TABLE 2—EFFECT OF C.D. ON REGENERATION OF Cr^{6+}

Sl. no.	Current A	C.d. A dm^{-2}	Cell voltage V	Reaction time (h) Theoritical	Reaction time (h) Practical	Cr^{VI} %	C.E. %
1.	0.5	7.14	3	3.1	7 0	78.3	62.9
2.	1.0	14 2	4–5	1.6	3.5	81.3	61.5
3.	1.5	21.4	3–4	1.07	5.0	93.5	71.8

The results of Table 2 indicate that with the increase in current density the conversion of Cr^{III} to Cr^{VI} also increases (max 93.5% ; C.E. 71.8%). It has been also observed in a separate experiment that when current is passed for the theoretical time (3F mol^{-1}), only 20% conversion is achieved. The procedure of regeneration appears to be important in view of the large amount of oxidant used in industries. The result obtained by the oxidation with CrO_3 are quite similar. Here also under the above condition 92% chromic acid is regenerated with 30% current efficiency.

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References

1. D. J. LEE and U. A. SPITZER, *J. Org. Chem.*, 1970, 35, 3589.
2. S. CHIDAMBARAM, M. S. V. PATHY and H. V. K. UDUPA, *Indian J. Technol.*, 1968, 6, 12 ; *Indian J. Appl. Chem.*, 1971, 34, 1.
3. Organikum", Veb Deutscher Verlag der Wissenschaften, Berlin, 1970, p. 549.
4. MOORE and DALRYMPLE, "Experimental Methods in Organic Chemistry", 2nd. ed., W. B. Saunders, Philadelphia, 1976, pp. 168-169.
5. I. HEILBRON, "Dictionary of Organic Compounds", Eyre and Spottiswoode, London, 1935.
6. A. I. VOGEL "Text Book of Quantitative Inorganic Analysis", 2nd. ed , Longmans, London, p. 336.

C-Acylation of *p*-Acetotoluidide in Presence of Polyphosphoric Acid

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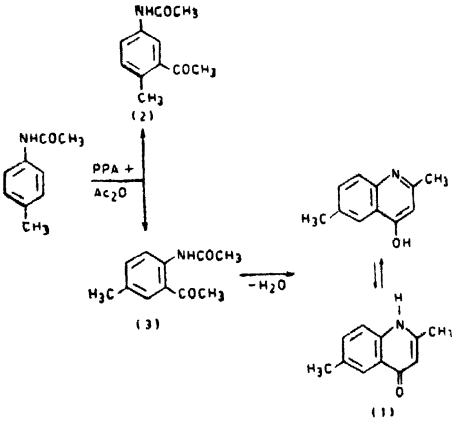
SACHA and Patel[1] carried out Friedel-Craft's acylation of different acetanilides, *p*-substitution predominating with respect to the amino group ; acylation, however, failed in case of aceto-*p*-toluidide. Desai and Desai[2] observed *N*-acyl migration in presence of polyphosphoric acid with different acetanilides in *para*-position to the amino group and also *N*-benzoyl migration. Further, in case of *p*-benzoyltoluidide, 2-hydroxy-4-phenyl-6-methylquinoline was formed, the intermediate ketone getting cyclised

In the present work, aceto-*p*-toluidide, when heated with PPA and acetic anhydride gave not only 2,6-dimethyl-4-hydroxyquinoline (1) but also two ketones, 5-acetamino-2-methylacetophenone (2) and 6-acetamino-3-methylacetophenone (3) ; the former could be easily obtained, but the latter with difficulty owing to its cyclisation into the corresponding 4-hydroxyquinoline. The formation of 2-hydroxy- or 4-hydroxy-quinoline is due to the cyclodehydration of the corresponding acetamino ketone being formed either due to benzoyl migration (loc cit) or to *C*-acylation of *p* acetotoluidide (Scheme 1).



Scheme 1

Experimental

2,6-Dimethyl-4 hydroxyquinoline : *p*-Toluidine (5 g) converted into acetotoluidide with acetic anhydride was heated with PPA (H_3PO_4, 25 ml ; P_2O_5, 40 g) at 170° for 4.5 h. After cooling, the mass was neutralised on acidic side giving precipitate, which after removal, was extracted with ethylacetate, the extract product being identified as *p*-acetotoluidide.

On basifying PPA solution, the product obtained was crystallised from ethanol, (1.510 g, 30%), m.p. 278–80° ; giving purple colouration with ferric chloride. Its mixed m p. with the authentic 2,6-dimethyl-4-hydroxyquinoline[3] prepared from *p*-toluidine and ethyl acetoacetate was found to be the same. However, its 4-chloroquinoline derivative with phosphorous oxychloride was prepared and the ir spectra of both were examined.

5-Acetamino-2-methylacetophenone : *p*-Toluidine (10 g) converted into its acetotoluidide was heated with PPA (H_3PO_4, 40 ml ; P_2O_5, 48 g) at 160° for 5 h. After treating the reaction mixture with ice-water, the filtrate (800 ml) on keeping overnight in a freezer gave a solid and crystallised from ethanol, (5.5 g, 30.8%), m.p 124° (Found : N, 7.41. $C_{11}H_{13}O_2$ calcd. : N, 7.32%) ; it could not be cyclised with PPA or Na-acetate and Ac_2O ; its oxime, m.p. 146 – 47° (Found : N, 13.10. $C_{11}H_{14}O_2N_2$ calcd. : N, 13.17%).

6-Acetamino-3-methylacetophenone : *p*-Toluidine, converted into its acetotoluidide was heated with PPA (H_3PO_4, 36 ml ; P_2O_5, 36 g) at 160° for 5 h. The turbid solution obtained after treating the reaction mass with cold water and on further cooling with ice gave a product, which was crystallised from ethanol, (2.2 g, 12%), m p. 105° (Found : N, 7.10. $C_{11}H_{13}O_2$ calcd. : N. 7.32%). It gave tests with hydroxylamine hydrochloride and 2,4-dinitrophenylhydrazine. Kohler[4] obtained a ketone (m.p. 105°) heating aceto-*p*-toluidide with acetic acid and syrupy phosphoric acid.

Ir spectra : 2,6-Dimethyl-4-hydroxyquinoline exists in tautomeric forms. Its ir spectra in solid state show band at 1 665 cm^{-1} corresponding to C=O stretch which does not appear with its 4-chloro derivative ; a weak band at 3 270 cm^{-1} due to NH stretch in keto form ; and medium bands at 2 865, 2 935 and 3 040 cm^{-1} due to C—H stretch, CH_3 group and ring CH, respectively.

For its chloro-compound, medium bands at 2 860, 2 980 and 3 040 cm^{-1} are due to C—H stretch, CH_3 groups and ring CH stretching, respectively. The C—H out-of-plane deformation in the chloroderivative is only due to one free H-atom in one ring, which absorbs very strongly at 831 cm^{-1}, corresponding to *p*-substituted aromatics. In addition, both show a second weak band at 900 – 850 cm^{-1} which may be associated with vibration of remaining ring H-atoms.

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References

1. H. J. Sacha and S. R. Patel, *J. Indian Chem. Soc.*, 1966, 33, 129, 867.
2. Kusum Desai and C. M. Desai, *Indian J. Appl Chem.*, 1970, 33, 373 ; *J. Indian Chem. Soc.*, 1971, 48, 863.
3. B. P. Bangadiwala and C. M. Desai, *J. Indian Chem. Soc*, 1953, 30, 655.
4. Kohler in "Beilstein Hand Book, Organic Chemistry", 1931, Vol. 14, p. 64.

Preparation of 2,4-Benzylidene-L-xylose

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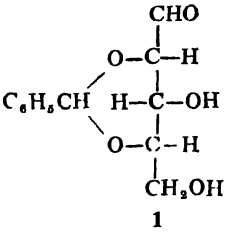
It was found by Malaprade that organic compounds containing two hydroxyl groups attached to two adjacent carbon atoms undergo a cleavage of the carbon-carbon bond when oxidised by sodium metaperiodate[1]. Another oxidising reagent which can be used is Criegee's reagent or lead tetra-acet te[2]. But in the case of carbohydrates and their derivatives sodium metaperiodate is more efficient because it is more quantitative and the yields are comparatively superior[3,4].

2,4-Benzylidene-D-sorbitol was prepared by the method of von Vargha[5], and it was then subjected to oxidative degradation with sodium metaperiodate to give 2,4-benzylidene-L-xylose (**1**).



1

Compound **1** is a starting material for the synthesis of ascorbic acid or vitamin C. This reaction can be used on a commercial scale.

Experimental

Oxidative degradation of 2,4-benzylidene-D-sorbitol to 2,4-benzylidene-L-xylose . 2 4-Benzylidene-D-sorbitol (100 g) was reacted with a solution of sodium metaperiodate (90 g) in water (1900 ml). The slight excess of sodium metaperiodate was removed with drops of glycerol. The solution was stirred for 1.5 h. It was then evaporated to a smaller volume. The resulting product was extracted with hot ethyl acetate. The extract was washed with water, dried with anhydrous sodium sulphate, and then ethyl acetate was evaporated to yield 2,4-benzylidene-L-xylose (80 g), m.p 162° (Found : C, 43.40 ; H, 8.52. $C_{12}H_{14}O_5$ calcd. for : C, 43.37 ; H, 8.43%), $[\alpha]_D$ 4.4°).

References

1. L. Malaprade, *Compt. Rend.*, 1928, 382, 186.
2. R. Criegee, *Chem. Ber* , 1931, 64, 260.
3. E. L Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, 1936, 58, 373.
4. E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, 1937, 59, 2049.
5. V. Vargha, *Chem. Ber.*, 1935, 68, 1377.