cyclohexanone[20] and dehydrated with thionyl chloride and pyridine.[27] The unsaturated ester was distilled, b.p. 122.5–123° (30 mm.), n^{26}_D 1.4600 (lit.[20] 108–112° (12 mm.)).

Lactone of 2-(2-Hydroxycyclohexylidene)-propionic Acid (X).—The lactone was prepared from 2-(2-ketocyclohexyl)-propionic acid according to the procedure of Cocker and Hornsby.[4] The material boils 121–124° (3 mm.), n^{25}_D 1.5060 (lit.[4] 133–134° (3 mm.)).

Attempted Reaction of Aniline and Pseudosantonin.—Following the general procedure of Kuehl, Linstead and Orkin,[25] 1.0 g. of pseudosantonin was allowed to stand for four days at room temperature with 1 g. of aniline. The reaction mixture was diluted with methylene chloride, the solution extracted with dilute hydrochloric acid and the solvent evaporated. The residue was recrystallized from methylene chloride to yield 0.8 g. of pseudosantonin, m.p. 188.0–190.4°.

BERKELEY 4, CALIFORNIA

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(27) This experiment was performed by Mr. Thomas Colby.

[CONTRIBUTION FROM THE H. FLETCHER BROWN LABORATORIES OF THE UNIVERSITY OF DELAWARE]

Isomerism in the Diels–Alder Reaction. II. The Bromination of Diels–Alder Adducts[1]

BY HAROLD KWART AND LLOYD KAPLAN

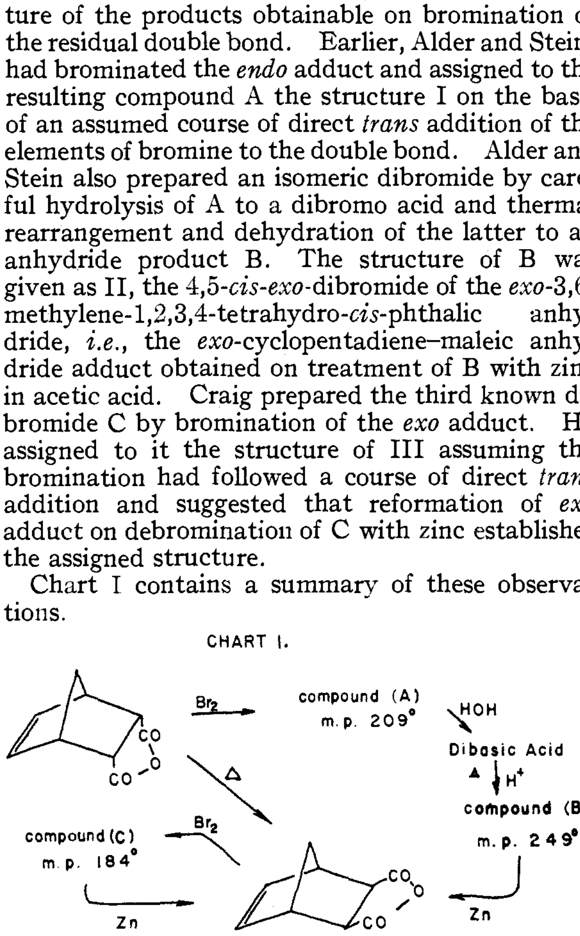
RECEIVED NOVEMBER 24, 1952

The steric course of bromination of the Diels–Alder adducts of cyclopentadiene and maleic anhydride has been examined. The previously reported structures of two of the three known dibromides in this series are found to be inconsistent with the measured dipole moments. Structural assignments are revised to bring all three structures into line with the dipole moment data and with modern concept on the steric course of addition and rearrangement reactions in related bicyclic systems.

Craig[2] has examined the reaction mechanism of the thermally induced transformation of the *endo* into the *exo* adduct of cyclopentadiene and maleic anhydride. Among other considerations taken into account in his examination, he discusses the nature of the products obtainable on bromination of the residual double bond. Earlier, Alder and Stein[3] had brominated the *endo* adduct and assigned to the resulting compound A the structure I on the basis of an assumed course of direct *trans* addition of the elements of bromine to the double bond. Alder and Stein also prepared an isomeric dibromide by careful hydrolysis of A to a dibromo acid and thermal rearrangement and dehydration of the latter to an anhydride product B. The structure of B was given as II, the 4,5-*cis*-*exo*-dibromide of the *exo*-3,6-methylene-1,2,3,4-tetrahydro-*cis*-phthalic anhydride, *i.e.*, the *exo*-cyclopentadiene–maleic anhydride adduct obtained on treatment of B with zinc in acetic acid. Craig prepared the third known dibromide C by bromination of the *exo* adduct. He assigned to it the structure of III assuming the bromination had followed a course of direct *trans* addition and suggested that reformation of *exo* adduct on debromination of C with zinc establishes the assigned structure.

Chart I contains a summary of these observations.

CHART I.



In the course of our work with this system it appeared that the structures of A, B and C previously assigned may be in error for two reasons; the experimental evidence did not seem to be complete or conclusive in some instances and the assumed reaction course for bromination of the double bond ignored the possibilities of rearrangement previously identified in other double bond addition reactions of this system.[4]

It seemed apparent also that a quick test of the validity of the assigned structure was obtainable through a comparison of the computed dipole moments of I, II and III with the experimental values we have determined and are reporting here for compounds A, B and C. Table I affords this comparison.

It is to be noted that a large discrepancy exists between the calculated and observed values in the cases of compounds A and B whereas good agreement is demonstrated for compound C. On this basis it is clear that the structure of compound C has been properly assigned, but the structures previously assigned for A and B are seriously in error.

What structures do accord with the observed dipole moments and how could these structures arise in the procedure used for their preparation? A tabulation of all other possible dibromo anhydrides that would possess the observed reactions[2,3] of the three isomers is contained in Table I together with their calculated dipole moments.

The limits of inaccuracy in our dipole moment measurement is estimated to be ±0.1 *D*. The structure dipole moment values (Table I) calculated from individual bond moments are not corrected in all cases for mutual polarizability of the bonds and internal field interaction effects.[5] We estimate from the magnitude of such effects that we have encountered in similar molecules[10b] a maximum correction of ±0.3 *D*. It is seen, therefore, that the upper limit of discrepancy between calculated and observed moments is ±0.4 *D*.

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(1) The research work being reported here has been supported by the Office of Naval Research under contract N-onr-567(00). *Cf.* previous paper in this series—THIS JOURNAL, **74**, 3094 (1952).

(2) D. Craig, *ibid.*, **73**, 4889 (1951).

(3) K. Alder and G. Stein, *Ann.*, **504**, 247 (1933).

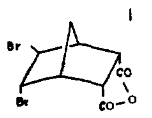
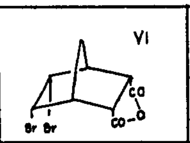
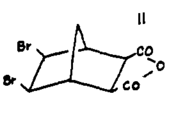
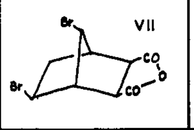
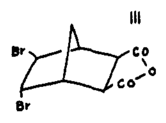
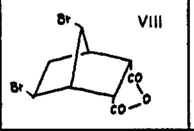
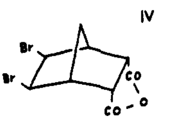
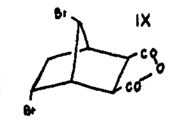
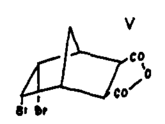
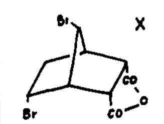
(4) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946); R. B. Woodward and H. Baer, *ibid.*, **70**, 1161 (1948).

(5) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942); R. J. W. LeFèvre, "Dipole Moments," Methuen and Co., London, 1948, Chap. III.

TABLE I

DIPOLE MOMENTS OF ALL POSSIBLE STRUCTURES

calculated

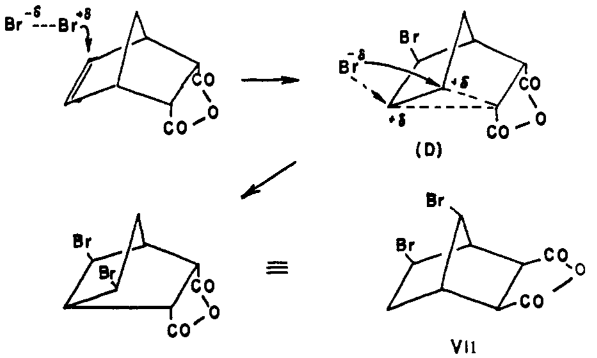
 I	6.1[c]	 VI	8.6
 II	4.4[b]	 VII	4.5
 III	2.5[c]	 VIII	4.5
 IV	4.3	 IX	3.0
 V	4.4	 X	6.0

	Observed	
Compound	μ_D, obsd.	Structure previously assigned[a]
A	4.5	I
B	3.2	II
C	2.3	III

[a] *Cf.* reference 2. [b] A value of 2.0 *D* for a normal C–Br bond moment is used in this calculation.[6] A value of 4.8 *D* is used for a normal bond moment for the anhydride obtained as a mean experimental value—*cf.* experimental section. [c] Value corrected for the known experimental moment of *trans*-2,3-dibromonorbornylane. Unpublished reports from these laboratories.

The observed moment of compound A is noted in Table I to be in agreement with five possible structures whose calculated dipole moments are within the estimated limits of discrepancy. On the other hand the observed dipole moments of compounds B and C correspond well to a single structure in each case. It seems reasonable by considering the mechanism of formation and the possibilities therein for rearranged products[7] ignored by the previous authors[2,3] to reconcile the dipole moment data with the structural assignments for compounds B and C and make a consistent choice among the possibilities for the structure of compound A.

Thus the addition of bromine to the *endo*-cyclopentadiene-maleic anhydride adduct would, in terms of the modern concept[8] of this reaction type, involve primary attack of an electrophilic bromine fragment on the double bond and consequent formation of a bridged cation intermediate[9] as pictured in equation (1).



EQUATION I.

That the initial attack on the double bond occurs at the *exo* side as represented above is consonant with many analogous observations in the stereochemistry of addition to multiple bonds in bicyclic systems.[10] Stabilization of the bridged cation complex D would be expected to occur by *trans* displacement of the delocalized electron pair by the accompanying halogen anion. It is of interest that the steric course of the reaction is in keeping with observations[10b] on the analogous chlorination of pinene. Displacement at the dotted arrow site would result in the unrearranged structure IV whereas displacement at the other site would lead to the structure VII indicated. Both IV and VII are consistent with the dipole moment data. Preference[11] for the rearranged structure over the unrearranged IV is dictated by many demonstrations of rearranged products on addition to the double bond in related bicyclic systems, *e.g.*, the observations of Bartlett and Schneider[4] on the addition of halogen in dicyclopentadiene and the results of bromination of norbornylene in this Laboratory.[10b] Furthermore only structures VII and IV lead reasonably and by means of well known analogous reactions in bicyclic systems to the unique structure IX consistent with the observed moment of compound B. A profound rearrangement of the sort necessary to explain the formation of structure IX on treatment of structure IV with acid appears to have no analogy in previous observations. However, treatment of VII with strong acid (HBr) at high temperature would be expected[10b] to promote the establishment of bornyl–isobornyl halide equilibrium[12] known to

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(6) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publishers, New York, N. Y., 1950, p. 215.

(7) W. E. Doering, Abstracts, 113th Meeting of the American Chemical Society, April 19–23, 1948, Chicago, Illinois, p. 44; T. P. Neville, E. DeSala and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); *cf.* also reference (10).

(8) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949, p. 141 *et seq.*

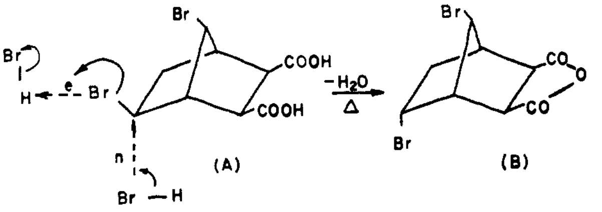
(9) For a comprehensive discussion of entirely analogous cases see S. Winstein, *et al.*, THIS JOURNAL, **74**, 11 (1952), and reference (10b).

(10) (a) K. Alder and G. Stein, *Ann.*, **515**, 191 (1935); *ibid.*, **525**, 183 (1936); (b) unpublished reports from these laboratories.

(11) A referee has contended that the unrearranged structure IV is equally acceptable. In our experience[10b] as well as in that cited[4] *cis* vicinal derivatives have never been obtained on addition to bicyclic double bonds with reagents that show a characteristic stepwise pattern to their reaction.[8] Gates and Malchik of the University of Rochester report in a private communication of their unpublished work that hydroxylation of dicyclopentadiene with performic acid, an entirely similar system, afforded no product that tested for vicinal diol with lead tetraacetate or periodic acid, the reaction apparently occurring entirely by rearrangement. *Cis* vicinal glycols have been obtained from bicyclic double bonds however by use of reagents (aq. $KMnO_4$ or H_2O_2 and OsO_4) which appear always to add simultaneously at both ends of the double bond, probably by a cyclic process (*cf.* K. Ziegler, *et al.*, *Ann.*, **551**, 1 (1942)).

(12) H. Meerwein and K. von Emster, *Ber.*, **55**, 2500 (1922).

favor the bornyl configuration. Equation (2) represents this acid-catalyzed isomerization.



EQUATION 2.

We picture this as a concerted solvolysis[13] and surmise that since a moderate amount of HBr is eliminated in a side reaction, the halogen acid is functioning as the electrophilic reagent as well as the source of nucleophilic reagent (Br^-). The considerably greater inertness in solvolytic reactivity of halogen on the methylene bridge[14] apparently prevents a similar inversion at the 7-position. The formation of an unrearranged product, structure III, on bromination of the *exo*-cyclopentadiene–maleic anhydride adduct would imply that a bridged ion intermediate similar to that postulated above for addition to the *endo* adduct does not obtain in bromination of the *exo* configuration and the normal *trans* course of halogen addition to a double bond occurs. A pertinent observation has been made by Bartlett and Barnes[15] in their studies of the solvolysis of the 2-tosylates of dihydrodicyclopentadiene. These authors have shown that greater assistance from participation of the neighboring bond in formation of a bridge cation intermediate is afforded the isomer in which the substituent ring is fused to the bicycloheptane system in the *endo* configuration.

Experimental[16]

Preparation of *endo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Anhydride (the *endo* Adduct).—The procedure of Diels and Alder[17] was followed using one mole of freshly distilled cyclopentadiene and one mole of maleic anhydride. The product was recrystallized from low boiling petroleum ether. A 95% yield of the *endo* adduct (m.p. 161–162°)[17] was obtained.

Bromination of the *endo*-Adduct.—The procedure of Bartlett and Schneider[4] was followed. From 0.1 mole (16.4 g.) of the *endo*-adduct and 0.12 mole (19.2 g.) of bromine there was obtained 22 g. (68%) of the dibromoanhydride, m.p. 205–206°.

Preparation of *endo*-3,6-Methylenehexahydro-*cis*-phthalic Anhydride.—The procedure of Bartlett and Schneider was followed. From 0.1 mole (16.4 g.) of the *endo*-adduct there was obtained 14.4 g. (87%) of the completely saturated compound (m.p. 165–167°).

Preparation of *exo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Anhydride (the *exo*-Adduct).—The procedure of Craig[2] was followed. One mole (164 g.) of the *endo*-adduct was heated in an open flask immersed in an oil-bath at 190 ± 2° for 1.5 hours as measured by a thermometer immersed in the reaction mixture. Some material was lost due to sublimation. The brown cake that remained on cooling was taken up in 500 cc. of boiling benzene and boiled with 3 g. of norit. The filtered solution yielded 35 g. of crystalline material (m.p. 122–126°) when cooled to room temperature. Concentration of the filtrate produced an additional 12.6 g. of crystals (m.p. 112–117°). The two crops of crystals were combined and recrystallized from 200 cc. of benzene, yielding 30.7 g. of the *exo*-adduct (m.p. 139–141°).

Bromination of the *exo*-Adduct.—The procedure followed was that of Bartlett and Schneider.[4] From 0.1 mole of the *exo*-adduct and 0.12 mole of bromine there was obtained 22 g. (68%) of the dibromoanhydride, m.p. 189–189.5°.

Preparation of *exo*-3,6-Methylenehexahydro-*cis*-phthalic Anhydride.—The procedure of Bartlett and Schneider[4] was followed. From 0.1 mole of the *exo*-adduct there was obtained 13.3 g. (80%) of the completely saturated compound (m.p. 85–86°).

Hydrolysis of the Dibromoanhydride (m.p. 205–206°).—The anhydride was hydrolyzed according to the procedure of Alder and Stein.[3] One tenth of a mole (32.4 g.) of the dibromoanhydride yielded 32 g. (94%) of the dicarboxylic acid (m.p. 181–182° dec.).

Preparation of the Dibromoanhydride (m.p. 248–249°).—The procedure of Bartlett and Schneider[4] was followed. Twelve grams of the dibromoacid (m.p. 181–182°) yielded 3.2 g. of the dibromoanhydride (m.p. 248–249°).

Determination of the Dipole Moments of the Various Adducts.—The apparatus used in determining the capacitance of the various solutions was similar to that of Smyth and Stranathan.[18] A 1000-cycle hummer was used to determine the null point when taking readings.

TABLE II

DIPOLE MOMENT DATA FOR THE VARIOUS ISOMERS

Compound	Concn., moles/cc. × 10^5	ϵ	n^2	S^0	μ_D
exo-3,6-Methylenehexahydro-*cis*-phthalic anhydride	0.00	2.2175	2.0161	0.027	4.8
	2.29	2.2805	2.0173		
	4.16	2.3318	2.0181		
	7.58	2.4221	2.0190		
	9.63	2.4777	2.0198		
endo-3,6-Methylenehexahydro-*cis*-phthalic anhydride	0.00	2.2145	2.0167	0.027	4.8
	2.21	2.2845	2.0175		
	4.50	2.3453	2.0187		
	6.86	2.4093	2.0192		
	9.90	2.4915	2.0201		
exo-Adduct dibromide (m.p. 183–184°)	0.00	2.2165	2.0170	0.006	2.3
	3.06	2.2372	2.0190		
	5.52	2.2549	2.0207		
	7.62	2.2718	2.0221		
	9.26	2.2825	2.0239		
	0.00	2.2194	2.0170		
	2.23	2.2350	2.0187		
	4.31	2.2488	2.0201		
	6.70	2.2684	2.0215		
	8.92	2.2849	2.0232		
endo-Adduct dibromide (m.p. 209°)	0.00	2.2164	2.0175	0.023	4.5
	3.01	2.2908	2.0204		
	6.02	2.3614	2.0224		
	7.78	2.4010	2.0244		
	9.58	2.4454	2.0261		
	0.00	2.2194	2.0170		
	1.89	2.2635	2.0187		
	4.38	2.3185	2.0201		
	6.30	2.3749	2.0218		
	9.35	2.4470	2.0244		
Dibromoanhydride (m.p. 249–250°)	0.00	2.2135	2.0170	0.012	3.2
	2.73	2.2461	2.0192		
	4.69	2.2708	2.0207		
	6.98	2.3002	2.0227		
	10.40	2.3433	2.0258		

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(13) C. G. Swain, THIS JOURNAL, **70**, 1119 (1948).

(14) J. D. Roberts, W. Bennet and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(15) P. D. Bartlett, Abstracts of the Twelfth National Organic Chemistry Symposium of the American Chemical Society, Denver, Colorado, June 12–15, 1951, p. 6.

(16) All melting points given are uncorrected and were taken with a hot stage microscope.

(17) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(18) (a) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939); (b) J. Stranathan, *Rev. Sci. Instruments*, **5**, 334 (1934).

Dioxane used as a solvent in the determinations was technical grade which was refluxed over sodium for a minimum of two days and then distilled from sodium as needed. The fraction boiling at 101.5° was used in this work. The benzene for one determination was obtained by distilling thiophene-free benzene from sodium. The fraction boiling at 80–80.5° was taken.

Calculations of the dipole moments from the dielectric constant and refractive index data in Table III were done by the Guggenheim method of initial slopes.[1]

Acknowledgment.—The authors wish to express their gratitude and appreciation for the generous support of this work by the Office of Naval Research.

(19) See reference 10b for further references and discussion.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Internal Condensation of 2,4-Diphenyl-1-butanesulfonyl Chloride to a Five- in Preference to a Seven-membered Cyclic Sulfone[1]

BY WILLIAM E. TRUCE, DONALD D. EMRICK AND ROBERT E. MILLER

RECEIVED FEBRUARY 6, 1953

The preference of five- rather than seven-membered ring sulfone formation by the Friedel–Crafts cyclization of ω-phenvlalkanesulfonyl chlorides is demonstrated by the formation of 2,3-dihydro-3-(β-phenylethyl)-benzothiophene-1-dioxide rather than 3-phenylhomothiochroman-1-dioxide from 2,4-diphenyl-1-butanesulfonyl chloride.

Cyclization of ω-phenylalkanesulfonyl chlorides by the Friedel–Crafts method proceeds best when forming the six-membered ring sulfone, while the five- and seven-membered ring compounds are formed in much lower, and approximately equal yields.[2] To determine whether the five- or seven-membered ring sulfone would be formed preferentially when in open competition, 1,5-diphenyl-2-pentanesulfonyl chloride was prepared as outlined.

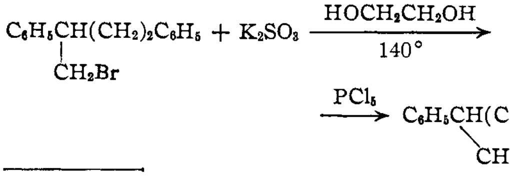
$$C_6H_5(CH_2)_3MgBr + C_6H_5CH_2CHO \longrightarrow C_6H_5(CH_2)_3CH(OH)CH_2C_6H_5 \xrightarrow{PBr_3}$$

$$C_6H_5(CH_2)_3CHBrCH_2C_6H_5 \xrightarrow[2,\ KOH,\ H_2O]{1,\ CS(NH_2)_2} C_6H_5(CH_2)_3CH(SH)CH_2C_6H_5 \xrightarrow[AcOH]{Cl_2,\ H_2O}$$

$$C_6H_5(CH_2)_3CH(SO_2Cl)CH_2C_6H_5$$

Unfortunately, the resulting sulfonyl chloride was unstable, losing sulfur dioxide even when stored in a refrigerator; therefore, this approach to the problem was abandoned.

In order to avoid this characteristic instability[3] of secondary sulfonyl chlorides, the primary sulfonyl chloride, 2,4-diphenyl-1-butanesulfonyl chloride, was prepared by the sequence of reactions

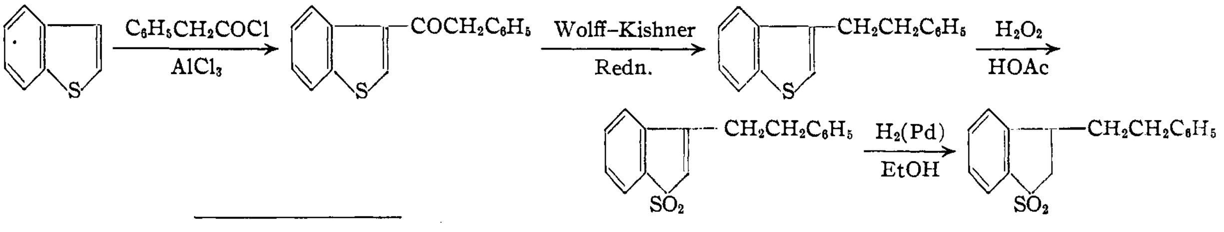


$$C_6H_5CH(CH_2Br)(CH_2)_2C_6H_5 + K_2SO_3 \xrightarrow[140°]{HOCH_2CH_2OH} \xrightarrow{PCl_5} C_6H_5CH(CH_2SO_2Cl)(CH_2)_2C_6H_5$$

Cyclization[2] of this sulfonyl chloride yielded 2,3-dihydro-3-(β-phenylethyl)-benzothiophene-1-dioxide; none of the isomeric 3-phenylhomothiochroman-1-dioxide was isolated. This indicates that the five-membered ring sulfone is formed in preference to the seven-membered ring sulfone in the Friedel–Crafts cyclization of phenylalkanesulfonyl chlorides.

2,4-Diphenyl-1-bromobutane was prepared by way of 2,4-diphenylbutyric acid. A new but inferior approach to this acid began by alkylating diethyl phenylmalonate with β-phenylethyl bromide. However, the product, diethyl phenyl-(β-phenylethyl)-malonate, was not saponified by prolonged refluxing with strong alkali; it was hydrolyzed and decarboxylated, with difficulty and in poor conversion, to 2,4-diphenylbutyric acid, using strong sulfuric acid–potassium bisulfate as the reagent.

That the product of the Friedel–Crafts cyclization was 2,3-dihydro-3-(β-phenylethyl)-benzothiophene-1-dioxide and not 3-phenylhomothiochroman-1-dioxide was established by the following independent synthesis of the former compound.



Experimental

1,5-Diphenyl-2-pentanesulfonyl Chloride.—The Grignard reagent[4] of γ-phenylpropyl bromide was treated with phenylacetaldehyde, and the product was distilled at reduced pressure; b.p. 159° (0.7 mm.), n^{20}_D 1.5593, yield 57% of theory.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.98; H, 8.41. Found: C, 84.90, 84.95; H, 8.20, 8.09.

This product, 1,5-diphenyl-2-pentanol, was treated with phosphorus tribromide[5] at −5 to 0°. Distillation of the

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(1) Taken from Mr. Emrick's and Mr. Miller's M.S. theses.

(2) W. E. Truce and J. P. Milionis, THIS JOURNAL, **74**, 974 (1952).

(3) M. H. Gold and L. J. Druker, *J. Org. Chem.*, **16**, 1510 (1951).

(4) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 306.

(5) *Ibid.*, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 358.