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base is now able to deproton on the former carbonyl C-atom: The second equivalent of aldehyde reacts with this carbanion; Removal of catalyst regenerates carbonyl compound at the end of reaction: Recent literature Chemoselective N-Heteocyclic Carbene-Catalyzed Cross-Benzoin Reaction: Meaning of fused ring in triazolium salt S.M. Langdon, M.M. D. Wilde, K. Thai, M. Gravel, J. Am. Chem. Soc., 2014, 136, 7359-7542. Lanthanum Tricyanide-Catalyzed Acyl Silane-Ketone Benzoin Additions J.C. Tarr, J.S. Johnson, Org. Lett., 2009, 11, 3870-3873. Kinetic Direct Control  $\alpha$ -Silyloxy Keton Synthesis: New Regiospecific Catalyzed Cross Silyl Benzoin Reaction X. Linghu, J.S. Johnson, Angew. Chem. Int. Ed., 2003, 42, 2534-2536. Highly Enantioelective benzoin condensation reactions involving bifunctional protic Pentafluorophenyl-Replacement Triazolium Precatalyst L. Baragwanath, C. A. Rose, K. Zeidler, S. J. Connon, J. Org. Chem., 2009, 74, 9214-9217. 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The reaction completely analogous to benzoin condensation occurs in our body, but it does not include cyanohydrin interme-diate or is catalyzed by cyanide ion. It is catalyzed by thethiazolium moiety coenzyme thiamine pyrophosphate (TPP). This article shows common links and inclusive aspects between cyanohydrin formation, cyanohydrins, conversion of cyanohydrins into ben-zoins/acyloins, the role of vitamin B1 (thiamine) and the use of benzoin/acyloin compounds. IntroductionCyano Group in natural products1. Cyanoglycoside hydrogen cyanide is a deadly poisonous substance. Various plant plants produce it, albeit in a hidden form of cyanoglycosides.sugar derivatives of cyanohydrins. Cyanohydrins are formally products of HCN other than ketones or aldehydes, the addi-ce being reversible. Cyanoglycosides hydrolyses enzymatically and nonenzymatically in the body on sugar and cyanohy-drins, which release hydrogen cyanide, scheme 1. Ingestion of cyanide in condensationKeywordsBenzoin, acyloincondensation, cyanide, cyanide, cyanide , vitamin B1kataly-sis, cyanide catalysis, thiazoliumsalt catazoliumsalt, nitril-containing products. Benzoin condensationTnikysnika connection with tapioca and vitamin B1Gopalpur NagendrappaG Nagendrappa, retired from Bangalore Univer-sity, Bangalore, isrepresentative professor of the Ahlava Department of FMedicinal Chemistry, SriRamachandra University,Porur, Chennai. His main work is in the field oforganosilicon chemistry, organic synthesis, reaction mechanism and synthetic surfaces. 356 RESONANT  $\nabla$ This 2008GENERAL  $\nabla$ ARTICLEbody exceeds the tolerance limit (see Box 1). It acts as a defense mechanism in plants because a high cyanoglycoside con-tent makes such parts of plants (seeds, roots, leaves, etc.) bitter. However, we consume many food materials that containcyanoglycosides. R1R2CNOSugarR1R2CNOHR1R2Osugar HCN+ +hydrolysisLinamarine: R1= R2= CH3; Sugar = $\blacktriangleright$ -D-glucoseAmygdalin: R1= Ph, R2= H; Sugar = $\blacktriangleright$ -D-gentiobiosePrunarin: R1= Ph, R2= H; Sugar = $\blacktriangleright$ -D-glucoseChem 1.Box 1. Toxicity and detoxification of the murder course of cyanide: Cyanide inhaled as HCN or consumed as its salts, such as NaCN, KCN, etc., or released in the body for hydrolysis of cyanogenous glycosides consumed as food, causes poisoning. Orl-hmn LDL0= 2857 $\blacklozenge$ gkg-1 for NaCN or KCN. This is How it Poisons: Cyanide ion binds very strongly to Fe3+ methoglobin in mitochondria and formanomemoglobin, which cannot transfer oxygen to tissues. Cellular respiration is arrested and deaths imminent.+HbFe3+ HbFe3+CNMethemoglobin CyanohemoglobinCNDetoxification: A small amount of cyanide present as glycosides in the foods we consume is detoxified by theenzyme rhodanase present in the liver, erythrocytes and other tissues by facilitating the conversion of cyanide tothiocyanate. Smaller qu cn-antities are removed b yox idace kyanate (CNO-) or c ombining with kyb alaminoto form cyanococbalabin (vitamin B12 ).++HbFe3+HbFe3+CN\_ CNCN\_ SCNRhodanasea Nitrite (NO2-) acts as an antidote to cyanide poisoning. Nitrite is given either by inhalation or injection, oxygen is given as a supplement together with or after NO2. Giving oxygen alone is not effective. 357RESONANCE  $\nabla$ This 2008General  $\nabla$ ARTICLERoots of manioc (tapioca), an important food crop in many countries around the world, including India, contain acetone cyanohy-drinkoside called linamarin. Tapioca that contains linamarininn over 100 mgkg-1 of fresh roots is not recommended for food use. Even in order to be suitable for edible purposes, it must be properly processed in order to reduce the toxin content to less than 50 mgkg-1, a limit considered acceptable. A long-recognized source of cyanogenous glucoside is the bitter trapezoid, the bitterness of which is caused by amygdial, or D-mandelonitrile--D-gentiobioside (Scheme 1). Historically, benzaldehyde was first obtained from bitter tonsils. Seeds of apples, peaches, plums, apricots, cherries, etc., contain the appropriate amount of amygdaline. Cyanoglycosides are also present in common edible plants such as sorghum, soybeans, limabeans, corn, bee, sweet potatoes, spinach, sugar cane and bamboo shoots. However, the toxin content in these is low and is henched by the liver and eliminated (see Box 1). Even in the case of Apple seeds, seeds of other fruits, and bitter tapioca, which have arelatively high levels of cyanoglycoside, it is necessary to consume hugequantities from them before they could pose a toxicity problem. The name cyanide evokes in laymen the spectre of poisoning and immediate death, made famous by the authors of detective stories. Cyanide is indeed one of the most toxic substances. Detoxification of smaller amounts of cyanide in the body is caused by the rhodanase enzyme present in the liver, erythrocytes, and other seals, through its rapid conversion to thiocyanate, (see Box 1). Some insects and molluscs eat plants containing cyanogenic glycosides and accumulate a sufficient amount of these glycostrans, which serve as a defense against their predators.2. Non-lycosid group Kyano CompoundsCyano is found in natural products not only in cyanohydringlycosides, but also in non-cyanohydrin form. Some examples are given in Figure 1.1 in the case of Apple seeds, seeds and other fruits, and bittersapioca, which have arelatively highcyanoglycosidecontent, one mustconsume hugequantities of them before they could appe toxicity problem. Detoxification of minorasy cyanide in the body is provoked by enzyme-thrown inliver, erythrocytes and other tissues. 358 RESONANT  $\nabla$ Dude 2008General  $\nabla$ ARTICLEVitamin B12N NNH NCo+CNH2NOCH2CMeCH2CONH2CH2CH2CONH2MeMeMeMeMeMeMCH2H2NOCNMeNPoMe HMeHCH2OHOHHHO-OH2CHNCOMeH2CCH2CCH2CH2CONH2HMeOHHNCNOCH3OH3CRicine (Alkaloid)(from castor oilseeds) Merisclausin Ehreticide B (name depends on R1, R2, R3)Non-cyanogenous OR1OR2Figure 1. Nitril-(Cyano Group) Containing drugsThis cyanohydrins present as much of a toxicity problem as inorganic cyan compounds (NaCN, KCN, HCN, Cu(CN)2, K3Fe-(CN)6, etc.), other types of organic nitrile must not be as toxic 359RESONANCE  $\nabla$ Duch 2008general  $\nabla$ ARTICLENNOOMeONHOOOOMeNCHHHONOHNNHOHOHOHOONME2OHOH OOMeCNHH2O3POOHOHHMEOCNCNR2R1OOR13Cyanopupe henoon(antiviral activity against HIV I)Saframycin A(antibiotic and anticancer activityR1= H, R2= R3 = CH2CH = C(CH3)2R1= R2= H, R3= CH2CH = C(CH3)2123EpurinsCalyculin J(antitumour activity)Figure 1. Continued... 360 RESONANCE  $\nabla$ Ducho 2008general  $\nabla$ ARTICLE because they do not release cyanide easily. In fact, a good number of common drug molecules contain cyano groups as animportant functional groups. A few examples are given inOcution 2.Nitrile (Cyano Group): Universal broker Func-tional GroupSynthetic routes even more drugs used nitrily asNPhCO2C2H5NCPPhPhFigure 2.NCH3H3CCH3CCH3COOCH3CH3H3CO (S)-Verapam il(Ca2+ channel blocker)ONNCH3CN(H/ KATP inhibitor NNNCNNOZaleplan (ultra-short acting sleep inducer)Diphenoxylate (antidiarrheal agent)NHNH3CSHNCH3NCNCimetidine (Tagame l)(antulcer drug) 361RESONANCE  $\nabla$ Thisould 2008GENERAL  $\nabla$ ARTICLIIntermediates due to their versatility for other useful trans formations. Nitrile can be converted into a number of other functions such as amine, carboxylic acid, ester, amide, ketone, aldehyde, heterocycle and more. As a result, nitriles are of great importance as intermediates in the production ofchemoricas, including medicines. As a strong electron towing group, cyano groupssphilizes the formation of carbanion and then ensures its resistance. It has been utilized in pole reversal (umpolung) ofaldehydic carbon from electrophilic nucleophilic, asreented in scheme 2.Cyanide: A good NucleophileCyano group can be introduced into organic molecules of avariety methods. Since cyanide is one of the very effective and effective classical nucleophils, the most common cyanide methods use this property, for example in (1) direct displacement of halides, tosylates or similar leaving groups with cyanide and (2) the addition of cyanide to aldehydes, ketones and their  $\blacktriangleright$  unsociable analogues. The high nucleophilic efficiency of cyanide is due to its easy effectiveness and low silverearm obstacle to its attack. (This is the smallest carbon nucleophile). It is classified high in nuclephilicityRCHO HCN LDAR1X+ R COHCNHR COR2CNR COR2CNR COR2CNR1R1CORHydrolysisR COR2CNRH\_R1X = Electrophile varietyR2=O.Scheme 2.Cyano groupfacilitates formation-carbanion and then ensures its stability. It was exploited in polereversal (umpolung) carbon aldehyde. 362 RESONANT  $\nabla$ The spirit of 2008general  $\nabla$ ARTICLEorder for SN2 reactions (in protectionist solvents), much higher than OH-, (Figure 3). Cyanide as a departure is a well-known fact that many good nuclephilcs, such as ashalides, are also good groups that leave. (Of course, all nuclephilcsare also leaving the group, in principle, although the two characters do not match in all cases). Carbanions, on the other hand, are goodnucleophiles, but generally not good leaving the group. Exceptions are carbon groups bound to strong electrone-gative atoms or groups. Some examples are given in 3.RS&gt; ArS&gt; I&gt; CN&gt; OH&gt; N3&gt; Br&gt; ArO&gt; Cl&gt; Pyr &gt; AcO&gt; H2OFigure 3.R 3.R 3.R C3ORCX3OCR CX3OOH ROHO+Cl3COHOCi3COO+ \_ Cl3C\_CO2OH\_OH\_x2x3Cx = halogenBasePh CH CH BrPh CH CH COOHBr BrPh CH CHBr BrOPh CH HCBBrBr \_BaseOONBrCOOHBaseONBrOONBrONBrONBrH+ \_ Scheme 3. (1) (2) (3) (4) 363RESONANCE  $\nabla$ <3> <4>Thousand 2008GENERAL  $\nabla$ ARTICLEGroup of cyanohydrins deviates very easily, which is the conversion of cyanide addition to the carbonyl ketonesand aldehydes forming cyanohydrins (Diagram 4). However, onlysize bases can eliminate HCN from alkyl nitriles, and it is used in one of the steps of vitamin B12 synthesis. Due to this dual nature (i.e. easy additions to aldehyde easy diversion from cyanohydrin), cyanide may have the ability to catalyze a useful reaction, benzoin condensation, in which two aldehyde molecules condense give -hydroxy ketone. BenzoincreaticCyanohydrins are normal end products of nucleophilic addi-ce NaCN, KCN or HCN to aldehydes or ketones in an aqueous salcoholic solution. However, in the case of aldehydes, the reaction may further add a second aldehyde molecule, topropduce -hydroxy ketones (Diagram 5, Table 1). The highlight of the reaction is the fascinating way in which it is facilitated and directed by ion inoccedituocide, in particular by converting the intermediate cyanohydrin adduct into a key type of nucleophilic carbanion N, which then adds to the next mol-eculu aldehyde to finally deliver benzoin. The mechanism for these reactions was proposed as early as 1903. Although the correctness of this mechanical mechanism was questioned at some stage, it was eventually adopted in 1971. Important steps are listed in the 5.CR R1CNOHCR R1CNORR1O+CN\_BaseH+H3CNCH2Ct-BuOKa reaction in vitamin Bsynthesis-HCNScheme 4. (5) (6) 364 RESONANT  $\nabla$ Duchi 2008General  $\nabla$ SPRSCHRCHA/KL CHR CNCOR CCNHOR1HOHOR CCNOHCOHR1R1CHOHCORabdc \_ CR CCNOCHOHR1(N) (7)Scheme 5. Table 1. Some examples of condensation benzoin vScheme 5.R R1Yield (%) 365RESONANCE  $\nabla$ Auben 2008General  $\nabla$ ARTICLEThe most idiosyncratically successful role of cyanide ion in the catalysing of benzoinreaction is determined by its four properties, namely (1) high nucleophilic activity, (grade a), (ii) facilitating the transmission of proton a, (phase b),iii) the ability to stabilize negative charge in active aldehyde inter-mediate N, (stage c), and (iv) the ability to finally leave, (phase e). Vitamin B1 and thiazole salts as catalystsIn principle, any chemical entity that all four substances should be able to deliver benzoin condensation. In fact, Nature performs this task effectivelyamally by analogy using (vitamin B1)1thiamine pyro-phosphate, TPP, (Figure 4), coenzym present in our body, and other living organisms. TPP catalyzes several reactions that h-clude decarboxylation of pyruveic acid to acetaldehyde, conver-sion pyruveic acid to acetoin, (Scheme 6), Transmission 2-carbonNSRH3CR1\_ ++NSRH3CR1+CH3CCCOOO\_OHH3COO\_NSRH3C R1C CHOH3CONSRH3CR1C COH3COHNSRH3CR1\_ +HCH3\_CH3H\_NSRH3CR1CHOCH3OH+H3C COCOHCH3A1Pyruvate ++NN2H3CNSOH+H3CENN2H3CNSOPOO \_ Vitamine 6.1Preparation of benzoinusive thiamine (vitamin B1) is one of the experi-ements carried out by our l. m es t er M Sc. Medi cin alChemistry students. This is a neatreaction that h gives a clean, crys-talline bezoin high yield. Pre-existing for cedure is fol-lowed is mentioned in[7] mentioned in Suggested Reading.It is a highly ins tructive experiment in terms of chemistry, bio-chemistry, environm ental chem-istr y, and bio- and org o-catalysis. 366 RESONANT  $\nabla$ This 2008GENERAL  $\nabla$ ARTICLEgroup from sedoheptalosis-phosphate to glyceraldehyde-3-phosphate k production of xylose-5-fospbate (acyloin reaction) (Scheme 7), which include acyl ion or its equivalent intermediates in the reaction of benzoin catalyzed cyanide. A key feature of thiazolium moieta in facilitating these reactions is that hydrogen on carbon between carbon between hydrogen and nitrogen (i.e. position 2) is acidic enough to be exchanged with deutenium in D2O. Removal of this protonby base transmits forward reaction, as shown in schemes 6-8,in a way that is quite similar to cyanide catalyzed one. (Scheme 5). CH2OHCHHOHHCH2O PNSH3CR1NSRH3CR1COHCH2OHCHOOHCH2HOPNSH3CR1CH2OHOHHOHHHHHH2CH2CHOHOHHHOHHOHOCH 2OPOOPOHCOHHOHHOHHCH2-O -PoRGE\_FCBDA= Thiamine pyrophosphateB= sedoheptalosis-7-phosphate (ketosis donor)C= TPP-keto sedonor adductD= Ribose-5-phosphate= Resonant stabilized carbanionF= Glyceraldehyde-3-phosphate (aldose acceptor)G= Xylose-5 5-phosphateScheme 7. The key feature ofthiazolium moiety infacilitating thisreaction so effectively in that hydrogen on the uhusudrose and nitrogen (ie. position 2) jeacidic. 367RESONANCE  $\nabla$ Auben 2008General  $\nabla$ ARTICLERecoutation that thiazolium ion in the TPP catalyzes these reac-tions has led to the development of improvised thiazolium ion-based catalysts (Figure 5), which are simpler than TPP but bring obenzoincondenation effectively (Scheme 8). In fact, thiazoliumcatalysts show a greater range of applicability in that they are able to catalyze the condensation of a wider range of aldehydes and not just aromatic aldehydes. Another advantage is that condensation at room temperature and without the risk of environmental pollution posed by cyanide. Replacing cyanide with harmless thiazole salts with ascatalysts for benzoin condensation is one of the best examples of green chemistry in action. SNRH3COHX+R = Ph-CH2, X = Cl (T-1)R = C2H5, X = Br (T-2)R = CH3, X = I (T-3)Figure 5.N SRH3COH+N SRH3C+N SRH3COH+\_ E13NR1HOOR1N SRH3COH+CHO R1\_R2HOR1COCHOHR2R1CHHOCCR2O+CHOOOHC9H19 COCHOH C9H19+AR COCHOHR+AR CHOHCORRCHOC9H19CHOARCHOET3N, EtOHEi3N, EtOHET3N, EtOHT\_1\_T\_2Scheme 8.OH 368 RESONANCE  $\nabla$ Thinking 2008General  $\nabla$ reading proposals[1] T Laird, in complex organic chemistry, (Series Editor d h rbarton and w d ollis), vol.1 (editor: J F Stoddart), p. 1142–1147,Pergamon Press, Indian Press, 2007. [2] G Tennant, in Complex Organic Chemistry , (Series Editors: D HR Barton and W D Ollis), Vol.2 (Editor: I O Sutherland), pp.528-550,Pergamon Press, Indian Press, 2007. 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