

$K = 0.841, 0.832, 0.825, 0.837$  and  $90, 100, 110$  and  $120^\circ$ , respectively. The agreement between the high and low temperature results is all that can be desired in view of the somewhat vague nature of the parameter  $K$ ; thus the theory appears to be in accord with facts in a hitherto untested region.

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RECEIVED AUGUST 2, 1948

### A NEW SYNTHESIS OF SULFONYL CHLORIDES

Sir:

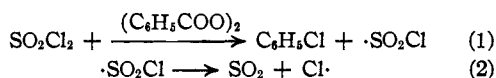
It has been established in previous publications from this Laboratory<sup>1</sup> that under certain conditions sulfonyl chloride is a useful reagent for the chlorination and sulfonation of saturated hydrocarbons, and for the addition of chlorine to olefins to produce dichloro compounds.<sup>2</sup> In the preparation of the dichloro derivatives from the olefins and sulfonyl chloride, the suggested procedure was to mix equimolecular quantities of the reactants, and a small quantity (1–2 mole per cent.) of a diacyl peroxide and to heat the mixture.

We now find that if to the mixture of the olefin and the diacyl peroxide (1–2 mole per cent.) maintained at  $60\text{--}70^\circ$ , sulfonyl chloride (dissolved in the olefin) is added dropwise, there is formed besides the dichloro derivative a considerable quantity of a compound containing two molecular equivalents of the olefin to one of the sulfonyl chloride, as well as some other, as yet unidentified, products.

A mixture of octene-1 (45 g.) and dibenzoyl peroxide (2 g.) is heated to  $60^\circ$ , and sulfonyl chloride (30 g.), dissolved in octene-1 (50 g.), is added dropwise over a period of six hours, while a slow stream of sulfur dioxide is passed through the reaction mixture. The heating is continued for two hours longer. Distillation of the reaction mixture gave 13 g. of dichlorooctane (b. p.  $67\text{--}71^\circ$  (4 mm.),  $n_D^{20}$  1.4531, Cl 38.38%, mol. wt. 183) and a residue. The major part of this residue sublimed readily when heated to  $110\text{--}140^\circ$  ( $10^{-5}$  mm.). When crystallized from alcohol a white crystalline material (22 g.) was obtained which melted at  $57\text{--}58^\circ$ .

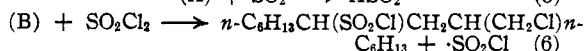
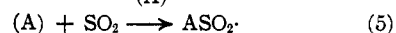
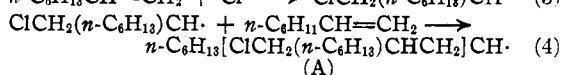
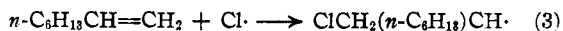
*Anal.* Calcd. for  $C_{16}H_{32}O_2SCl_2$ : Cl, 19.73; mol. wt., 359.4; neut. eq., 179.7. Found: Cl, 19.58, 19.67; mol. wt., 365; neut., eq., 180.

The formation of the compound  $C_{16}H_{32}O_2SCl_2$  from octene-1, sulfonyl chloride and a small amount of benzoyl peroxide, probably proceeds as follows



(1) Kharasch and Brown, *THIS JOURNAL*, **61**, 2142 (1939); **61**, 3432 (1939); **62**, 925 (1940); Kharasch and Read, **61**, 3089 (1939).

(2) The original papers should be consulted for the mechanisms of these reactions.



The analyses, molecular weight, neutralization equivalent, and the fact that the compound is soluble in sodium hydroxide and is not subsequently precipitated by acid, indicate that the compound is a sulfonyl chloride and not a chlorinated sulfone.

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### ULTRAVIOLET SPECTRUM OF FLUORINATED BENZENES

Sir:

The spectra of fluorinated benzenes and toluenes have been measured in the  $1700\text{--}2800 \text{ \AA}$ . region. Because of the current interest in fluorocarbons, we present a preliminary comparison of the spectra of perfluorotoluene<sup>1</sup> (b. p.  $103.5^\circ$ ) and toluene (API-NBS)<sup>2</sup> in *n*-heptane solution in Table I, where  $\epsilon$  is the molecular extinction coefficient and  $f$  the oscillator strength.

TABLE I  
MAIN FEATURES OF SPECTRA

	Toluene	Perfluorotoluene
${}^1A_{1g}\text{--}{}^1B_{2u}$ type forbidden transition		
Onset	37,300	near 36,800 $\text{cm.}^{-1}$
$\epsilon_{\text{max}}$	230	1,080
$f$	0.004	0.021
${}^1A_{1g}\text{--}{}^1B_{1u}$ type forbidden transition		
Onset	46,300	near 47,500
$\epsilon_{\text{max}}$	8,100	7,000
$f$	0.12	0.12
${}^1A_{1g}\text{--}{}^1E_{1u}$ type allowed transition		
Peak	53,000	56,100
$\epsilon_{\text{max}}$	55,000	48,000
Total $f$	1.09	0.91

The previously studied simple substituents on benzene, such as alkyls, halides, etc., which do not conjugate with the ring, cause little change in the position of the  $2600 \text{ \AA}$ . forbidden transition ( ${}^1A_{1g}\text{--}{}^1B_{2u}$ ). They cause some red shift in the  $2100 \text{ \AA}$ . forbidden transition ( ${}^1A_{1g}\text{--}{}^1B_{1u}$ ), and larger red shifts in the allowed  $1835 \text{ \AA}$  N  $\rightarrow$  V ( ${}^1A_{1g}\text{--}{}^1E_{1u}$ ) transition.<sup>2</sup> Increasing shifts in the shorter wave length bands are noted here except that they are in the opposite direction, *i. e.*, "toward the blue." Saturated fluorocarbon spectra show blue shifts compared to the corresponding hydrocarbon as seen in the extension of solu-

(1) Kindly supplied by Dr. E. T. McBee.

(2) J. R. Platt and H. E. Klevens, *Chem. Rev.*, **41**, 301 (1947).