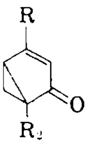
Communications TO THE EDITOR

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.)].

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING HOWARD E. SMITH
STANFORD UNIVERSITY RICHARD H. EASTMAN
STANFORD, CALIFORNIA

Received May 21, 1956

---

[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)$_n$M, 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]

---

[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.