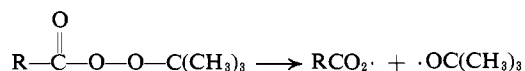


be off by as much as a factor of three or four. Furthermore, the possibility of backside attack of the methylazo radical by the α -phenylethyl radical to give N_2 and cumene while in the cage was neglected because of the lack of knowledge of this type of reaction. Inclusion of such a displacement in the scheme as an important reaction lowers the limit for k_9 .

Activation Parameters. The entropy of activation and the Arrhenius energy of activation for III were measured and are shown together with those for I and II in Table V. In reactions involving similar compounds capable of giving two or three fragments it might be expected that the entropy of activation would be greater when three particles are being produced than when two particles are being formed, due to the increase in rotational freedom. This is not the case. The general order is similar to that observed for the decomposition of peresters by Bartlett and co-workers.³⁷ In a series of compounds, they noted a decrease of energy of activa-



tion with concurrent decrease of entropy of activation as R varied. When R is phenyl, the incipient carboxy radical could be stabilized in the transition state by delocalization of the free electron on the ring. This can be seen as a lowering of the activation energy in the rupture of the oxygen-oxygen bond when compared to the parent molecule, *t*-butyl peracetate. Such stabilization, however, generally creates steric restrictions in the transition state in that the phenyl group is not free to rotate; it was suggested that this is the cause for the simultaneous decrease in ΔS^* .³⁷ Similar arguments can

(37) P. D. Bartlett, *Experientia Suppl.*, 7, 275 (1957). The authors thank Dr. Leon Gortler for citing this paper.

be made to explain the trends in entropy and energy of activation for the decomposition of I, II, and III. In I, both phenyl groups help to delocalize the free electrons on the benzylic carbons. Therefore rotation of both rings is restricted in order that its π -orbitals overlap with the half-filled p-orbital being formed at the benzylic carbon. The isotope effects in the decomposition of II were interpreted as showing little progress in the rupture of the nitrogen-2-propyl-carbon bond. This would mean little requirement for stabilization of the hardly formed 2-propyl radical and in turn little restriction on the geometry of the isopropyl group; the energy and entropy of activation increase in going from I to II. Finally in the decomposition of III we have shown that only the benzylic carbon-nitrogen bond ruptures in the slow step. The methyl group contributes little stabilization and therefore is free to rotate, as seen by the increase in energy and entropy of activation.

Table V. Activation Parameters in the Thermal Decomposition of Azo Compounds

	E_a , kcal./ mole	ΔS^* , e.u.	Ref.
$C_6H_5CH(CH_3)N=N(CH_3)CHC_6H_5$ (I)	32.6	7.0	15
$C_6H_5CH(CH_3)N=NCH(CH_3)_2$ (II)	36.5	9.3	5c
$C_6H_5CH(CH_3)N=NCH_3$ (III)	38.6	14.0	This work

Acknowledgment. The authors are indebted to Mr. Theodore Middleton for mass spectrometric determinations and to Dr. D. R. Christman and Mrs. C. Paul for v.p.c. analyses.

The Optical Activity of Butylethylhexylpropylmethane¹

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Contribution from the Department of Organic Chemistry of The University, Bloemensingel 10, Groningen, The Netherlands. Received March 8, 1965

A synthetic route to an asymmetric hydrocarbon, butylethylhexylpropylmethane, is described. Within the limits of experimental error it is established that both enantiomers exhibit no rotation of plane-polarized light between 280 and 580 m μ . This finding is in accord with predictions based on empirical calculations.

Most textbooks introduce the subject of stereoisomerism by stating that an asymmetric carbon atom in a molecule gives rise to rotation of the plane of polarized light. The two enantiomers differ from one another by the fact that their rotation is opposite in direction.

However, van't Hoff³ in his first publications nearly a century ago already recognized that the degree of

difference between the four substituents at the asymmetric center might determine whether optical activity would be observed or not.

A particularly instructive test case appeared to be a tetraalkyl methane of type A. The question we wished to answer was "Is the difference in the length of the four alkyl groups a sufficient condition for optical activity to be observed with present day instruments?" It has been predicted⁴ that a paraffin with three or four flexible chains at the asymmetric center should be almost completely optically inactive.

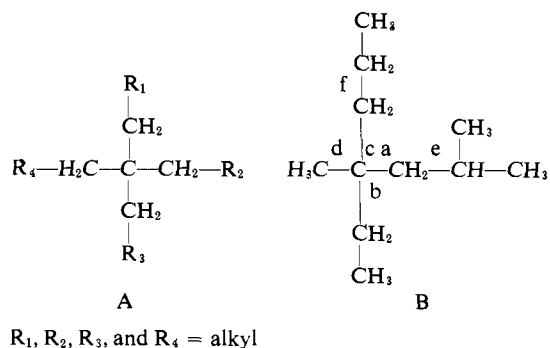
An asymmetric hydrocarbon of a somewhat dif-

(3) J. H. van't Hoff, "Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuurformules in de ruimte," Utrecht, 1874; "La chimie dans l'espace," Rotterdam, 1875; *Bull. soc. chim. France*, 23, 295 (1875).

(4) (a) J. H. Brewster, *J. Am. Chem. Soc.*, 81, 5475, 5483, 5493 (1959); *Tetrahedron*, 13, 106 (1961); (b) D. H. Whiffen, *Chem. Ind. (London)*, 964 (1956).

(1) Part of this work was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 31-Sept. 4, 1964.

(2) To whom inquiries should be sent.



ferent type, ethylisobutylmethylpropylmethane (B), had been prepared by Streitwieser starting from 25% optically pure ethylisobutylmethylacetic acid.⁵ This compound was shown to have a molecular rotation of $0.05 \pm 0.03^\circ$ at the sodium D-line. If we assume Brewster's analysis⁴ to be applicable to quaternary hydrocarbons, this rotation is due to "atomic asymmetry" since the contribution of "conformational asymmetry" to the rotation turns out to be zero.⁶

In order to examine the optical activity of a quaternary hydrocarbon at shorter wave lengths than the sodium D-line we have synthesized asymmetric butyl-ethylhexylpropylmethane (I). The differences in polarizability of the alkyl groups in I are small. It is these differences in polarizability which are responsible for atomic asymmetry in Brewster's sense.⁴ Here again the contribution of conformational asymmetry to the optical activity can be expected to be negligible.⁷

Synthetic approaches to quaternary hydrocarbons have been limited,^{5,8} while those which lend themselves to resolution into enantiomers at an appropriate intermediate stage are rare indeed.

Our route solves both problems as shown in Scheme I. The condensation of thiophene with ketones described in the literature⁹⁻¹¹ was applied to hexanone-3 furnishing, in 52% yield, 3,3-di(2'-thienyl)hexane (II) as a nearly colorless oil. Monoacylation was best accomplished using slightly more than one-half the required amount of acetic anhydride in the presence of a few drops of 60% perchloric acid.^{12,13} The

(5) A. Streitwieser, Jr., and T. R. Thomson, *J. Am. Chem. Soc.*, **77**, 3921 (1955).

(6) Conformational analysis of this hydrocarbon according to Brewster⁴ reveals that within the 22 molecular conformations of lowest energy there is complete cancellation of conformational asymmetry contributions to optical rotation. The bondings a, b, c, and d (B) show (necessarily) the prohibited double skew pattern whereas the conformation of bonding e cannot be consistent with Brewster's "5-atom" rule.

(7) The conformational asymmetry contribution to the rotation of the 459 molecular conformations of lowest energy of I cancel each other completely. The conformations of the bondings attached to the asymmetric atom show (necessarily) the forbidden double skew pattern.

(8) (a) N. Rabjohn and M. J. Latina, *J. Am. Chem. Soc.*, **76**, 1389 (1954); (b) R. Ya. Levina, A. A. Faïnzil'berg, and E. G. Treshchova, *J. Gen. Chem. USSR*, **22**, 430 (1952); *Chem. Abstr.*, **47**, 2678i (1953); (c) R. Ya. Levina, T. I. Tantsyeva, and A. A. Faïnzil'berg, *J. Gen. Chem. USSR*, **22**, 571 (1952); *Chem. Abstr.*, **47**, 2679d (1953); (d) R. Ya. Levina and N. P. Shusherina, *J. Gen. Chem. USSR*, **22**, 577 (1952); *Chem. Abstr.*, **47**, 2679h (1953); (e) J. C. Maire and G. Desgrandchamps *Rec. trav. chim.*, **83**, 233 (1964)

(9) J. W. Schick and D. J. Crowley, *J. Am. Chem. Soc.*, **73**, 1377 (1951).

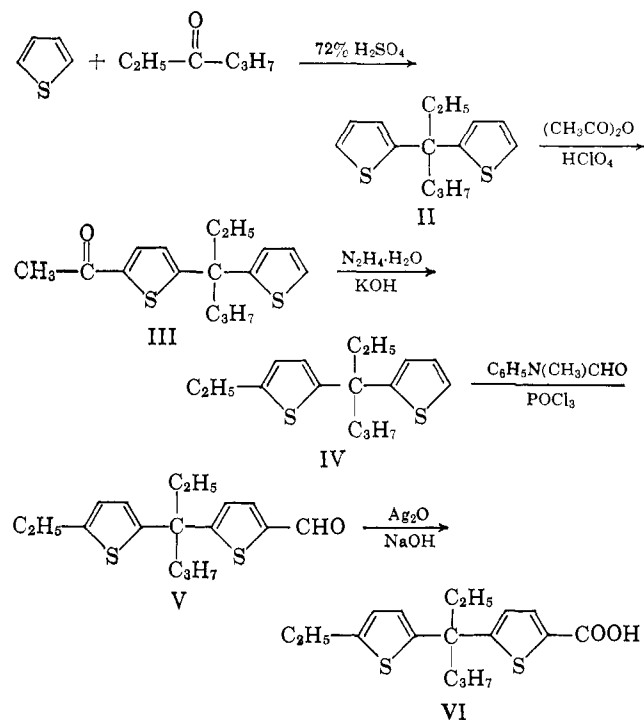
(10) G. M. Badger, H. J. Rodda, and W. H. F. Sasse, *J. Chem. Soc.*, 4162 (1954).

(11) N. P. Buu-Hoi, M. Sy, and N. D. Xuong, *Rec. trav. chim.*, **75**, 463 (1956).

(12) G. N. Dorofejenko, *J. Gen. Chem. USSR*, **31**, 918 (1961).

(13) H. Burton and P. F. G. Prall, *J. Chem. Soc.*, 1203 (1950).

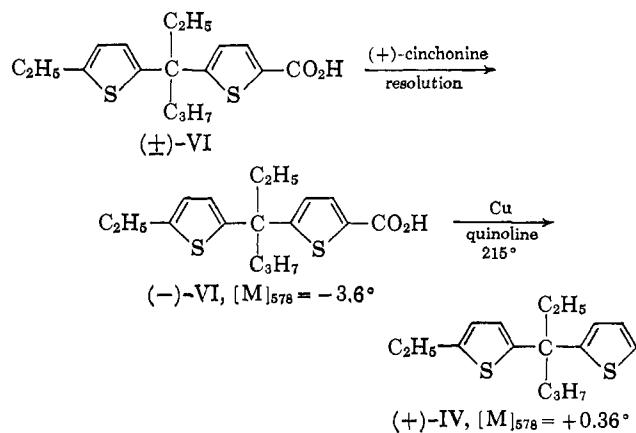
Scheme I



(±)-ketone III was obtained in 31% yield (83% based on recovered starting material) as a straw-colored liquid which could be reduced in 79% yield using the Wolff-Kishner method in diethylene glycol.^{14,15} The product, racemic 3-(2'-thienyl)-3-(5'-ethyl-2'-thienyl)hexane (IV), was resolved *via* the acid VI. The latter was best prepared by the mild oxidation of the aldehyde V. Although several alternate procedures for preparing acid VI were tried (carbonation of the lithium derivative and hypohalite oxidation of the acetyl derivative), the procedure indicated was superior.

After several resolving agents were tried, resolution was successfully accomplished using (+)-cinchonine. Decarboxylation of (−)-3-(5'-ethyl-2'-thienyl)-3-(5'-carboxy-2'-thienyl)hexane ((−)-VI), $[M]_{578} = -3.6^\circ$, by heating with copper powder in quinoline¹⁶ gave (+)-3-(2'-thienyl)-3-(5'-ethyl-2'-thienyl)hexane ((+)-IV), $[M]_{578} = +0.36^\circ$, in a yield of 80% (Scheme II).

Scheme II



(14) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(15) Ya. L. Gol'dfarb and M. L. Kirmalova, *J. Gen. Chem. USSR*, **29**, 881 (1959)

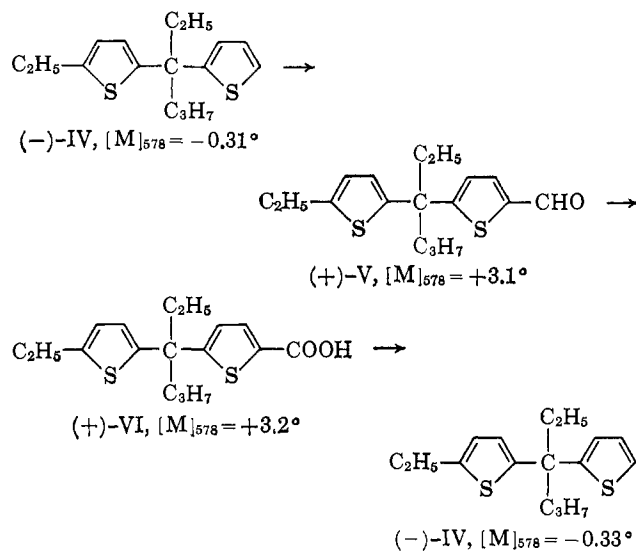
(16) I. J. Rinkes, *Rec. trav. chim.*, **51**, 1134 (1932).

The crude (+)-3-(5'-ethyl-2'-thienyl)-3-(5'-carboxy-2'-thienyl)hexane ((+)-VI) similarly gave (-)-3-(2'-thienyl)-3-(5'-ethyl-2'-thienyl)hexane ((-)-IV), $[M]_{578} = -0.31^\circ$, in a yield of 69%.

In order to assure that no racemization had occurred during the drastic decarboxylation step, optically active (-)-IV was carboxylated and decarboxylated by the same route and found to have the same molecular rotation within experimental error (Scheme III).

It may be said that no racemization *can* occur, *i.e.*, there is no known mechanism whereby racemization at quaternary carbon atom can take place. Nevertheless it is essential to establish that the (small) rotation observed at this stage is meaningful.

Scheme III



The rotations of the optically active compounds IV, V, and VI, measured with a Zeiss photoelectric polarimeter, are collected in Table I.

Table I. Rotations of Optically Active Intermediates^a

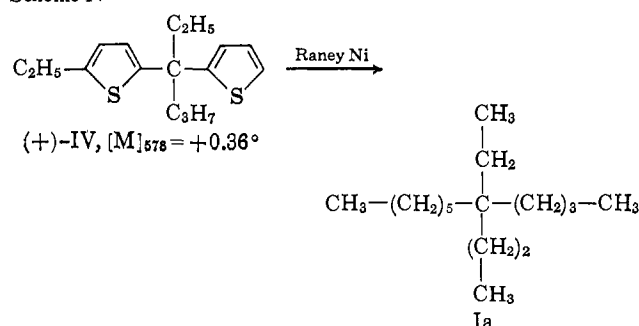
	λ , $m\mu$	(+)-Enantiomer			(-)-Enantiomer		
		α	$[\alpha]$	$[M]$	α	$[\alpha]$	$[M]$
IV	578	0.140	0.13	0.36	0.120	0.11	0.31
	546	0.155	0.14	0.39	0.140	0.13	0.36
	436	0.245	0.23	0.64	0.220	0.21	0.57
	405	0.280	0.26	0.72			
Concentration and solvent		Neat			Neat		
V	578	0.105	1.00	3.1			
	546	0.120	1.13	3.5			
	436	0.335	3.16	9.7			
		c 10.6, ethanol					
Concentration and solvent							
VI	578	0.120	1.00	3.2	0.110	1.10	3.6
	546	0.140	1.18	3.8	0.130	1.30	4.2
	436	0.290	2.44	7.9	0.280	2.80	9.0
	405				0.355	3.55	11.5
Concentration and solvent		c 11.9, benzene			c 10.0, benzene		

^a Measured with a Zeiss photoelectric polarimeter provided with a 10-cm. tube at 20° .

Desulfurization of (+)-IV, $[M]_{578} = +0.36^\circ$, was accomplished with Raney nickel in boiling alcohol¹⁷ (Scheme IV).

(17) For a general review of desulfurization reactions, see G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, **12**, 356 (1962).

Scheme IV



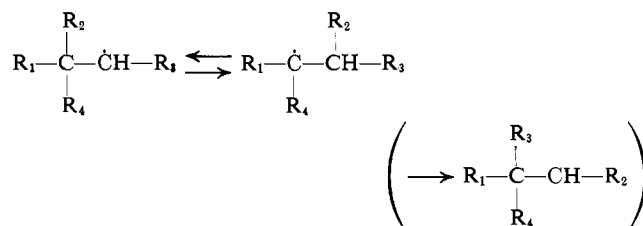
The product Ia, b.p. $263.5\text{--}264.5^\circ$, n_{D}^{20} 1.4412, d_{4}^{20} 0.791, was purified by preparative gas-liquid chromatography and by passage through a column filled with alumina. This purification gave an analytically pure hydrocarbon. The molar absorptivity (ϵ) was about 6 at $214\text{ m}\mu$. If we assume only olefinic impurities with molar absorptivities near 10^4 at this wave length, the hydrocarbon Ia is better than 99.9% spectroscopically pure. The rigorous purification was essential in order to measure rotation at the lowest possible wave length with the longest possible path.

The structure of Ia was unambiguously proved by the mass spectrum. This showed no peak above m/e 197; this peak is due to loss of the ethyl group. Similarly, peaks at m/e 183, 169, and 141 are due to loss of the propyl, butyl, or hexyl group, respectively.

The enantiomeric hydrocarbon Ib was similarly obtained by desulfurization of (-)-IV, $[M]_{578} = -0.32^\circ$.

Using a Bendix-Ericsson Polaromatic 62 spectropolarimeter, provided with a tube of 1 cm., we did not observe optical rotation of the hydrocarbon Ia (neat) against its enantiomer Ib with air as intermediate reference in the wave-length region of $280\text{--}580\text{ m}\mu$. Since the noise level at $280\text{ m}\mu$ is about 0.0015° , the experimental error is approximately 0.006° . This means that $2\alpha_{280} \leq 0.006^\circ$,¹⁸ $[\alpha]_{280} \leq 0.04^\circ$, and $[M]_{280} \leq 0.09^\circ$. At $580\text{ m}\mu$ the noise level is about 0.0002° and the experimental error 0.0008° ; $2\alpha_{580} \leq 0.0008^\circ$, $[\alpha]_{580} \leq 0.009^\circ$, and $[M]_{580} \leq 0.02^\circ$.

The possibility of racemization during the desulfurization of optically active IV appears highly unlikely.¹⁹ We are forced to conclude that, within the



limits of our experimental conditions, the hydrocarbon I, though asymmetric, does not exhibit optical activity between 280 and $580\text{ m}\mu$.²⁰ With Thomson's formula²¹

(18) Although the hydrocarbon Ib is somewhat less optically pure than Ia, we have assumed for convenience the difference between the rotations of both hydrocarbons to be 2α .

(19) There appears to be no known mechanism which could reasonably be advanced for racemization during this final step. Assuming the radical nature of the desulfurization reaction a rearrangement of possible intermediate radicals as shown below seems to be remote indeed.

(20) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Am. Chem. Soc.*, **86**, 1733 (1964), especially p. 1740. These authors also present rigorous evidence of an asymmetric molecule which exhibits no rotation over a considerable spectral range. The difference

we calculated $[M]_D = 0.00002^\circ$ for butylethylhexyl-propylmethane, and this value is in accordance with our results.

The difference in the length of the alkyl groups in hydrocarbons of type A is therefore by itself an insufficient condition for rotation to be observed with present day instruments.

Experimental

All temperatures are uncorrected. Microanalyses were performed in the analytical section of our department under the supervision of Mr. W. M. Hazenberg. The infrared absorption spectra were run on a Perkin-Elmer Infracord 137 E. The ultraviolet absorption spectra were obtained with a Zeiss spectrophotometer, Type PMQ II. Optical rotations were determined with a Zeiss photoelectric polarimeter (accuracy 0.005° , lines at 578, 546, 436, 405, and 365 μ) or with a Bendix-Ericsson Polarmatic 62 spectropolarimeter at 20° ; concentrations are given as g./100 ml. and 10-cm. tubes were used unless otherwise stated.

3,3-Di(2'-thienyl)hexane (II). When 106 g. (1.26 moles) of thiophene and 74 g. (0.74 mole) of hexanone-3 were vigorously stirred with 160 ml. of 72% sulfuric acid⁹⁻¹¹ for 4.5 hr. at $70-75^\circ$, 97 g. (0.39 mole, 52% based on hexanone-3) of 3,3-di(2'-thienyl)hexane (II), b.p. $124-126^\circ$ (1.5 mm.), n_D^{20} 1.5690, was obtained; $\lambda_{\max}^{\text{CHCl}_3}$ 241 μ (ϵ 14,300).

Anal. Calcd. for $C_{14}H_{18}S_2$ (250.40): C, 67.15; H, 7.25; S, 25.60. Found: C, 67.4; H, 7.1; S, 25.5.

3-(2'-Thienyl)-3-(5'-acetyl-2'-thienyl)hexane (III). A mixture of 76 g. (0.30 mole) of 3,3-di(2'-thienyl)hexane (II) and 16 g. (0.16 mole) of freshly distilled acetic anhydride was stirred with 10 drops of 60% perchloric acid^{12,13} for 2.5 hr. under anhydrous conditions at room temperature. The purple-colored reaction mixture was carefully neutralized with 80 ml. of 2 N sodium hydroxide and the organic layer was separated. The aqueous layer was extracted twice with 50 ml. of ether and the combined organic fractions were washed, dried over magnesium sulfate, and concentrated under reduced pressure. The residue upon distillation furnished 48 g. (0.19 mole, 63%) of unreacted starting material, b.p. $126-128^\circ$ (1.5 mm.), n_D^{20} 1.5700, and 27 g. (0.092 mole, 31%) of the ketone III as a straw-colored oil, b.p. $170-178^\circ$ (1.4 mm.), n_D^{20} 1.5874, $\nu_{C=O}$ 1650 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 240 μ (ϵ 10,100) and 298 μ (ϵ 12,400).

Anal. Calcd. for $C_{16}H_{20}OS_2$ (292.44): C, 65.71; H, 6.88; S, 21.93. Found: C, 65.7; H, 6.9; S, 22.2.

3-(2'-Thienyl)-3-(5'-ethyl-2'-thienyl)hexane (IV). Using 30 g. (0.10 mole) of the ketone III the Wolff-Kishner reduction was carried out in the usual manner with 60 g. of potassium hydroxide in 250 ml. of diethylene glycol and 55 ml. of 100% hydrazine hydrate.^{14,15} After a reflux period of 2 hr., water and diethylene glycol were distilled until the temperature of the mixture reached 190° . After another 5-hr. reflux period, 100 ml. of water was added and the crude product was isolated by extraction with ether. The organic fraction was washed twice with 100 ml. of

2 N hydrochloric acid and once with 100 ml. of a 10% sodium bicarbonate solution, and dried over magnesium sulfate. The ether was evaporated and the residue yielded upon distillation 22 g. (0.079 mole, 79%) of 3-(2'-thienyl)-3-(5'-ethyl-2'-thienyl)hexane (IV), b.p. $128-130^\circ$ (0.6 mm.), n_D^{20} 1.5608, $\lambda_{\max}^{\text{EtOH}}$ 238 μ (ϵ 15,600).

Anal. Calcd. for $C_{18}H_{22}S_2$ (278.47): C, 69.00; H, 7.97; S, 23.03. Found: C, 69.2; H, 7.9; S, 23.4.

3-(5'-Ethyl-2'-thienyl)-3-(5'-formyl-2'-thienyl)hexane (V). Formylation of 90 g. (0.32 mole) of the thiophene derivative IV using 64 g. (0.47 mole) of N-methylformanilide and 58 g. (0.38 mole) of phosphorus oxychloride^{16,22} afforded 87 g. of crude aldehyde V, b.p. $160-170^\circ$ (0.2 mm.), n_D^{20} 1.5835-1.5873. Redistillation yielded 80 g. (0.26 mole, 82%) of pure product as a slightly yellow oil, b.p. $164-170^\circ$ (0.2 mm.), n_D^{20} 1.5877, ν_{CHO} 2740 and $\nu_{C=O}$ 1675 cm^{-1} , $\lambda_{\max}^{\text{EtOH}}$ 249 μ (ϵ 8300) and 301 μ (ϵ 8800).

Anal. Calcd. for $C_{17}H_{22}OS_2$ (306.48): C, 66.62; H, 7.24; S, 20.92. Found: C, 66.5; H, 7.1; S, 20.9.

The 2,4-dinitrophenylhydrazone prepared from this aldehyde melted at $153-154^\circ$.

Anal. Calcd. for $C_{23}H_{26}N_4O_4S_2$ (486.61): C, 56.77; H, 5.39; N, 11.52. Found: C, 56.7; H, 5.5; N, 11.5.

3-(5'-Ethyl-2'-thienyl)-3-(5'-carboxy-2'-thienyl)hexane (VI). To a suspension of silver oxide, prepared²³ by combining a solution of 51 g. of silver nitrate in 100 ml. of water and a solution of 24 g. of sodium hydroxide in 100 ml. of water, 25 g. (0.082 mole) of the aldehyde V dissolved in 200 ml. of ethanol was added. The reaction mixture was stirred for 4 hr. at 40° . Excess silver oxide and the silver formed were removed by filtration and the major part of the ethanol was distilled from the filtrate. The residue was diluted with 2 N sodium hydroxide, washed with 100 ml. of ether, and carefully acidified with concentrated sulfuric acid. The insoluble acid VI was isolated with ether. The organic fraction was washed with water and dried over magnesium sulfate. After evaporation of the ether 24 g. (0.073 mole, 88%) of solid product, m.p. $74-81^\circ$, was obtained. Recrystallization from methanol gave the acid VI as colorless crystals, m.p. $80-81^\circ$, ν_{OH} broad band from 3000 to 2100 and $\nu_{C=O}$ 1660 cm^{-1} (in carbon tetrachloride), $\lambda_{\max}^{\text{EtOH}}$ 245 μ (ϵ 15,000) and 280 μ (ϵ 12,500).

Anal. Calcd. for $C_{17}H_{22}O_2S_2$ (322.49): C, 63.31; H, 6.88; S, 19.89. Found: C, 63.3; H, 6.6; S, 19.6.

The S-benzyl isothiuronium salt melted at $148-149^\circ$.

Anal. Calcd. for $C_{23}H_{32}N_2O_2S_3$ (488.72): C, 61.44; H, 6.60; S, 19.69. Found: C, 61.6; H, 6.6; S, 19.4.

Resolution of 3-(5'-Ethyl-2'-thienyl)-3-(5'-carboxy-2'-thienyl)hexane (VI). A mixture of 109 g. (0.34 mole) of racemic acid VI and 98 g. (0.33 mole) of cinchonine, $[M]_{578} = +706^\circ$, was dissolved in 9 l. of boiling ethyl acetate. The hot solution was filtered and after crystallization 104 g. of cinchonine salt, m.p. $183-187^\circ$,

between these two cases appears to be that there is a quantitative predictability in our case.

(21) T. R. Thomson, *J. Am. Chem. Soc.* **75**, 6070 (1953).

(22) A. Vilsmeier and A. Haack, *Ber.*, **60**, 119 (1927).

(23) E. Campaigne and W. M. Le Suer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1964, p. 919.

was collected. The mother liquor yielded on concentration to 6.5 l. another 18.5 g. of salt, m.p. 183.5–187°. The combined salt fractions (122.5 g.) were recrystallized from 5.5 l. of ethyl acetate and 70 g. of salt, m.p. 184.5–187°, $[M]_{578} = +583^\circ$, $[M]_{436} = +1121^\circ$, and $[M]_{405} = +1337^\circ$ (*c* 3.10, methanol), was obtained. A second recrystallization from 2.5 l. of ethyl acetate afforded 47.5 g. of the cinchonine salt, m.p. 185.5–187°, $[M]_{578} = +580^\circ$, $[M]_{436} = +1122^\circ$, and $[M]_{405} = +1320^\circ$ (*c* 3.00, methanol).

Anal. Calcd. for $C_{36}H_{44}N_2O_3S_2$ (616.86): C, 70.09; H, 7.19; S, 10.40. Found: C, 69.8; H, 7.2; S, 10.3.

A solution of 43 g. (0.070 mole) of this last cinchonine salt in benzene was thoroughly washed with 2 *N* sulfuric acid and water. Concentration under reduced pressure after drying afforded 22.5 g. (0.070 mole, 21% based on inactive acid) of (–)-3-(5'-ethyl-2'-thienyl)-3-(5'-carboxy-2'-thienyl)hexane as a slightly yellow-colored oil, solidifying on standing, $[M]_{578} = -3.6^\circ$, $[M]_{436} = -9.0^\circ$, and $[M]_{405} = -11.5^\circ$ (*c* 10.0, benzene).

From the mother liquor of the first crystallization of the cinchonine salt, the crude (+)-acid was obtained as a dark colored oil in a yield of 42.5 g. (0.130 mole, 38% based on inactive acid). Because of the impure state rotation could not be measured (see below, however).

(+)-3-(2'-Thienyl)-3-(5'-ethyl-2'-thienyl)hexane ((+)-IV). To 20 g. (0.062 mole) of (–)-acid VI 37 g. of quinoline and 1.2 g. of copper powder were added.¹⁶ The mixture was heated at 215° until the calculated amount of carbon dioxide had evolved (about 10 min.). The cooled reaction mixture was filtered; the filtrate was diluted with ether, extracted with excess of 2 *N* sulfuric acid, washed with 100 ml. of a saturated solution of sodium bicarbonate and 100 ml. of water, and dried. The product was obtained after distillation in a yield of 13.8 g. (0.050 mole, 80%), b.p. 114–119° (0.2 mm.), n_{20}^D 1.5597, d_{20}^{20} 1.07, $[M]_{578} = +0.36^\circ$, $[M]_{436} = +0.64^\circ$, and $[M]_{405} = +0.72^\circ$ (neat). The infrared absorption spectrum was identical with that of the optically inactive material.

(–)-3-(2'-Thienyl)-3-(5'-ethyl-2'-thienyl)hexane ((–)-IV). Similarly 42.5 g. (0.13 mole) of crude (+)-acid VI furnished 25.7 g. (0.093 mole, 70%) of the (–)-thiophene derivative IV, b.p. 114–118° (0.2 mm.), n_{20}^D 1.5615, $[M]_{578} = -0.31^\circ$ and $[M]_{436} = -0.57^\circ$ (neat).

(+)-3-(5'-Ethyl-2'-thienyl)-3-(5'-formyl-2'-thienyl)hexane ((+)-V). Formylation of 15 g. (0.054 mole) of the (–)-thiophene derivative IV in the way described before afforded 12.9 g. (0.042 mole, 78%) of (+)-aldehyde V, b.p. 158–173° (0.3 mm.), n_{20}^D 1.5872, $[M]_{578} = +3.1^\circ$ and $[M]_{436} = +9.7^\circ$ (*c* 10.6, ethanol).

(+)-3-(5'-Ethyl-2'-thienyl)-3-(5'-carboxy-2'-thienyl)hexane ((+)-VI). Oxidation of 12.9 g. (0.042 mole) of (+)-aldehyde V with silver oxide yielded 12.5 g. (0.039 mole, 92%) of the (+)-acid VI as a slightly yellow-colored viscous oil, $[M]_{578} = +3.2^\circ$ and $[M]_{436} = +7.9^\circ$ (*c* 11.9, benzene).

Of this acid 6.5 g. (0.020 mole) was decarboxylated and 4.2 g. (0.015 mole, 75%) of the (–)-thiophene derivative IV, b.p. 116–121° (0.3 mm.), n_{20}^D 1.5615, $[M]_{578} = -0.33^\circ$ and $[M]_{436} = -0.60^\circ$ (neat), was obtained.

Desulfurization of (+)-3-(2'-Thienyl)-3-(5'-ethyl-2'-thienyl)hexane ((+)-IV). To a suspension of 500 g. of Raney nickel W-5²⁴ in 1500 ml. of ethanol 7.5 g. (0.027 mole) of the (+)-thiophene derivative IV was added. After 40 hr. of stirring at 80° the cooled reaction mixture was filtered and the filtered nickel was washed with ethanol. The filtrates were combined and the ethanol was removed by distillation. The residue was diluted with hexane, washed with 0.5 *N* sulfuric acid and water, and dried over magnesium sulfate. Evaporation of the hexane yielded 7.3 g. of residue which was purified by gas chromatography ($\frac{3}{8}$ in. \times 20 ft. aluminum column, packed with 30% Carbowax 20 M on 60–80 mesh Chromosorb P, 190°, 100 ml./min. helium outlet flow). The butylethylhexylpropylmethane (Ia) thus obtained was slightly colored and column chromatography over neutral alumina with hexane (E. Merck, Uvasole) as eluent yielded, after evaporation of the hexane, 3.0 g. (0.013 mole, 50%) of the hydrocarbon as a colorless oil, b.p. 263.5–264.5°, n_{20}^D 1.4412, d_{20}^{20} 0.791, MR 75.63 (calcd. 75.78). This product proved to be gas chromatographically pure.

The ultraviolet absorption spectrum, measured neat in a 1-mm. cell with hexane (E. Merck, Uvasole) as reference, showed maxima at 267 (O.D. 0.117) and 214 $m\mu$ (2.4).

Anal. Calcd. for $C_{16}H_{34}$ (226.43): C, 84.86; H, 15.14. Found: C, 84.8; H, 15.0.

Desulfurization of (–)-3-(2'-Thienyl)-3-(5'-ethyl-2'-thienyl)hexane ((–)-IV). In a similar way, starting from 7.0 g. (0.025 mole) of the (–)-thiophene derivative IV and using 300 g. of Raney nickel, the butylethylhexylpropylmethane (Ib) was obtained in a yield of 2.0 g. (0.090 mole, 33%), n_{20}^D 1.4410.

The ultraviolet spectrum showed a maximum at 223 (O.D. 3.2), whereas at 280 $m\mu$ the optical density was 0.195 (measured neat in a 1-mm. cell with hexane as a reference).

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