uct (32%), mp 70–71°. Thin layer chromatography of the product in the solvent system Skellysolve F–ether (60:40, v/v) showed that only traces of the 1,2 isomer were present.

Anal. Calcd for $C_{10}H_{38}O_3$: C, 72.61; H, 12.10. Found: C, 73.10; H, 12.00.

1,2-O-Hexadecylidineglycerol-3-phosphorylcholine.—To 0.37 ml (4.0 mmoles) of freshly distilled phosphorus oxychloride, cooled by an ice bath and vigorously stirred by a magnetic stirrer, was added drop by drop under anhydrous conditions a solution containing 1.18 g (4.0 mmoles) of 1,2-O-hexadecylidineglycerol,[17] 0.52 ml (4.4 mmoles) of anhydrous quinoline, and 20 ml of anhydrous chloroform. The cold bath was then replaced by a water bath at 35° and the reaction mixture was kept at this temperature for 1 hr. To the solution was then added quickly 5 ml of anhydrous pyridine, 0.871 g (4.5 mmoles) of finely powdered choline iodide, and 15 ml of glass beads (4-mm diameter). The stirring was continued for 20 additional hr at room temperature and then 0.1 ml of distilled water was added. The solution was stirred for an additional 30 min. The reaction mixture was then filtered and the residue was washed twice with 15-ml portions of cloroform. The chloroform solution was first evaporated under vacuum using a rotary evaporator from a water bath at 37°, followed by a final drying at a vacuum of 0.1 mm until a semisolid, yellow residue was obtained. The residue was triturated at 0° with 1 *N* hydrochloric acid and immediately filtered. This was washed with cold water until the washings were free of mineral acid and dried under vacuum. The residue was dissolved in a mixture of chloroform and 95% ethanol and to the solution was then added 1.5 g of finely powdered silver carbonate and the mixture was stirred for 1 hr. The solution was filtered and the solvent was evaporated under vacuum from a water bath at 35°. The resultant residue was dissolved in a minimum amount of chloroform and acetone was added and kept at 0° to precipitate the 1,2-acetal choline phosphatide. The product was obtained by filtration on a Büchner funnel to give 1.2 g of 1,2-acetal choline plasmalogen.

The crude 1,2-acetal choline phosphatide was fractionated by silicic acid column chromatography according to the method of Hanahan, *et al.*[14] Thus, using 20 g of silicic acid and 10 g of Celite, 0.096 g (25% over-all yield) of product was obtained from 0.265 g of crude acetal phosphatide by elution with 1000 ml of a mixture of chloroform and methanol (3:2, v/v).

Anal. Calcd for $C_{24}H_{52}NO_7P$: N, 2.81; P, 6.22. Found: N, 2.33; P, 5.88.

Registry No.—1,2-O-Hexadecylidineglycerol-3-phosphorylcholine, 7731-07-9; 1,3-O-hexadecylidineglycerol, 7731-06-8.

The Thermal Decomposition of Crotyldi-*t*-butylcarbinol

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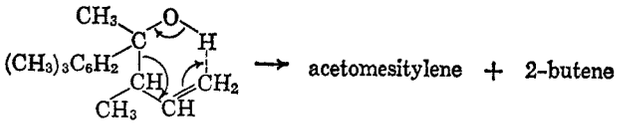
In 1950, Wilson, Roberts, and Young[1] reported that butenylmagnesium bromide reacts with hexamethylacetone to form crotyldi-*t*-butylcarbinol in 69% yield. This reaction remains of considerable interest since it is the only example of the formation of a product derived exclusively from the primary form of this Grignard reagent.[2] It was also disclosed[1] that pyrolysis of crotyldi-*t*-butylcarbinol at 215° produced 1-butene. Previously, similar thermal decompositions for compounds like α-methylallylmesitylmethylcarbinol to acetomesitylene and 2-butene had been demonstrated.[3] A cyclic process had been invoked to explain the products of such decompositions.



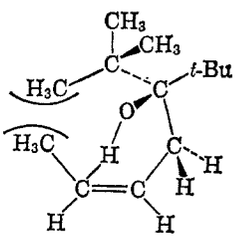
Recently we found that crotyldi-*t*-butylcarbinol is formed from butenyl Grignard reagents and hexamethylacetone predominantly in the *cis* form.[4]

We now wish to report that the thermal decomposition of a mixture of *cis*- and *trans*-crotyldi-*t*-butylcarbinol is selective, in that the *trans* alcohol decomposes to hexamethylacetone at a faster rate than the *cis* isomer. This trend is clearly delineated in Table I.

TABLE I
THERMAL DECOMPOSITION OF CROTYLDI-*t*-BUTYLCARBINOL
COMPOSITION OF CARBINOL

Time, hr	Temp, °C	*cis*	*trans*	Hexamethylacetone, %
0	246	71	29	0
1.17	248	71	28	1
2.00	248	71	24	5
3.00	245	72	20	8
4.17	244	71	15	14
5.17	245	70	13	17
6.08	245	70	12	18
7.08	245	71	10	19
10.00	244	74	7	19

If the intramolecular cyclic transition state which has been proposed[3] for these decompositions is correct, a cursory examination of molecular models provides a possible explanation for the differences in decomposition rates which are observed. The *cis* isomer (**1**)



1

would suffer severe steric interactions between one of the methyls of the *t*-butyl group and the terminal methyl of the crotyl group as shown. A considerable amount of this strain would be relieved in the *trans* isomer wherein the methyl of the *t*-butyl group would be opposed only by one of the vinylic hydrogens.

Further work is obviously necessary to decide whether these interesting decompositions are truly intramolecular and whether the steric proposals invoked here are valid.

Experimental Section

General.—All samples were analyzed by vpc using a 20-ft, 20% stainless steel DEGS column on 60–80 AW-DMCS treated

(1) K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **72**, 218 (1950).

(2) See J. E. Nordlander, W. G. Young, and J. D. Roberts [*ibid.*, **83**, 494 (1961)] who discuss the structural problems associated with this Grignard reagent.

(3) W. G. Young and J. D. Roberts, *ibid.*, **68**, 1472 (1946).

(4) The butenyl Grignard prepared from either *trans*-1-chloro-2-butene or 3-chloro-1-butene forms crotyldi-*t*-butylcarbinol in about the same *cis*/*trans* ratio, namely 2.2:1. Details of these and similar results will be published shortly.

Chromosorb W at 150° with a carrier gas flow of 100 ml/min. Accurately weighed samples of pure di-*t*-butyl ketone and crotyldi-*t*-butylcarbinol were analyzed under the same conditions to determine the thermal conductivity correction factor. It was found that the area of the ketone peak had to be multiplied by 1.069 in order to arrive at correct relative per cent values.

Decomposition Reaction.—A mixture[5] of 71.2% *cis*- and 28.8% *trans*-crotyldi-*t*-butylcarbinol was placed in a 15-ml conical flask with a side arm to which a small Friedrichs condenser was attached. To the side arm was connected an open capillary tube with a ground-glass joint, the tip of the capillary being positioned below the surface of the alcohol mixture. At the top of the capillary was a rubber stopple through which a length of 3-mm glass tubing was attached *via* a bubbler to a tank of dry, purified nitrogen which was bubbled slowly through the reaction mixture during heating.

The flask containing the alcohols was lowered into a hot oil bath and that time taken as t_0. Samples were withdrawn at intervals of about 1 hr by puncturing the rubber stopple with a small hypodermic syringe, sliding the needle down through the capillary, and removing about 0.1 ml of the reaction mixture. Aliquots of exactly 4.0 μl were then subjected to vpc analysis, the total areas of ketone and alcohol peaks remaining constant within 2%. Thus it was concluded that no high-boiling products remained behind on the column.

This procedure was continued until the concentration of di-*t*-butyl ketone (bp 153°) became great enough that it was being lost through the condenser. This point was noted by the increase in the relative proportion of *cis*-crotyldi-*t*-butylcarbinol in the reaction mixture. The data are presented in Table I.

Registry No.—Crotyldi-*t*-butylcarbinol: *cis* isomer, 7634-94-8; *trans* isomer, 7634-95-9.

Acknowledgment.—This research was supported by the U. S. Army Research Office (Durham) to whom the authors are deeply indebted.

(5) This mixture was obtained from the reaction of crotylmagnesium chloride with di-*t*-butyl ketone. Separation of the two isomers was effected by vpc (see conditions above). The infrared spectrum of the *cis* isomer showed absorption at 13.8 and no band at 10.3–10.4 μ, whereas the reverse was true for the *trans* isomer. *Anal.* Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found (*cis*): C, 78.45; H, 13.39. Found (*trans*): C, 78.20; H, 13.33.

Organic Disulfides and Related Substances. XXI. Sulfuryl Chloride in the Preparation of Thiolsulfonates from Disulfides[1a,b]

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The Douglass–Farah reaction for the preparation of aliphatic thiolsulfonates ($AlkSO_2SAlk$) affords an elegant and valuable synthesis for this class. It involves chlorinolysis of a disulfide in acetic acid and subsequent treatment with water.[2] In a recent communication we showed that this method could be extended to aromatic disulfides and thus is a good general route to symmetrical thiolsulfonates.[3] Since sulfuryl chloride has been used to convert disulfides and thiols to sulfenyl chlorides,[4] key intermediates in the Douglass–Farah reaction,[2] and since it is very easily handled, it presented a useful alternative to chlorine in the Douglass–Farah synthesis; there is also the prospect of greater flexibility in conditions than with a gas, and of useful differences in selectivity. The over-all reaction presumably occurs according to eq 1 and 2 (*cf.* ref 2).

$$\mathrm{RSSR + AcOH + 2SO_2Cl_2 \longrightarrow \underbrace{RS(O)Cl + RSCl + AcCl}_{2H_2O\downarrow} + HCl + 2SO_2} \quad (1)$$

$$\mathrm{RSO_2SR + AcOH + 3HCl} \quad (2)$$

Results are shown in Table I. To test the versatility of the procedure, the reactants were selected to be as diverse as possible in their illustration of various classes of sulfur compounds. No attempt was made to optimize conditions; hence it is likely that improvement in yields would be possible.

Preparation of *p*-tolyl *p*-toluenethiolsulfonate (**1**) shows that an aromatic thiol can be used. Oxidation of the thiol to the disulfide presumably occurs according to eq 3. The preparations of **1** and of *p*-nitrophenyl

$$\mathrm{2RSH + SO_2Cl_2 \longrightarrow RSSR + 2HCl + SO_2} \quad (3)$$

p-nitrobenzenethiolsulfonate (**2**) show that aromatic thiolsulfonates with either electron-donating or electron-attracting groups can be made. However, the low yield of **2** shows that sulfuryl chloride is less effective in this instance than chlorine (75% yield),[3] and thus its use should be considered an alternative to chlorine and not a substitute for it. Possibly the low yield of **2** is a consequence of lower electrophilic character of sulfuryl chloride than of chlorine toward the sulfur atom with its reduced basicity caused by the nitro group. The low yield of 21% with a 20% excess of sulfuryl chloride suggests that the yield might be further improved by a greater excess; pure **2** could not be isolated when no excess was used.

Ethyl ethanethiolsulfonate (**3**), a primary alkyl thiolsulfonate, and isopropyl 2-propanethiolsulfonate (**4**), a secondary alkyl thiolsulfonate, were made from the disulfides. However, the reaction shown in eq 4[5]

$$\mathrm{(RCH_2S)_2 + SO_2Cl_2 \longrightarrow 2RCH(Cl)SCl} \quad (4)$$

conceivably could become troublesome in the preparation of certain alkanethiolsulfonates and is worth being kept in mind as a possible side reaction with alkyl disulfides.

Treatment of ethanethiol by the process using sulfuryl chloride also gave thiolsulfonate **3** in reasonable yield, showing the reaction can be extended to the use of alkanethiols as starting materials. However, treatment of 2-acetamidoethanethiol failed to give the

(1) (a) This investigation was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under Research Contract No. DA-49-193-MD-2030. Taken partly from the Ph.D. dissertation of J. D. B., Vanderbilt University, June 1966. (b) Paper XX: J. D. Buckman and L. Field, *J. Org. Chem.*, **32**, 454 (1967). (c) Du Pont Postgraduate Teaching Assistant, 1964–1965. (d) To whom correspondence should be addressed.

(2) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **24**, 973 (1959).

(3) L. Field and T. F. Parsons, *ibid.*, **30**, 657 (1965).

(4) N. Kharasch, U. S. Patent 2,929,820 (1960); *Chem. Abstr.*, **54**, 15318 (1960).

(5) H. Brintzinger and H. Ellwanger, *Chem. Ber.*, **87**, 300 (1954).