(15%), and a stereoisomeric di-addition product melting at 223° (12%). In a similar experiment in which the reacting mixture was boiled for six hours the yields were 22% of mono-addition product, 26% of product melting at 178° and 32% of product melting at 196°. Both of the di-addition products are sparingly soluble in common organic solvents. The lower melting—which is the less soluble—crystallizes from acetone in small prisms and the higher melting crystallizes in six-sided tables containing acetone of crystallization.

Anal. Calcd. for $C_{33}H_{28}O_3S$: C, 78.6; H, 5.6. Found: C, 78.6; H, 6.0. Calcd. for $C_{33}H_{28}O_3S{\cdot}C_3H_6O$: C, 77.1; H, 6.0; C_3H_6O, 10.3. Found: C, 77.1; H, 5.7; C_3H_6O, 10.1.

The structure of the di-addition products was established by converting them into triphenyl indene. To this end a solution of each in glacial acetic acid containing a small quantity of sulfuric acid was heated on a steam-bath for half an hour, then diluted first with methyl alcohol and finally with water. In each case the product was identified by comparison with a sample on hand.

Summary

The paper contains a comparison of $C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5$ and $C_6H_5COCH{=}CHSO_2C_6H_5$ with respect to their stereoisomerism, the facility with which they enter into addition reactions, the mode of addition of hydrogen compounds and the mode of addition of Grignard reagents.

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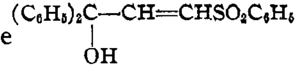
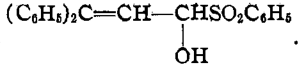
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Physical Investigation of β-Hydroxy-β,β-diphenylvinyl Phenyl Sulfone

BY H. E. BENT, E. S. LARSEN AND H. BERMAN

In a recent paper Kohler and Larsen[1] described two compounds which "are interesting by reason of the very remarkable ease with which they undergo the allylic rearrangement.... Most solutions, on chilling, deposit a mixture of both isomers but by slow crystallization from properly selected solvents it is possible to secure both isomers in a pure condition—the tertiary alcohol VIII from benzene and the secondary alcohol X from methyl or ethyl alcohol." The tertiary alcohol, β-hydroxy-β,β-diphenylvinyl phenyl sulfone, has the structure  $(C_6H_5)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CH{=}CHSO_2C_6H_5$ and the secondary alcohol, α-hydroxy-β,β-diphenylpropenyl phenyl sulfone, X, has the structure  $(C_6H_5)_2C{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}}HSO_2C_6H_5$. The melting point of the tertiary alcohol is given as 193° and of the secondary alcohol as 164°. Both compounds crystallize readily but differ greatly in appearance. This apparent reversal of the direction of transformation by different solvents at the same temperature is, however, thermodynamically impossible, and we have therefore reëxamined more carefully the physical properties of these two substances.

Crystallographic measurements were made as follows:

OPTICAL CRYSTALLOGRAPHY

	Cpd. VIII	Cpd. X
α	1.608	1.607
β	1.656	1.657
γ	1.710	1.706
Opt. sign	(+) 2*V* med.	(+) 2*V* med.
Orientation	*Z* = *b*	*Z* = *b*
	*X*Λ*C* = 23°	*X*Λ*C* = 23°

CRYSTALLOGRAPHY

Measurements on X

Forms: (010)(100)(110)(011)(101) Monoclinic-holohedral

$a:b:c = 1.0597:1:0.3277 \qquad \beta = 99° 05'$

$p_0 = 0.30926 \quad q_0 = 0.32362 \quad e = 0.15784$

Form	Observed (averages) φ	Observed (averages) ρ	Calculated φ	Calculated ρ	Number of observations
(010)	0°	90° 00′	0°	90° 00′	4
(100)	90° 00′	90° 00′	90° 00′	90° 00′	1
(110)	43° 42′	90° 00′	43° 42′	90° 00′	12
(011)	26° 00′	20° 02′	26° 00′	20° 02′	6
(101)	90° 00′	25° 17′	90° 00′	25° 19′	1
Ranges: for (110)			43° 32′ to 43° 55′		
(011)			25° 40′ to 26° 41′	19° 47′ to 20° 10′	

Measurements on a single crystal of VIII

Form	φ	ρ
(010)	0°	90° 00′
(110)	39° 49′	90° 00′
(011)	25° 51′	20° 09′

Crystals X are much superior in quality and the angles of these are to be relied upon for a good axial ratio for the substance. Crystals VIII were difficult to measure since they were of the order of 0.1 mm. in maximum size. Several crystals

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[1] Kohler and R. G. Larsen, THIS JOURNAL, 57, 1448 (1935).

yielded rather poor measurements, the best being given above. The data given above indicate that substances VIII and X are crystallographically identical and that although they do have a different superficial appearance they are actually similar in habit as well as in the prevalence of particular forms.

The melting points were carefully re-determined, first by conventional methods and second by the use of the copper block. The results obtained with an ordinary melting point tube depend upon the rate of heating, rapid heating giving much higher results. The following table gives typical results obtained with a copper block.

	Time required for melting, in sec.	
T, °C.	VIII	X
159	180	60
165	120	30
170	120	30
178	75	22
188	50	15
193	50	12
195	25	12
199.5	2–3	2–3

It is clear from these results that the melting points as determined in tubes are really decomposition or rearrangement points and as usual are greatly affected by variations in the rate of heating. Since decompositions are known to be very sensitive to the presence of impurities, the low apparent melting point of substance X may well be due to an impurity present in it when recrystallized from methyl alcohol, but absent or present in smaller amounts when recrystallized from benzene.

Finally, the solubilities of VIII and X were determined in benzene and methyl alcohol at several temperatures. The saturation was accomplished by shaking the solutions in a small container of about 10-cc. capacity surrounded by a jacket containing a boiling liquid. This vessel was conveniently made like a small Dewar flask with the boiling liquid in the space usually evacuated, to which a reflux condenser was sealed. To prevent evaporation of the solvent there was a ground glass stopper halfway down the neck of the flask. The whole apparatus was mounted on a shaker which not only served to agitate the solution but also to minimize superheating. The temperatures were read on a thermometer immersed in the solution itself and these remained constant to ±0.1°. One cubic centimeter samples were removed by means of a filter pipet and evaporated to constant weight on a steam-bath. Duplicate determinations usually agreed to about ±1 mg. depending on the concentration of the solution. The results are given in Table I.

TABLE I

Temp., °C.	Time of shaking	Vol. of soln. 1 cc. C_6H_6	Wt. of solute VIII, g.	Wt. of solute X, g.
34.4	10 min.	"	0.0054	0.0043
55.2	5	"	.0114	.0108
64.4	4	"	.0167	.0163
80.3	5	"	.0303	.0293
0	12 hr.	CH_3OH	.0030	.0027
0	12	C_6H_6	.0015	.0015
0	25 min.	satd. CH_3OH	.0030	.0032

These results are not as precise as perhaps one might wish, and if it seemed worth while a somewhat greater expenditure of time would doubtless improve them considerably. However, the values given for the solubilities of the two materials agree as well as values obtained on successive runs on the same material. The time was intentionally made as short as five minutes for the shaking in order to diminish the chance of a rearrangement taking place in solution. Perhaps the last row in the table is the most significant. In this case a saturated solution of one compound in methyl alcohol was shaken with the other solid. Unless there is a rapid equilibrium established at 0° one would have expected the total amount of solute to be about twice that observed. The only alternative is that both materials are the same.

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