectra providing a

(1) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967). This article contains an excellent discussion of and leading references to the thermal rearrangement of cyclopropyl ketones, carboxaldehydes, and carboxylate esters.

(2) W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).

(3) D. L. Garin, *ibid.*, **34**, 2355 (1969).

(4) F. Bickelhaupt, W. L. DeGraaf, and G. W. Klumpp, *Chem. Commun.*, 53 (1968).

(5) A Perkin-Elmer R-20 spectrometer was used for nmr measurements in $CDCl_3$ using TMS as internal standard. Wilkens A-700 (Autoprep) instruments were used for vpc analyses and separations utilizing silicone gum rubber (SE-30) and fluorosilicone (QF-1) as stationary phase materials.

(6) R. T. LaLonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **86**, 4068 (1964); D. L. Garin, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1964.

(7) D. L. Garin, Abstracts, 149th National Meeting of the American Chemical Society, Houston, Texas, 1970, Orgn 137 (submitted for publication).

rapid determination of purity. The aldehydes were readily oxidized to the known carboxylic acids for conclusive identification *via* mixture melting point determinations.[8]

Vpc Results.—The injection of up to 50 μl of **3** (n = 1, 2) into the vpc at 190° with an injection port temperature of 230° resulted in apparently quantitative rearrangment of the *endo* isomers to **4** (n = 1, 2) without affecting the *exo* isomers.[9] Typical retention times (min) for a 20 ft × 3/8 in. 30% QF-1 column under a helium gas flow rate of 100 cc/min were: *exo*-**3** (n = 1), 18; **4** (n = 1), 12; *exo*-**3** (n = 2), 28; **4** (n = 2), 17. Samples were collected from the vpc and subjected to spectral analysis. The *exo* isomers were shown to be unchanged while the nmr and infrared spectra ($CHCl_3$) of **4** (n = 1, 2) were identical with that of authentic material.[3]

Pyrolysis Results.—The dropwise addition of the *endo* isomer of **3** (n = 1) onto a 9 in. column of glass beads in a temperature controlled oven at 240° under helium gas flow and flushing with ether gives a crude pyrolysate containing 25% of **4** (n = 1) and 75% of starting material determined by integration of the aldehydic protons at δ 9.85 (t) and 9.55 (d), respectively. At 300°, the nmr spectrum of the crude pyrolysate is identical with that of **4** (n = 1). The *exo* isomer of **3** (n = 1) remains unchanged at temperatures as high as 400° determined by nmr analysis of the crude pryolysate.

Photochemical Rearrangements.—A solution of 60 mg of *endo*-**3** (n = 1) in 7 ml of ether was irradiated with 3000 Å light in a quartz tube in a Rayonet reactor for 5 hr. Some polymeric material had formed on the sides of the tube. The ether was removed *in vacuo* and $CDCl_3$ added to the residue (54 mg). Comparison of the nmr spectrum of this material with that of **4** (n = 1) allowed an estimation of *ca.* 30% of **4** (n = 1) in the crude mixture from integration of the aldehydic and olefinic protons against the total proton count in the nmr spectrum of the crude reaction mixture. Similar irradiation of 65 mg of *exo*-**3** (n = 1) in 7 ml of ether gave a product mixture whose nmr spectrum showed that more than 90% of the starting material had reacted but there were no olefinic absorptions.

Registry No.—*endo*-**3** (n = 1), 4729-42-4; *endo*-**3** (n = 2), 24874-09-7.

Acknowledgment.—The support of the Petroleum Research Fund (1207-G1) and the Research Committee-UMSL is gratefully acknowledged.

(8) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963); J. A. Berson and E. S. Hand, *ibid.*, **86**, 1978 (1964). The author is indebted to Professor Berson for an authentic sample of bicyclo-[4.1.0]heptan-7-*endo*-carboxylic acid.

(9) No other peaks are observed in the chromatogram but preparative collection from the vpc results in 80–90% recovery. This loss, due to incomplete trapping of the effluent, is not unusual.

Chloromethyl Sulfoxides and Sulfones from 1,2-Dichlorovinyl Sulfoxides and Sulfones

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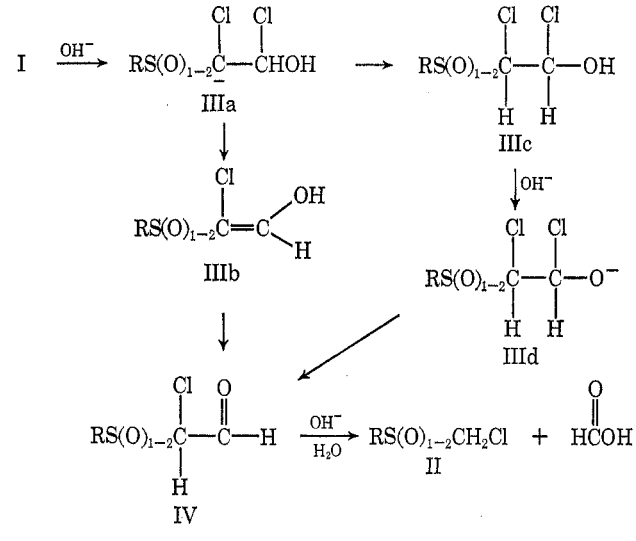
There has been considerable recent interest in the preparation and chemistry of α-chloro sulfoxides[1] and in the chemistry of sulfoxides in general.[2] We report here the facile preparation of α-chloro sulfoxides and sulfones from the corresponding 1,2-dichlorovinyl compounds by treatment with dilute aqueous base. In Table I are listed a number of examples of this reaction and the recrystallized yields of the products.[3–6] Crude yields were generally 10 to 15% higher, and the crude products were quite clean, impurities being soluble in the basic aqueous phase. Identification of products was made by elemental analyses and spectral (ir and nmr) and melting point comparison with authentic samples prepared by oxidation of the corresponding α-chloro sulfides.[7,8]

In only one case, that of the *t*-butyl sulfoxide IIc, was a relatively poor yield obtained. Part of the starting material was converted into unidentified base-soluble products under all conditions explored. The use of organic solvents such as dioxane, tetrahydrofuran, dimethyl sulfoxide, and dimethylformamide in conjunction with the aqueous base for the hydrolysis of Ia–c led uniformly to lower yields of IIa–c. Milder conditions were necessary with the benzyl derivatives Ie–f, as heating led to styrene from the chloromethyl sulfone IIf *via* a Ramberg–Backlund reaction and to unidentified products from the sulfoxide IIe.



The chemistry of β-chlorovinyl sulfones has been extensively investigated and reaction with various nucleophiles (RO^-, RS^-, RSO_2^-, R_2NH) leads to β-substituted vinyl sulfones with displacement of chloride.[4,9] Thus, it is reasonable to postulate that the initial step in the present reaction is nucleophilic attack by hydroxide to give the carbanion IIIa, which can be converted to the aldehyde IV either by direct elimination of chloride to give the tautomeric enol IIIb, or by protonation to give IIIc followed by elimination of HCl through IIId. The aldehyde would be highly susceptible to attack by hydroxide followed by cleavage to give formic acid and the α-sulfinyl or sulfonyl anion which

(1) (a) R. N. Leoppky and D. C. K. Chang, *Tetrahedron Lett.*, 5415 (1968); (b) M. Hojo and Z. Yoshida *J. Amer. Chem. Soc.*, **90**, 4496 (1968); (c) T. Durst, *ibid.*, **91**, 1034 (1969).

(2) C. R. Johnson and J. R. Sharp, "The Chemistry of Sulfoxides," Intra Science Research Foundation, Santa Monica, Calif., 1969.

(3) E. Ayca, *Fac. Sci. Univ. Istanbul, Ser. C*, **22**, 371 (1957); *Chem. Abstr.*, **53**, 11287*f* (1959).

(4) H. J. Backer, *et al.*, *Rec. Trav. Chim. Pays-Bas*, **72**, 813 (1953); *Chem. Abstr.*, **49**, 11538*g* (1955).

(5) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5187 (1964).

(6) J. Metivier, U. S. Patent 2,793,234 (1957).

(7) H. Bohme, *Ber.*, **69**, 1610 (1936).

(8) In agreement with Durst,[1c] we find that *m*-chloroperbenzoic acid oxidation, using chloroform or methylene chloride as solvent, gives excellent yields of the sulfoxides.

(9) F. Montanari and A. Negrini, *Gazz. Chim. Ital.*, **87**, 1068 (1957); *Chem. Abstr.*, **52**, 9987*g* (1958). L. Maioli and G. Modena, *ibid.*, **89**, 854 (1959); *Chem. Abstr.*, **54**, 22451*i* (1960).