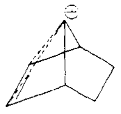
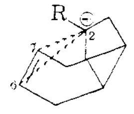
STABLE NON-CLASSICAL CARBONIUM IONS

Sir:

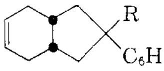
The impressive difference shown in the rate of solvolysis of the tosylates of anti-7-norbornenol and 7-norborneol[1] (a factor of 10^{11}) indicates non-classical stabilization of the intermediate carbonium ion, I, of about 15 kcal. This value is of a similar order to that involved in several other stable classical carbonium ions[2] and suggests that salts of non-classical carbonium ions might also be capable of isolation. We wish now to report the formation of such a stable non-classical carbonium ion.



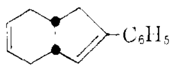
I



II



III



IV

Models indicated that in the molecular system II, a p_z orbital of carbon atom 2 could effectively overlap with the π molecular orbital of the 6:7 double bond if the ring fusion were *cis*, but could not in the corresponding *trans* isomer

Accordingly, we have synthesized the *cis* phenyl carbinol III (R = OH) and its *trans* ring fused isomer. The *cis* compound readily dissolves in strong acids giving deep yellow solutions; the ultraviolet absorption curve in 60% H_2SO_4 (Fig. 1, curve A) shows two strong peaks at 386 and 427 mμ. The *trans* isomer, however, shows no strong absorption beyond 300 mμ in 60% H_2SO_4 (curve D). The spectrum of the *cis* diene, IV, in 60% H_2SO_4 is identical with that of the *cis* carbinol; both solutions presumably contain the non-classical carbonium ion II (R = phenyl).

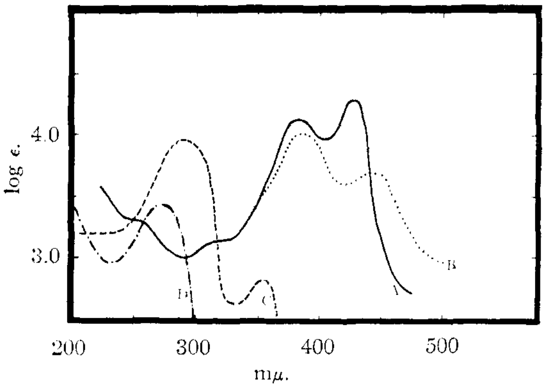


Fig. 1.

Treatment at 0° of the chloride III (R = Cl) with $AgClO_4$ in benzene caused immediate precipitation of AgCl together with a yellow solid. From its mode of formation and the following properties, this yellow solid is undoubtedly the perchlorate salt of the carbonium ion II (R = phenyl). The yellow solid contains the perchlorate anion, it is insoluble in hexane, $CHCl_3$, CCl_4 and benzene; it dissolves readily in nitromethane to give yellow solutions, the ultraviolet spectrum of which shows two peaks at 382 and 435 mμ (curve B), but which rapidly change with time. In 60% H_2SO_4 the spectrum is identical to that of the carbinol (curve A). Treatment of the yellow solid with water, alcohol or ether causes immediate decolorization and formation of the diene IV. The yellow solid is stable below −40° but decomposes at room temperature, especially on exposure to air.

The *cis* methylcarbinol, analogous to the phenylcarbinol, also forms stable yellow solutions in 60% H_2SO_4; these again show strong absorption beyond 200 mμ (curve C) suggesting formation of a similar non-classical carbonium ion II (R = methyl).

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[1] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955).

[2] For references see D. Bethell and V. Gold, *Quart. Rev.* (*London*), **12**, 173 (1958).

CHROMIUM TETRA-*t*-BUTOXIDE

Sir:

We have obtained a new tetravalent chromium compound, chromium tetra-*t*-butoxide, in the course of experiments on the catalytic action of bis-benzenechromium. Inorganic compounds of tetravalent chromium are known,[1] but tetravalent chromium with organic groups has not been isolated heretofore.

A solution of bis-benzenechromium in benzene (or petroleum ether) was heated with di-*t*-butyl peroxide in a sealed tube at 90° for 20 hr. After solvent had been removed, the green residues were sublimed under reduced pressure at 70–90°. The sublimed deep blue crystals (80% yield based on $Cr(C_6H_6)_2$) melt at 30–35° and give *t*-butyl alcohol on decomposition with dilute sulfuric acid. These crystals contain a small amount of biphenyl as an impurity. The experimental results strongly indicate that this biphenyl is derived from the benzene in bis-benzenechromium. It is interesting that π-bonded benzene shows a different chemical behavior from that of benzene itself. The contaminated biphenyl was freed from the blue crystals by means of the formation of adduct with 2,4,7-trinitrofluorenone. The purified blue crystals showed no characteristic absorption bands of biphenyl in the infrared spectrum.

Analytical results of the purified blue crystals are as follows. Calcd. for $C_{16}H_{36}O_4Cr$: Cr, 15.1; C, 55.79; H, 10.56; mol. wt., 345. Found: Cr, 15.2; C, 55.57; H, 10.27; mol. wt., 330. This compound has been found to be paramagnetic to the extent of 2.88 Bohr magnetons, suggesting the presence of two unpaired electrons in the molecule.[2]

From these results, the blue crystals should be chromium tetra-*t*-butoxide, $Cr[OC(CH_3)_3]_4$. This

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[1] E. Huss and W. Klemm, *Z. anorg. u. allgem. Chem.*, **262**, 25 (1950); H. Bode and E. Voss, *ibid.*, **286**, 136 (1956); R. Scholder and W. Klemm, *Angew. Chem.*, **66**, 461 (1954).

[2] We are indebted to Drs. H. Takagi and M. Mekata of Kyoto University for this magnetic measurement.