dioxide oxidation of the corresponding methyl ketones[5] was the new compound *p*-fluorophenylglyoxal hydrate, white crystals, decomposing at 93–94°.

Anal. Calcd. for $C_8H_7FO_3$: C, 56.65; H, 4.13. Found: C, 56.80; H, 4.57.

We are indebted to Dr. M. J. Shear and Dr. J. L. Hartwell of the National Cancer Institute, and Dr. Louis H. Goodson of Midwest Research Institute, and their associates for suggestions and for arranging screening tests.

(5) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509.

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The Steric Configuration of Brominated 3-Ketosteroids[1]

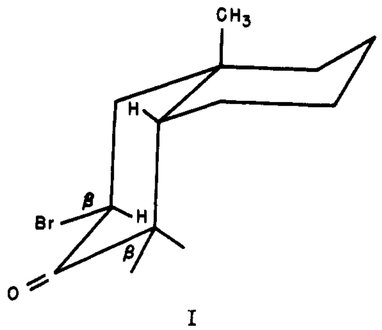
BY R. NORMAN JONES

RECEIVED APRIL 23, 1953

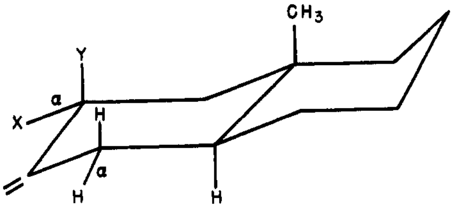
To explain the effects of vicinal bromination on the C═O stretching band in the infrared spectra of ketosteroids, it was postulated[2] that when the C—Br and C═O bonds are coplanar the frequency of the carbonyl band is increased by 15–20 cm.$^{-1}$, but when the C—Br and C═O bonds are perpendicular, bromination does not change the frequency of this band. This observation was subsequently confirmed by Corey who has generalized it to other cyclic α-haloketones.[3]

For the chair conformations I and II conventionally assigned to the A rings of normal and allo-3-ketosteroids, a positive frequency shift should occur on bromination at the equatorial C_2- and C_4-positions, and on this basis the configurations 4β-bromocoprostan-3-one and 2α-bromocholestan-3-one were predicted.[2] The 4β-bromocoprostan-3-one structure has been substantiated by Fieser and Dominguez[4] on the basis of chemical evidence. These investigators assigned a 2β-configuration to 2-bromocholestan-3-one, but Fieser and Wei-Yuan Huang[5] now regard this compound as 2α-bromocholestan-3-one, in accord with spectrographic considerations.

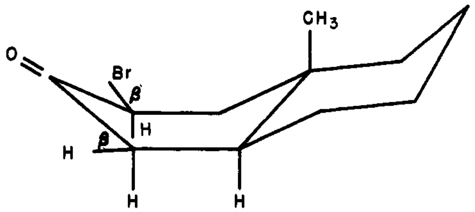
The validity of the general assumption of a chair conformation for ring A in allo-steroids has been questioned by Fieser and Dominguez.[4] In assigning the bromine configurations spectrographically this assumption was specifically made and it is the object of this note to draw attention to the fact that if 2β-bromo-3-ketoallosteroids have a boat conformation IV the C—Br bond will be coplanar with the C═O bond and the conditions for a positive carbonyl frequency shift will be satisfied. It is therefore to be anticipated that the position of the C═O stretching band will fail to distinguish between 2α-bromocholestan-3-one in the conventional chair configuration, and 2β-bromocholestan-3-one in the boat configuration IV.



I



II X = Br Y = H
III X = H Y = Br



IV

There can be little doubt that the non-halogenated 3-ketoallosteroids will possess the stabler chair structure, but in the 2β- and 4β-bromo derivatives the bromine atoms approach closely to the C_{19} angular methyl group in the chair form and repulsion between these groups may be sufficient to stabilize the boat structure.

Although at present it is not possible to differentiate between boat and chair conformations of ring A by infrared spectroscopy, the carbonyl absorption strongly suggests that these vicinal bromo-ketones must exist predominantly or exclusively in one conformation only. A labile equilibrium of the type III $\rightleftarrows$ IV should reveal itself by a broadening, asymmetry or doubling of the carbonyl band. Although such an effect has been looked for it has not been observed.

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THE NATIONAL RESEARCH COUNCIL OF CANADA
OTTAWA, CANADA

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(1) Published as Contribution No. 3060 from the Laboratories of The National Research Council of Canada.

(2) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952).

(3) E. J. Corey, *ibid.*, **75**, 2301 (1953).

(4) L. F. Fieser and X. A. Dominguez, *ibid.*, **75**, 1704 (1953).

(5) L. F. Fieser and Wei-Yuan Huang, *ibid.*, **75**, 4837 (1953).

Platinum–Olefin Compounds

BY BODIE E. DOUGLAS

RECEIVED APRIL 3, 1953

Chatt[1] and Chatt and Wilkins[2] reviewed the various structures which have been proposed for olefin coördination compounds and reasons for rejecting each of these were presented. The ob-

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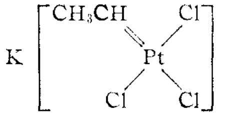
(1) J. Chatt, *J. Chem. Soc.*, 3340 (1949).

(2) J. Chatt and R. G. Wilkins, *Nature*, **165**, 859 (1950).

jections to all of the structures except the Winstein–Lucas[3] or Pitzer[4] type structures seem to be valid. In a later publication Chatt[5] proposed a new stucture and considered in detail the experimental evidence that seemed significant.

Chatt's structure necessitated the migration of a hydrogen atom from one carbon adjacent to the double bond to the other so that an ethylidene group could attach to the platinum. The platinum is pictured as sharing a pair of electrons from the carbon atom and in addition a pair of d-electrons from the platinum is shared with the carbon.



Chatt mentioned that this structure would require isomerization of *cis*-olefins during coördination to and subsequent liberation from platinum(II) salts. Anderson[6] found that a golden-yellow crystalline complex was formed between platinum(II) chloride and a compound which he stated to be presumably *trans*-2-pentene. However, unpublished results of Oppegard[7] indicate that *cis*-2-pentene gave a crystalline complex with platinum(II) chloride, while *trans*-2-pentene gave a red oil. The infrared spectra for the two complexes were also found to differ. This seems to be conclusive evidence that isomerization does not take place during coördination and that *cis*- and *trans*-olefins can form different complexes. It is known that olefins do not isomerize during reactions involving silver–olefin coördination compounds. Oppegard's results rather conclusively eliminate Chatt's structure.

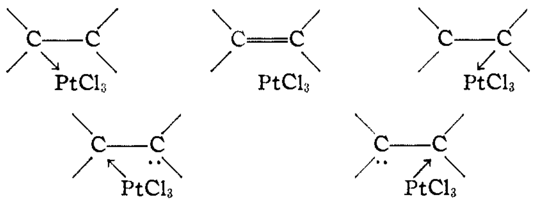
The similarity between the Winstein–Lucas structure involving resonance and Pitzer's structure involving an argentated double bond has been mentioned by others.[8,9] Bateman[8] included the platinum–olefin compounds in the group of complexes having such a structure. Chatt ruled out Pitzer's structure on the basis that the platinum has no unhybridized vacant s-orbital for bond formation. Pitzer pointed out that silver could be bonded to an olefin molecule in a manner similar to the bonding of the protons in diborane. The silver ion and the proton each have a vacant s-orbital which is non-directional and could be expected to combine into the protonated double bond type of orbitals better than directed orbitals. However, Pitzer did not rule out the possible use of directed orbitals for such bond formation.

Dr. Pitzer has clarified the interpretation of his views by a recent statement.[10]

"Because of their non-directional property, s-orbitals can be combined into the protonated double bond type of orbitals better than p- or d-orbitals. This is not to imply that it is impossible to use p- or d- or hybrid orbitals for this purpose—indeed I now feel that there is adequate evidence in favor of bridge bonds of this type.

"I believe we should use caution in assuming larger and more complex groups to be bonded to a pair of electrons in a double bond. However, I do not pretend to prescribe any particular limit and I feel it probable that a limitation to single atoms with s-orbitals available would be incorrect."

Pitzer's structure or the formulation of Winstein and Lucas seems very reasonable except that they do not offer an explanation for those properties of the platinum ethylene compounds which seem to indicate that the ethylene shares d-electrons from the platinum. Ethylene complexes resist oxidation to about the same extent as platinum(IV) compounds and are similar to the carbonyl compounds where presumably bonding involving d-electrons from the platinum also occurs. If one formulates the structure in a manner similar to the Winstein and Lucas structure for silver–olefin complexes, one can add two resonance structures which involve donation of d-electrons from the platinum to the ethylene, giving a total of five resonance structures



In this structure, the platinum could still be in the planar dsp^2-hybridized state as in the case of Chatt's structure. The ethylene could be compared to a large group such as the iodide ion and distortion of the planar arrangement might be expected to be comparable.

It seems likely that the participation of platinum as a donor would be at least partly responsible for the much greater stability of the olefin compounds of platinum as a compound with those of silver. This type of bonding also helps to maintain electrical neutrality of the atoms involved.

The ease of replacement of one olefin by another olefin or by a typical ligand such as CN^- or pyridine is difficult to explain on the basis of Chatt's structure because it involves rearrangement within the olefin molecule. Such replacement is readily understood if one adopts the suggestion made here.

Chatt mentioned that substitution in the ethylene molecule markedly weakens its tendency to coördinate except in the case of styrene which has a phenyl group conjugated with the double bond and in the case of butadiene which involves two conjugated double bonds, but does not form a chelate ring. These two exceptions were cited as support for his structure because of the expected increased stability of the ethylidene form of such compounds. These exceptions are also in accord with the structure proposed here, since a double bond conjugated with an aromatic or unsaturated system might be expected to play the dual role of electron donor and electron acceptor more readily than one in other substituted olefins.

The evidence in support of the attachment of the

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(3) S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

(4) K. S. Pitzer, *ibid.*, **67**, 1127 (1945).

(5) J. Chatt, *Research* **4**, 180 (1951).

(6) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

(7) A. Oppegard, Ph.D. Thesis, University of Illinois, 1946.

(8) L. Bateman, *Nature*, **160**, 56 (1947).

(9) A. E. A. Werner, *ibid.*, **160**, 644 (1947).

(10) K. S. Pitzer, private communication, Sept 17, 1952.

olefin by one carbon atom only is based on the decomposition of Zeise's salt to produce acetaldehyde, but no symmetrically substituted ethanes.[11] The mechanism of decomposition for a symmetrically coördinated olefin might well cause the formation of unsymmetrical products if the reaction involves attack on one carbon.

Similar resonance structures could be written for an end-on association between the olefin and the platinum, but the number of resonance structures would be smaller.

(11) J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

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α-(N-Alkylamino)-nitriles

BY LAWRENCE J. EXNER, LEO S. LUSKIN AND PETER L. DEBENNEVILLE

RECEIVED MAY 7, 1953

The preparation of α-N-substituted aminonitriles is common in the literature.[1] No extensive study of the α-N-monoalkylaminonitriles has been made, nor have preparative methods been described which involve the use of anhydrous hydrogen cyanide or those cyanhydrins which are now commercially available. Methods which utilize these common reagents have now been studied and a number of new α-N-alkylaminonitriles have been prepared. In addition physical data, which are often lacking on previous preparations of members of this series, have been obtained.

The compounds which are listed in the accompanying table, have been prepared by the reaction of amines, carbonyl compounds and hydrogen cyanide, or their equivalent combinations, usually in equimolar amounts. Thus, anhydrous hydrogen cyanide may be added as a liquid to the imine or trimer formed by the combination of amine and carbonyl compound. The addition of the amine to commercially available 50 or 70% aqueous glycolonitrile, lactonitrile or acetone cyanohydrin is a convenient and satisfactory alternative.[2] Since the reactions are exothermic, temperatures are held below about 40°. Catalysts are not required, since the amine will promote cyanohydrin formation, if this is necessary to the selected route.

The expected side-reaction of bis-cyanoalkylation is a minor one, particularly as the molecular weight of any component increases, and is of no consequence when a ketone reactant is involved. This is probably because of the much reduced basicity which obtains when one cyanoalkyl group is introduced into the amine, so that the product does not compete successfully with the more basic starting amine for the other reactants.

Lower yields in the accompanying table mainly reflect either difficulty of isolation or some decomposition on distillation at higher temperatures. The products are stable to storage, particularly at refrigerator temperatures, although some darkening may occur due to the formation of hydrogen cyanide polymers.

Experimental

The two examples illustrate the procedures used. Analysis for nitrogen was by the Kjeldahl method. Neutralization equivalents were measured by titration in acetic acid with standard perchloric acid–acetic acid.[3]

α-N-Methylaminoisobutyronitrile.—Methylamine was bubbled rapidly into acetone cyanohydrin (722 g., 8.5 moles) which was stirred and cooled to maintain the temperature between 23 and 32°. In 75 minutes, the absorp-

α-(N-ALKYLAMINO)-NITRILES

Compound	Empirical formula	Yield, %	B.p. °C.	Mm.	$n^{25}\text{D}$	d^{25}_{25}	Nitrogen, % Calcd.	Nitrogen, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
CH_3NHCH_2CN	$C_3H_6N_2$	58	65–67^a	23	1.4184	0.9171	40.0	39.5	70	72
$CH_2{=}CHCH_2NHCH_2CN$	$C_5H_8N_2$	67	74–76^b	12	1.4484	.9188	29.1	28.9	96	96
n-$C_3H_7NHCH_2CN$	$C_5H_{10}N_2$	40	65	15	1.4289	.8858	28.5	28.0	98	99
$CH_3NHCH(C_2H_5)CN$	$C_5H_{10}N_2$	91	66	15	1.4258	.8860	28.5	28.0	98	98
$CH_3NHC(CH_3)_2CN$	$C_5H_{10}N_2$	93	60^c	24	1.4174	.8600	28.5	28.1	98	99
n-$C_4H_9NHCH_2CN$	$C_6H_{12}N_2$	70	105–110^d	29	1.4311	.8818	25.0	25.1	112	114
$(CH_3)_3CNHCH_2CN$	$C_6H_{12}N_2$	71	90–99^e	22	1.4294	.8756	25.0	24.8	112	113
$CH_3NHC(CH_3)(C_2H_5)CN$	$C_6H_{12}N_2$	68	75–77^f	28	1.4270	.8698	25.0	24.6	112	112
$CH_2{=}CHCH_2NHC(CH_3)_2CN$	$C_7H_{12}N_2$	77	80–82	30	1.4393	.8766	22.6	22.3	124	125
n-$C_4H_9NHCH(CH_3)CN$	$C_7H_{14}N_2$	90	95–97	31	1.4286	.8589	22.0	21.7	126	128
Cyclohexyl $NHCH_2CN$	$C_8H_{14}N_2$	66	77–82^{d,g}	1	1.4735	.9657	20.2	20.2	138	140
n-$C_4H_9NHC(CH_3)_2CN$	$C_8H_{16}N_2$	87	86–88	28	1.4262	.8483	20.0	19.5	140	141
Cyclohexyl $NHC(CH_3)_2CN$	$C_{10}H_{18}N_2$	77	M.p. 56–57°	^{h}			16.9	16.8	166	166
n-$C_8H_{17}NHCH_2CN$	$C_{10}H_{20}N_2$	66	120–125	2	1.4425	.8611	16.7	16.2	168	170
$C_4H_9CH(C_2H_5)CH_2NHCH_2CN$	$C_{10}H_{20}N_2$	75	99–101	1.5	1.4448	.8667	16.7	16.0	168	168
1,1,3,3-$(CH_3)_4C_4H_5NHCH_2CN$	$C_{10}H_{20}N_2$	91	99–102^e	5	1.4509	.8808	16.7	16.4	168	167
3,5,5-$(CH_3)_3C_6H_{10}NHCH_2CN$	$C_{11}H_{22}N_2$	74	92	0.6	1.4453	.8561	15.4	15.5	182	182

[a] A. H. Cook and S. F. Cox, *J. Chem. Soc.*, 2334 (1949), b.p. 65° at 20 mm. [b] H. Z. Lecher and R. S. Long, Can. Pat. 477,792, b.p. 60° at 15 mm. [c] N. J. Leonard and E. Barthel, THIS JOURNAL, **72**, 3632 (1950), b.p. 54° at 18 mm., $n^{20}\text{D}$ 1.4176. [d] Mentioned but not described by N. C. Throdahl and M. W. Harman, *Ind. Eng. Chem.*, **43**, 421 (1951); Monsanto Chemical Co., Brit. pat. 640,158, b.p. 77–80° at 6 mm. [e] L. S. Luskin, *et al.*, paper in preparation. [f] Ref. *b*, b.p. 66–68° at 17 mm., $n^{21}\text{D}$ 1.4282. [g] R. A. Jeffreys and E. B. Knott, *J. Chem. Soc.*, 4632 (1952), b.p. 74–76° at 1 mm., m.p. 18°. We found m.p. 24°. [h] A. D. Ainley and W. A. Sexton, *Biochem. J.*, **43**, 468 (1948), m.p. 52–53. We recrystallized the crude solid product from Skellysolve A.

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(1) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," A.C.S. Monograph Series No. 105, Reinhold Publ. Corp., New York, N. Y., 1947, pp. 198–215.

(2) Glycolonitrile and acetone cyanohydrin are commercial products of the Rohm and Haas Co. Lactonitrile was obtained from the American Cyanamid Co.

(3) P. C. Markunas and J. A. Riddick, *Anal. Chem.*, **23**, 337 (1951).