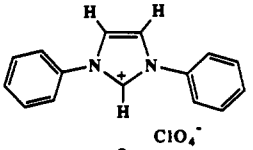
Table I. Selected Bond Lengths (pm) and Angles (deg) in 1-3[a]

property	1	2	3[5c]
$r(C_2-N_{1(3)})$	136.5 (4), 137.1 (4)	135.5 (3), 135.0 (3)	133.6
$r(C_4-C_5)$	133.1 (5)	131.3 (4)	133.9
$r(N_{1(3)}-C_{5(4)})$	138.1 (4), 137.8 (4)	138.2 (4), 138.4 (4)	138.0
$r(N_{1(3)}$-mesityl)	144.1 (4), 144.2 (4)	143.6 (3), 144.2 (3)	143.2 (phenyl)
$r(C_2-Al)$		203.4 (3)	
$\theta(N_1-C_2-N_3)$	101.4 (2)	104.2 (2)	109.2
$\theta(C_{5(4)}-N_{1(3)}-C_2)$	112.8 (3), 112.8 (3)	110.5 (3), 110.8 (3)	108.0
$\theta(N_{1(3)}-C_{5(4)}-C_{4(5)})$	106.5 (3), 106.5 (3)	107.5 (3), 107.0 (3)	106.5
$\theta(C_2-N_{1(3)}$-mesityl)	121.8 (2), 122.6 (2)	124.2 (2), 124.5 (2)	126.6 (phenyl)

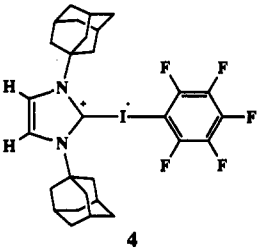
[a] The numbering scheme for all compounds is as indicated for 1.

X-ray quality colorless crystals of 2 were obtained from a THF/toluene solution at -25 °C.[6] The X-ray crystal structure is illustrated with the KANVAS[7] drawing in Figure 1. Selected bond lengths and angles are given in Table I.

The C_2-Al distance is 203.4 (3) pm, which is slightly longer than the Al-C(terminal) distance of 195.8 pm observed for $(AlPh_3)_2$.[8] The geometry around C_2 is planar with an average $N_{1(3)}-C_2-Al$ angle of 127.9° and an $N_1-C_2-N_3$ angle of 104.2 (2)°. The $C_2-N_{1(3)}$ bond distances (Table I) are intermediate between those in the free carbene and in representative 1,3-diarylimidazolium ions (3).[5c] The two mesityl groups in 2 are nearly perpendicular to the imidazole ring with twist angles of 82° and 85°.



3



4

The intermediate ring geometry, which is reflected in both the angles and bond lengths of 2, is similar to the geometry observed for a nucleophilic carbene-derived reverse iodine ylide 4.[9] It is remarkable that the ring internal angle at C_2 of 4 was 104.1° (very close to the same angle in 2) even though the substituents at N_1, N_3, and C_2 are very different. The generality and significance of this type of intermediate imidazole ring geometry are under study.

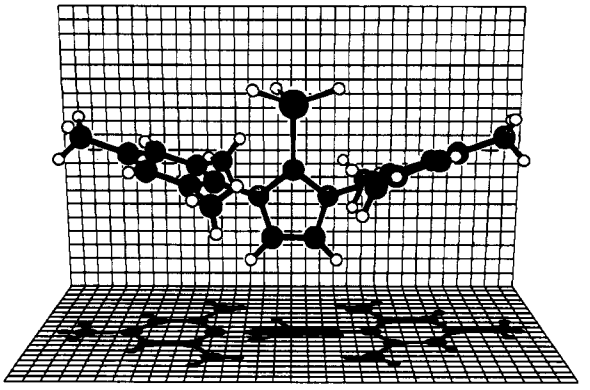


Figure 1. KANVAS[7] drawing of 2.

Structurally well characterized alane adducts are rare,[10] and their carbene complexes are unknown. Compound 2 represents the first example of a main group III-carbene complex and an interesting example of a well-characterized monomeric alane adduct. The stability of 2 is remarkable, considering the fact that it contains a potential hydride donor adjacent to an electrophilic carbon center.

Acknowledgment is made for the excellent technical assistance of H. A. Craig and W. F. Marshall.

Supplementary Material Available: Complete description of the X-ray crystallographic determination on 2, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles and ORTEP drawings (10 pages). Ordering information is given on any current masthead page.

(3) Solid 1 (0.201 g, 0.66 mmol) was added as a single portion to a solution of $AlH_3 \cdot NMe_3$ (0.059 g, 0.66 mmol) in toluene (30 mL) at room temperature under a dry nitrogen atmosphere. The mixture was stirred for 2 h. Volatiles were removed under vacuum to afford a white residue (0.22 g, 100%): mp 246-247 °C; ^1H NMR (THF-d_8) δ 2.06 (s, 12 H, o-CH_3), 2.32 (s, 6 H, p-CH_3), 2.7 (br s, 3 H, AlH_3), 6.98 (s, 4 H, m-H), 7.42 (s, 2 H, NCH); ^{13}C NMR δ 17.74 (s, o-CH_3), 21.16 (s, p-CH_3), 124.32 (s, NCH), 129.65 (s, Mes $C_{3,5}$), 135.76 (s, Mes $C_{2,6}$), 136.08 (s, Mes C_1), 139.85 (s, Mes C_4), 175.29 (br s, NCN); ^{15}N NMR (ref $NH_4{}^{15}NO_3$) δ -179.26; ^{27}Al NMR (ref $^{27}Al(H_2O)_6^{3+}$) δ 107 (br); IR (KBr) 1743 cm^{-1} (br AlH). Anal. Calcd for $C_{21}H_{27}N_2Al$: C, 75.42; H, 8.14; N, 8.38. Found: C, 75.41; H, 8.08; N, 8.26.

(4) *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; p 279.

(5) For structures of representative imidazolium ions, see: (a) 1,3-Dimethylimidazolium chloride (ref 1, supplementary material). (b) 1,3-Di(1-adamantyl)imidazolium tetraphenylborate (Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361; supplementary material). (c) 1,3-Diphenylimidazolium perchlorate (3) (Luger, P.; Ruban, G. *Z. Kristallogr.* **1975**, *142*, 177). (d) Langer, V.; Huml, K.; Reck, G. *Acta Crystallogr., Sect. B* **1982**, *38*, 298. (e) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753.

(6) Crystal data for 2 at -70 °C with Mo Kα radiation: a = 840.9 (4), b = 1525.1 (3), c = 1645.9 (8) pm, β = 104.11 (2)°, monoclinic, $P2_1/n$, Z = 4, 2065 unique reflections with $I > 3\sigma(I)$. The final R factors were R = 0.051 and R_w = 0.045. There was a rotational disorder of the three hydrogens on Al that was modeled by two equally populated rotamers. The largest residual electron density in the final difference Fourier map was 0.19 e/Å^3 near C_2. Further details of the crystal structure are available in the supplementary material.

(7) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful. Only one rotamer for the disordered AlH_3 group is shown.

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Biocatalysis and Nineteenth Century Organic Chemistry: Conversion of D-Glucose into Quinoid Organics

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By combining a newly created biocatalyst with nineteenth century chemical methodology,[1] quinoid organics such as quinic

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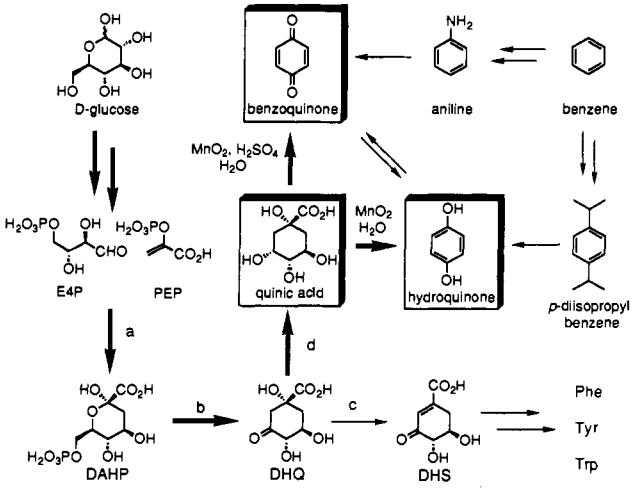
Scheme I[a]



[a] (a) DAHP synthase (*aroF*); (b) DHQ synthase (*aroB*); (c) DHQ dehydratase (*aroD*); (d) quinic acid dehydrogenase (*qad*).

acid, benzoquinone, and hydroquinone can now all be derived from D-glucose. A class of industrially important organics can thus be made from a nontoxic feedstock derivable from renewable resources such as corn starch and biomass. Current industrial routes to benzoquinone[2] and hydroquinone[2b,3] use a carcinogenic feedstock which can only be derived from nonrenewable fossil fuels.

Quinic acid is an invaluable chiral starting material in multistep chemical synthesis.[4] It is obtained by an expensive isolation from plant sources.[5] Benzoquinone is used as a building block for construction of a variety of industrial organics.[2a] Largely due to its use in photography, over 4.0×10^4 metric tons of hydroquinone are produced annually.[2b,3] Benzoquinone and hydroquinone are mainly produced (Scheme I) from oxidation of aniline or Hock-type oxygenation of *p*-diisopropylbenzene.[2b,3] Both of these organics are, in turn, obtained from a benzene feedstock.

Creation of a new, common route to the quinoid organics began with the ability of certain microbes such as *Klebsiella pneumoniae* to utilize quinic acid as the sole source of carbon during growth.[6] The first step in catabolism of quinic acid entails this molecule's oxidation (Scheme I) into 3-dehydroquinate (DHQ), which is catalyzed by NAD^+-requiring quinic acid dehydrogenase (EC 1.1.1.24).[7] Since reduction of DHQ to quinic acid is actually the thermodynamically preferred direction of reaction,[7] expression of the gene (*qad*) encoding quinic acid dehydrogenase in a microbe incapable of catabolizing quinic acid was anticipated to result in a heterologous[8] microbe capable of quinic acid synthesis. Construction of such a biocatalyst began with isolation of the *qad* gene from *Klebsiella pneumoniae* A170-40. Subcloning provided plasmid pTW8090A, which carries a 2.9-kb insert encoding quinic acid dehydrogenase.

Escherichia coli AB2848 *aroD*/pKD136 was chosen as the host strain for expression of pTW8090A and its *qad* locus encoding quinic acid dehydrogenase. Competing synthesis and degradation of quinic acid is avoided in *E. coli* since this microbe is not capable of using quinic acid as a carbon source. The flow of carbon into the common pathway of aromatic amino acid biosynthesis is increased by the elevated levels of transketolase,[9] DAHP synthase, and DHQ synthase resulting from expression of the *tkt*, *aroF*, and *aroB* loci encoded on plasmid pKD136.[10] The *aroD* mutation in AB2848 prevents competition between *qad*-encoded quinic acid dehydrogenase and *aroD*-encoded 3-dehydroquinate (DHQ) dehydratase (Scheme I) for available DHQ. Therefore, all of the carbon flow initially directed into the common pathway of aromatic amino acid biosynthesis is directed into quinic acid synthesis.

Construct AB2848*aroD*/pKD136/pTW8090A catalyzed the conversion of D-glucose (80 mM) into quinic acid (25 mM). The purity of the microbially synthesized quinic acid was noteworthy even in the crude culture supernatant (Figure 1 of the supplementary material). After cell removal, quinic acid in the crude culture supernatant was converted into benzoquinone in a yield of 40% after addition of sulfuric acid and technical grade manganese(IV) dioxide and heating at 100 °C for 1 h. Conversions of quinic acid to benzoquinone as high as 70% were achieved using similar conditions when quinic acid was purified prior to oxidation. In the absence of acidification, aqueous solutions of purified quinic acid were converted into hydroquinone in 10% yield upon heating at 100 °C for 18 h with technical grade manganese dioxide. Hydroquinone can also be obtained by reduction of benzoquinone.[3a]

Construct AB2848*aroD*/pKD136/pTW8090A is the first example of a microbe capable of synthesizing as opposed to catabolizing quinic acid. This conversion of D-glucose into quinic acid formally transforms multistep chemical syntheses which begin with quinic acid[4] into syntheses effectively utilizing D-glucose as a starting material. In addition, overall conversion of D-glucose into quinic acid is of potential significance to industrial synthesis. The *quin* route of both benzo*quin*one and hydro*quin*one actually reflects their derivation from quinic acid, which was first reported in 1838.[1] New life may be given to this almost forgotten transformation by AB2848*aroD*/pKD136/pTW8090A and its efficient derivation of quinic acid from inexpensive, nontoxic D-glucose.

Acknowledgment. Research was supported by a grant from the Environmental Protection Agency.

Supplementary Material Available: Experimental procedures and ^1H NMR analysis of crude culture supernatant (Figure 1) (2 pages). Ordering information is given on any current masthead page. Construct AB2848*aroD*/pKD136/pTW8090A is available upon request from the American Type Culture Collection (ATCC 69086).

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