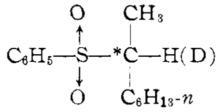
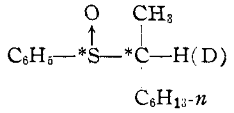
respectively did not impart any special stereochemical properties to their corresponding anions.[3] The current study was initiated to determine whether the configurational stability of the sulfonyl carbanion was independent of leaving group.



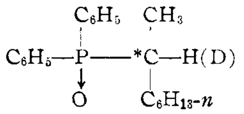
$$C_6H_5-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-{}^*\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-H(D)$$

I



$$C_6H_5-{}^*\overset{\overset{O}{\uparrow}}{S}-{}^*\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-H(D)$$

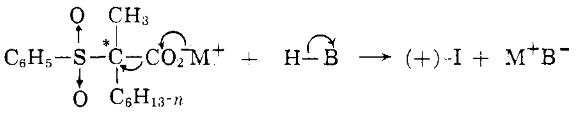
II



$$C_6H_5-\overset{C_6H_5}{\underset{\underset{O}{\downarrow}}{P}}-{}^*\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-H(D)$$

III

Acid IV was prepared by successive alkylations of ethyl benzene-sulfonylacetate[4] with *n*-hexyl bromide followed by methyl iodide, and hydrolysis of the resulting ester.[5] This acid (m.p. 97–98°) was resolved through its quinine salt to maximum rotation, $[\alpha]^{29}_{546} + 15.6°$ (c 8. $CHCl_3$). The optically active acid is an oil.



$$C_6H_5-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-{}^*\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-CO_2^-M^+ + H-B \longrightarrow (+)\text{-I} + M^+B^-$$

(+)-IV

Decarboxylations of (+)-IV were performed at 90° in *tert*-butyl alcohol, methanol, ethylene glycol, water and dimethyl sulfoxide. The substrate concentrations were 0.20 *M* in all solvents except water, in which the concentration was 0.04 *M*. Enough dry potassium carbonate was added in all runs to give solutions 0.17 *M* in potassium ion, except in the case of water, in which the final solution was 0.034 *M*. In an additional run in dimethyl sulfoxide, tetramethylammonium hydroxide was substituted for the carbonate (concentrations were the same as when potassium carbonate was used). Product was isolated as described previously[2] in yields from 10–99%, depending on how long the reaction was allowed to go. Control experiments demonstrated the product ((+)-I)[2] to be optically stable under conditions of its formation and, further, that acid IV did not decarboxylate in the absence of base. In all runs, product of 97 ± 3% optical purity[2] was obtained, the smallest observed rotation being $[\alpha]^{26}_{546} + 0.65°$ (l 1 dm., c 5, $CHCl_3$). The reaction occurred under all conditions with stereospecificities experimentally indistinguishable from one another and from 100%.[6] These results coupled with those obtained previously[2] leave little doubt that this reaction occurs with high retention, and that the sulfonyl carbanion possesses considerable configurational stability. In fact, in methanol and dimethyl sulfoxide as solvents, the decarboxylations occurred with greater stereospecificity than the isotope exchange reactions.[2]

The present results have a bearing on the unresolved problem of the type of hybridization at carbon in sulfonyl carbanions. In the exchange reaction,[2] the leaving group and attacking electrophile differed only isotopically. Thus the bond-making and breaking processes should involve essentially the same transition states. Application of the principle of microscopic reversibility indicates the two processes should be the exact reverse of one another, except for isotope effects. In the decarboxylation reaction, the two processes are quite different, and therefore the stereospecificity of the reaction in no way depends on a reversible process. If the carbanion is hybridized sp^2-p, and depends for its asymmetry on rotamer stability, the proton would have to attack on the same side of the flat carbanion from which the carbon dioxide molecule left. This adds one more condition to use of an sp^2-p-rotamer stability explanation[2] for the configurational stability of the sulfonyl anion.

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RECEIVED FEBRUARY 23, 1962

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[3] D. J. Cram, D. Partos, S. Pine and H. Jager, *J. Am. Chem. Soc.*, in press (1962).

[4] W. C. Ashley and R. L. Shriner, *ibid.*, **83**, 4410 (1932).

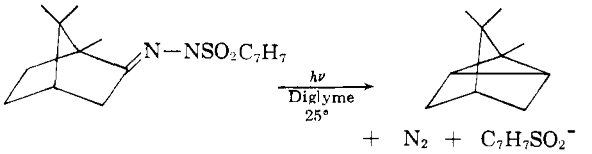
[5] All intermediates and the final compound gave carbon and hydrogen analyses that differed from theory by less than 0.30%.

[6] In an earlier study, J. E. Taylor and F. H. Verhoek [*ibid.*, **81**, 4537 (1959)] observed that the anion of optically active 2-methyl-2-benzenesulfonylbutyric acid decarboxylated at high temperatures to give optically active 2-butyl phenyl sulfone of undetermined optical purity.

PHOTOCHEMICAL TRANSFORMATIONS. XII. THE DECOMPOSITION OF SULFONYLHYDRAZONE SALTS[1,2]

Sir:

It has been established by Powell and Whiting[3] and Friedman and Schechter[4] that *p*-toluenesulfonylhydrazones of aliphatic aldehydes and ketones react at elevated temperatures (130–180°) with bases in aprotic solvents to give diazo compounds and in protic solvents to yield diazonium ions. The diazo and diazonium species formed at the high temperatures immediately decompose *via* carbenoid and cationoid routes, respectively. It has now been found that the potassium salt of a *p*-toluenesulfonylhydrazone upon irradiation with ultraviolet light at *room temperature* yields products similar to those in the thermal reaction.



At room temperature, a solution of camphor *p*-toluenesulfonylhydrazone (I) in 0.1 *N* methanolic potassium hydroxide is stable for many hours in the dark, but such a solution upon exposure to a quartz 500-watt Hanovia high pressure mercury lamp is transformed rapidly into a mixture of hydrocarbons and ethers. The composition of the hydrocarbon

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[1] For Paper XI, see W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, in press.

[2] This work was supported, in part, by Grant No. A-709, U. S. Public Health Service.

[3] J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

[4] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

TABLE I

HYDROCARBON COMPOSITION FROM CAMPHOR *p*-TOLUENESULFONYLHYDRAZONE IRRADIATION

Solvent	Light source	Hydrocarbon, %	Tricyclene,[d] %	Camphene,[d] %
Aqueous 0.1 *N* KOH[a]	Unfiltered	8	18	82
	Filtered	Trace	..	..
Methanolic 0.1 *N* KOH[a]	Unfiltered	36	36	64
	Filtered	44	20	80
Diglyme 0.1 *N* NaOMe[b,c]	Unfiltered	93	99	1
	Filtered	70	87	13

[a] In methanol the other products were methyl ethers and in water the other products were alcohols. In the latter solvent, the main product appeared to be camphene hydrate. [b] In diglyme the *p*-toluenesulfinate anion decomposes photochemically to give toluene and other minor products. These decomposition products were the only species present other than tricyclene and camphene. [c] The sodium salt of the hydrazone is insoluble in diglyme and the irradiations were conducted on the suspended solid. [d] Each entry is an average of two runs which differed by no more than 2%.

fraction obtained by irradiation of I under different conditions and in different solvents is summarized in Table I.

It is to be noted that as the concentration of available protons increases the amount of tricyclene, the product formed by carbenoid decomposition, decreases and the amounts of camphene and alcohols or ethers, the products formed by cationoid decomposition, increase. Such a result is in line with the results obtained by thermal decomposition of the hydrazone.[3,4] Of particular interest is the increase in cationoid decomposition when a Pyrex filter is employed.

Photolysis of I in pure methanol or diglyme (no base added) using a quartz probe proceeded more slowly than the reaction of the salt. The reaction product was contaminated with sulfur-containing materials which must have arisen from the *p*-toluenesulfinic acid generated in the reaction. (No reaction occurred when a Pyrex filter was employed.)

As in the case of the thermal decomposition of the salt of the *p*-toluenesulfonylhydrazone, the room temperature photochemical reaction can be viewed as first forming diazocamphane. The diazocamphane, in turn, either can undergo direct photolysis in the usual fasion to yield a carbene or can react with a proton-donating solvent to yield a diazonium cation which decomposes in the usual fashion. Some evidence for the intermediate formation of the red diazocamphane was found in the irradiations in diglyme with filtered light where a transient red color developed. The utilization of ultraviolet light energy rather than the usual thermal energy for excitation of a bond capable of cleavage again points to the utility of photochemical processes.

In a typical reaction, a solution or suspension of I in an alkaline medium is irradiated until the characteristic maxima of *p*-toluenesulfinate anion at 261 and 268 mμ appear and remain at approximately constant intensity for 15 minutes. For a 2-g. sample, about 20 minutes is required using unfiltered light and 150 minutes using filtered light. The temperature of the solution remains between 25–35°. The reaction mixture is processed as described by Powell and Whiting[3] and the hydrocarbons analyzed by gas-liquid chromatography using a column containing tris-(2-cyanoethoxy)-propane as a stationary phase.

(5) National Foundation Predoctoral Fellow.

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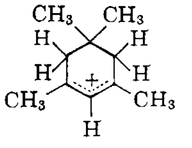
ALIPHATIC ALKENYL (ALLYLIC) CATIONS[1]

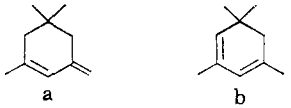
Sir:

Cation I has been prepared and its structure demonstrated with such certainty that its properties should serve as prototypes for those of other aliphatic alkenyl cations.

I is formed by adding to concentrated sulfuric acid the diene mixture (IIa and IIb) obtained from the Grignard addition of methyl iodide to isophorone.[2] I also was formed by shaking a dichloromethane solution of II with moist aluminum chloride.[3] Concentrated (10%) solutions in either medium are stable as evidenced by n.m.r. spectra that are unchanged after one hour.



I



II

The n.m.r. spectrum of a dichloromethane solution of I has four bands at 1.98, 6.67, 6.93, and 8.79 τ[4] (bands in nearly the same relative positions are exhibited in the spectrum of a 96% sulfuric acid solution of I) with relative areas of 1:4:6:6. The sharp band corresponding to one hydrogen is at lowest field (1.98 τ) as would be expected for a hydrogen attached to a carbon that is both multiply bonded and part of a positively charged conjugated system. The four methylene hydrogens and six of the twelve methyl hydrogens are alpha to the allylic system and exhibit bands at 6.67 and 6.93 τ (both bands show partially resolved fine structure), the τ-values reflecting the proximity of a positive charge. The six hydrogens (gamma to the allylic system) of the gem-dimethyl grouping gave a sharp band at 8.79 τ, a value only slightly lower than that of hydrogens of methyl groups of saturated hydrocarbons.[5]

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(2) M. S. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941); J. Schmitt, *Ann.*, **547**, 256 (1941); J. P. Ferrin, T. B. Tom, N. L. Koslin, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Org. Chem.*, **19**, 923 (1954); G. Chiurdoglu and A. Maquestiau, *Bull. soc. chim. Belges*, **63**, 357 (1954); O. H. Wheeler, *J. Org. Chem.*, **20**, 1672 (1955).

(3) This procedure has been used to prepare stable solutions of a number of carbonium ions (Herman G. Richey, Jr., unpublished work).

(4) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, N. Y., 1959.