but Michael and Noyes[5] have reaffirmed the original suggestions. If the energy-transfer mechanism from benzophenone outlined in reactions 1 to 3 is correct, then the triplet state of the carbonyl compounds decomposes to free-radical products. These results show that it does not yield type 2 products. It can be inferred, therefore, that the type 2 decomposition takes place through a singlet intermediate as was originally suggested.

The free-radical products in the normal photodecomposition may well arise from a triplet state, but it is clear from the work of Parmenter and Noyes[6] that the type 1 products (alkane and carbon monoxide) also arise from singlet excited states.

Acknowledgment.—The author wishes to thank the D.S.I.R. and the London Chemical Society for apparatus grants.

(5) J. L. Michael and W. A. Noyes, *J. Am. Chem. Soc.*, **85**, 1027 (1963).
(6) C. S. Parmenter and W. A. Noyes, *ibid.*, **85**, 416 (1963).

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An X-Ray Diffraction Study of Nonplanar Carbanion Structures

Sir:

Recently, spectroscopic investigations of the compound $KC(CN)_3$ have been reported by Long, Carrington, and Cravenor,[1] and Miller and Baer.[2] An assignment can be made, on the basis of both infrared and Raman spectra, for either a planar trigonal or a pyramidal model for the anion. Both sets of investigators favor the planar structure. A preliminary X-ray diffraction study by Anderson and Klewe[3] of $KC(CN)_3$ also favors a planar anion within rather large experimental limits.

We have determined, by X-ray diffraction techniques, the crystal structure of the compounds ammonium tricyanomethide, $NH_4C(CN)_3$, and pyridinium dicyanomethylide, $C_5H_5N^+-C^-(CN)_2$. Complete three-dimensional refinements of both structures show the trigonal carbon atom environments to be significantly nonplanar.

Both compounds crystallize in the monoclinic system with the unit cell constants shown in Table I. Both structures were solved through Patterson projections down the short axis followed by a three-dimensional analysis based on packing and other considerations.

TABLE I

Space group	$NH_4C(CN)_3$ C^5_{2h}–$P2_1/c$	$C_8H_5N_3$ C^2_{2h}–$P2_1/m$
a	9.055 ± 0.007 Å.	7.87 ± 0.02 Å.
b	3.87 ± 0.010 Å.	12.512 ± 0.004 Å.
c	17.325 ± 0.014 Å.	3.86 ± 0.01 Å.
β	$104.6 \pm 0.2°$	$114.8 \pm 0.1°$
Z	4	2

The structure of $NH_4C(CN)_3$ was refined by two-dimensional Fourier and least-squares techniques fol-

(1) D. A. Long, R. A. G. Carrington, and R. B. Cravenor, *Nature*, **196**, 371 (1962).
(2) T. A. Miller and W. K. Baer, *Spectrochim. Acta*, **19**, 73 (1963).
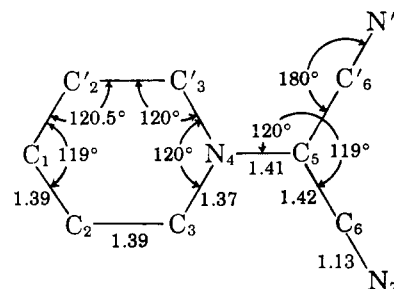(3) P. Anderson and B. Klewe, *Nature*, **200**, 464 (1963).

Fig. 1.—Bond distances and angles in pyridinium dicyanomethylide.

lowed by a complete full matrix isotropic weighted least-squares. The final R value for the 112 independent $(h0l)$ data was 8%. The R value for the 429 independent three-dimensional data was 10%. The observed dimensions of the $C(CN)_3^-$ ion are: C–C bond length, 1.40, 1.40, and 1.40 $\pm$ .01 Å.; C–N bond length, 1.15, 1.14, and 1.16 $\pm$ 0.1 Å.; C–C–C bond angle $119°40'$, $119°31'$, and $119°32' \pm 1°$; C–C–N bond angle 180, 180, and 180 $\pm 1°$. If one passes a plane through the three nitrogen atoms of this ion, the central carbon atom is found to be 0.13 Å. above this plane and the cyanocarbon atoms are all 0.08 Å. above this plane. Each C–C–N unit makes an angle of 3° with respect to its projection in this plane. There are no abnormal interionic distances.

The structure of $C_5H_5N^+-C^-(CN)_2$ was refined by the same procedure as that employed for $NH_4C(CN)_3$. The final value of R, based on 325 independent (hkl) data was 12%. The observed dimensions of the molecule are shown in Fig. 1. The molecule lies across a crystallographic mirror plane through atoms 1 and 4. The pyridinium ring as well as the trigonal carbon atom are coplanar within $\pm$ 0.01 Å. The two cyano groups are inclined with respect to this plane such that the distance from the plane to atoms 6 and 7 are 0.08 Å. and 0.13 Å., respectively. All distances reported in this molecule have an associated estimated standard deviation of $\pm$ 0.01 Å.

It thus appears that in both these systems a significant deviation from planarity of the carbanion group exists, even though the possibility of resonance stabilization of a planar configuration is possible. Detailed accounts of these results will be presented elsewhere.

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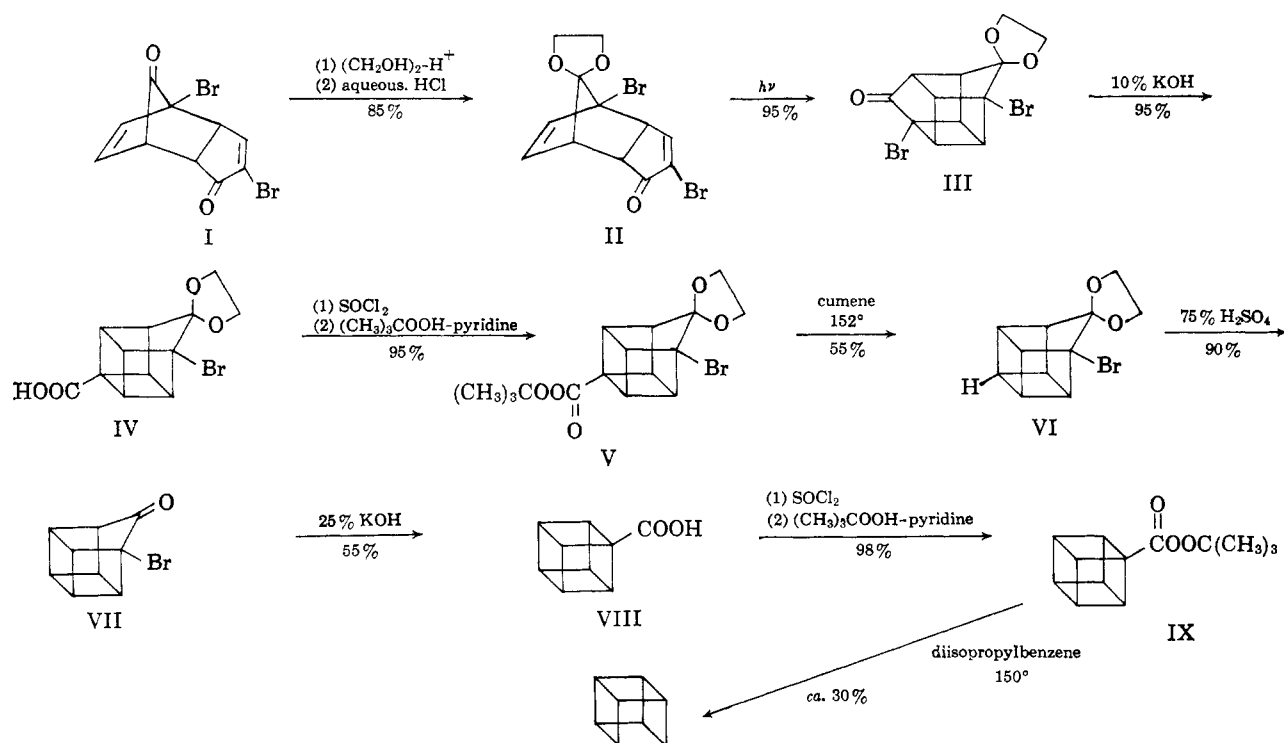

Cubane

Sir:

We have completed the synthesis and fundamental characterization of the hydrocarbon cubane.

The bromocyclopentadienone dimer I, prepared as described in an earlier communication,[1] is converted

(1) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962 (1964).

Reaction scheme:

I →[(1) (CH₂OH)₂-H⁺ / (2) aqueous. HCl / 85%]→ II →[hν / 95%]→ III →[10% KOH / 95%]→

IV →[(1) SOCl₂ / (2) (CH₃)₃COOH-pyridine / 95%]→ V →[cumene 152° / 55%]→ VI →[75% H₂SO₄ / 90%]→

VII →[25% KOH / 55%]→ VIII (COOH) →[(1) SOCl₂ / (2) (CH₃)₃COOH-pyridine / 98%]→ IX (COOC(CH₃)₃)

IX →[diisopropylbenzene 150° / ca. 30%]→ (cubane)

to the bisethylene ketal by prolonged reflux in benzene with ethylene glycol and excess p-toluenesulfonic acid. Selective regeneration of the 1-carbonyl group with concentrated aqueous hydrochloric acid gives the 1-keto-8-ethylene ketal II, 85%, m.p. (from ether) 172–173°, $\lambda_{max}^{CH_2Cl_2}$ 5.78 and 6.28 μ.

Ultraviolet irradiation of II in benzene solution leads quickly to the cage compound III in nearly quantitative yield; m.p. (from methylene chloride–hexane) 148–150, $\lambda_{max}^{CH_2Cl_2}$ 5.53 (sh), 5.61, and 5.63 (sh) μ.

Hot aqueous 10% potassium hydroxide readily converts III to the acid IV, 95%, m.p. (from methylene chloride–hexane) 187–189°, $\lambda_{max}^{CH_2Cl_2}$ 5.70 and 5.79 μ, τ_{CDCl_3} −1.1 (1H, singlet), +6.0 (4H, symmetrical multiplet), 6.3 (5H, multiplet), and 7.2 (1H, multiplet) p.p.m.

The t-butyl perester V, prepared by reaction of the acid chloride of IV with t-butyl hydroperoxide and pyridine in anhydrous ether, undergoes ready radical fragmentation in boiling cumene. Some of the alkyl radicals thus formed (40%) combine with the connate t-butoxy radicals,[2] but the major fraction (55%) escapes this and extracts hydrogen from the solvent to give VI, m.p. (from pentane) 64–65°, τ_{CCl_4} 6.0 (4H, symmetrical multiplet), 6.5 (6H, multiplet), and 7.2 (1H, multiplet) p.p.m.

Hydrolysis of the ketal VI in 75% aqueous sulfuric acid gives the hydrate of VII. The anhydrous ketone is obtained after desiccation in boiling benzene and crystallization from hexane; 90%, m.p. 90–91°, $\lambda_{max}^{CCl_4}$ 3.23, 5.32 (w), 5.45 (m), 5.60 (s), 5.65 (s) and 5.73 (w) μ; the complex carbonyl absorption probably derives from coupling with the vibrations seen at 10.22, 10.51, 10.77, and 10.98 μ, τ_{CCl_4} 6.3 (6H, multiplet) and 6.9 (1H, multiplet) p.p.m.

Cubanecarboxylic acid (VIII), a most versatile intermediate, forms slowly from VII on reflux with 25% aqueous potassium hydroxide; 55%, m.p. (from pentane) 124–125°, $\lambda_{max}^{CCl_4}$ 5.91 μ, τ_{CCl_4} −2.2 (1H, singlet) and +5.6 to 6.2 (7H, multiplet) p.p.m.

Cubane is produced by thermal decomposition at 150° of the t-butyl perester (IX) of cubanecarboxylic acid in diisopropylbenzene. The hydrocarbon is removed from the solvent as it is formed entrained in a nitrogen stream and then captured in an ice trap. Crystallization from methanol and sublimation just above room temperature at atmospheric pressure gives pure material as glistening rhombs, m.p. (sealed capillary) 130–131°.[3]

The identity of cubane follows unmistakably from the parent peak in the mass spectrum at m/e 104, from the diagnostic simplicity of the infrared spectrum in which the only noticeable absorptions in the region from 4000 to 660 cm.$^{-1}$ appear at 3000, 1231, and 851 cm.$^{-1}$, from the single-line proton magnetic resonance spectrum in which the one and only absorption appears at τ 6.0 p.p.m. with width at half-height of 0.3 c.p.s., and from the threefold symmetry axis of the monomolecular 5.34 Å. rhombohedral unit cell.

(2) Evidently the combination with t-butoxy radical occurs within a solvent cage; the distribution of products is unchanged with variation in concentration.

(3) The hydrocarbon is not thermally stable; significant decomposition is evident at 200°.

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