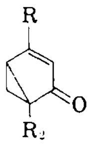
Communications TO THE EDITOR

Synthesis of an Isomer of Umbellulone

Sir:

In view of current interest in the chemical and spectroscopic properties of cyclopropane compounds we wish to report[1] that we have confirmed the structure[2] of umbellulone [I, $R_1 = CH_3$, $R_2 = CH(CH_3)_2$] by the synthesis of an isomer [I, $R_1 = CH(CH_3)_2$, $R_2 = CH_3$] which contains the [3.1.0.]-bicyclohexenone chromophoric system (I) and has an ultraviolet absorption spectrum [$\lambda\lambda_{max}^{alc}$ 216 mμ (ϵ 7800), 262 (3200), sh. 320 (184)] practically identical with the anomalous absorption spectrum reported[3] for umbellulone [$\lambda\lambda_{max}^{alc}$ 220 (5900), 265 (3290), sh. 330 (210)].



I

Diazomethyl isopropyl ketone reacted with methyl methacrylate to give after thermal decomposition of the intermediate pyrazoline, 1-carbomethoxy-2-isobutyryl-1-methylcyclopropane (II) (C, 65.27; H, 8.82) in 35% yield. II was hydrolyzed with alkali to a syrupy mixture of *cis* and *trans*-2-isobutyryl-1-methyl-1-cyclopropane carboxylic acids from which the crystalline *trans* isomer III (m.p. 56–57°, C, 63.83, H, 7.84) was isolated. After structure proof by oxidation to the known[4] *trans*-1-methyl-1,2-cyclopropanedicarboxylic acid, III was converted *via* reaction of its acid chloride (C, 57.94, H, 7.30) with the cadmium methyl Grignard reagent[5] to 1-acetyl-2-isobutyryl-1-methylcyclopropane (b.p. 120–122° at 2 mm. n_D^{21} 1.4670, C, 71.42, H, 9.80) which underwent aldol cyclization on treatment with dilute base to yield 1-methyl-4-isobutyrylbicyclo[3.1.0.]-4-hexenon-6 (I, $R_1 = CH(CH_3)_2$, $R_2 = CH_3$), [b.p. 54°at 1 mm.; n_D^{21} 1.4853; C, 79.48, H, 9.57; $\lambda\lambda_{max}^{film}$ 5.90 μ (C=O), 6.28, (C=C, conj.)].

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[1] Reported in part at the 125th meeting of the American Chemical Society in Dallas, Texas, March, 1956.

[2] F. W. Semmler, *Ber.*, **40**, 5017 (1907).

[3] A. E. Gillam and T. F. West, *J. Chem. Soc.*, 98 (1945); R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954).

[4] C. K. Ingold, *J. Chem. Soc.*, 398 (1925).

[5] J. Cason, *J. Am. Chem. Soc.*, **68**, 2078 (1946); R. H. Eastman and S. K. Freeman, *J. Am. Chem. Soc.* **77**, 6642 (1955).

The Infrared Spectra of Aromatic Organoalkali Compounds

Sir:

Kross and Fassel reported recently that a plot of absorption frequencies in the region 1045–1185 cm.$^{-1}$ *versus* the electronegativity squared of the substituent element yielded linear energy relationships for a series of compounds of the type $(phenyl)_nM$, where n is the valence of the substituent M.[1] They studied three to five compounds in each periodic group from IV B through VII B. In each group they obtained linear relationships and the lines for all four groups extrapolated to a common point at 984 cm.$^{-1}$. These workers suggest that the substituent-sensitive vibration being used arises from a C—H planar mode.

Similar linear energy relationships might be presumed to exist for aromatic organometallic compounds in groups I through III. A logical starting point is group I, but no infrared spectra of organoalkali compounds have been reported. Accordingly, spectra were run on phenyl-lithium, -sodium, and -potassium. Phenyllithium was prepared from bromobenzene, while the sodium and potassium compounds were prepared by metalation of benzene with amyl-sodium and -potassium respectively. Solvent-free Nujol mulls were prepared and spectra determined on a Perkin-Elmer (model 21) infrared spectrophotometer. Many bands were obtained for each compound, some of which could be identified as characteristic of a monosubstituted benzene. Phenylsodium, for example, gave medium intensity bands at 1590 and 3030 cm.$^{-1}$, characteristic of an aromatic structure. Strong bands appeared at 705 and 671 cm.$^{-1}$ and weak bands at 1970, 1880, 1850, and 1805 cm.$^{-1}$, all of which are characteristic of a monosubstituted benzene.[2]

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[1] R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, **77**, 5858 (1955).

[2] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954.

Bands were also observed whose positions were sensitive to the nature of the cation. Strong bands appeared at 1263, 1206, and 1163 cm.$^{-1}$ for the lithium, sodium, and potassium compounds respectively. A plot of those frequencies *versus* the electronegativity squared for lithium, sodium, and potassium[3] yielded points lying on a straight line within one per cent. The intercept of this line was 984 cm.$^{-1}$, identical with that reported by Kross and Fassel.

Kross and Fassel used their data and a band which occurs at 1030 cm.$^{-1}$ in monodeuterobenzene[4] to calculate an electronegativity value for deuterium. Considering deuterium as the highest member of the halogen series, they calculated a value of 2.06, which is close to the value 2.13 reported for hydrogen.[5] There is reason to doubt the validity of this calculation, since many monosubstituted benzene derivatives have bands close to 1030 cm.$^{-1}$ regardless of the nature of the substituent.[6] However, if the electronegativity quoted above for hydrogen is assumed to be the same as that for deuterium and if its square is plotted on the graph of the alkali metal compounds, a rather surprising result is obtained. In spite of the long extrapolation involved, the graph predicts a band in the spectra of monodeuterobenzene at 2256 cm.$^{-1}$, a value remarkably close to that of 2269 cm.$^{-1}$ assigned to the C—D fundamental vibration.[4] This result suggests that the bands used in plotting the linear relationship of the alkali reagents might be assigned to carbon-metal vibrations. However, assuming equal force constants for the C—D, C—Li, C—Na, and C—K bands, rough calculations indicate that C—Li should absorb about 1200 cm.$^{-1}$, C—Na about 700 cm.$^{-1}$, and C—K about 500 cm.$^{-1}$. Except for the C—Li bond the frequency values calculated by this method are much lower than those actually observed.

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(4) C. R. Bailey, R. R. Condon, J. B. Hale, N. Herzfeld, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, 299 (1946).

(5) W. Gordy, *J. Chem. Phys.*, **15**, 152 (1947).

(6) R. R. Randle and D. H. Whiffen, *Trans. Faraday Soc.*, **52**, 9 (1956).