698. *Pyrylium Salts obtained by Diacylation of Olefins. Part IV.*[1] *Di- and Tri-acetylation of Allylbenzene.*

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Acetylation of allylbenzene and treatment of the reaction mixture with ammonia yields two pyridines: 2,6-dimethyl-3-phenylpyridine by diacetylation, and 3-*p*-acetylphenyl-2,6-dimethylpyridine by triacetylation. The mechanism is discussed.

IT was previously reported[2] that 2-substituted propenes such as α-methylstyrene give γ-substituted pyrylium salts by diacylation with acid chlorides in the presence of aluminium chloride. Attempts to diacylate 1- and/or 3-substituted propenes under the same conditions failed.

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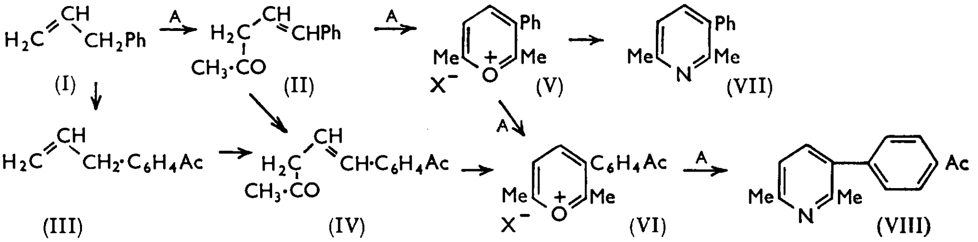
[1] Part III, preceding paper.

[2] Balaban and Nenitzescu, *Annalen*, 1959, **625**, 74.

In order to obtain 3-arylpyrylium salts for spectroscopic study * a milder acylating catalyst (perchloric acid) was tried. Introduction of 70% perchloric acid into a mixture of acetic anhydride and allylbenzene caused an energetic reaction, yielding two pyrylium salts instead of the expected one. Attempts to separate these salts by recrystallization were unsuccessful. Separation of the corresponding pyridines was, however, possible. The lower-boiling compound was the expected 2,6-dimethyl-3-phenylpyridine (VII), the other was the product (VIII) of triacetylation. The constitutions were assigned on the basis of the method of their formation and on their infrared absorption spectra which contain the characteristic bands of six-membered aromatic nuclei.[4,5]

The triacetylation product (VIII) has an intense carbonyl stretching vibration at 1696 and a further intense band at 1222 cm.$^{-1}$, both characteristic of aryl ketones.[5] The extra acetyl causes a splitting of the symmetrical and antisymmetrical methyl vibrations



in the 2850—2970 cm.$^{-1}$ region and a shift towards lower frequencies of the methyl bending vibrations in the 1350—1500 cm.$^{-1}$ region, but the ring frequencies in the latter region are unaffected. The comparative aspect of the 1660—2000 cm.$^{-1}$ region [6] indicates that the acetyl group is in the *para*-position.

Attempts to acetylate 1-phenyl- or 1,3-diphenyl-propene under the same conditions failed. Attempted acetylation of 1- and 3-phenyl-, 1,3-diphenyl-, and 2-chloro-1-phenylpropene with acetyl chloride and aluminium chloride was also unsuccessful. In the benzoylation of allylbenzene with benzoyl chloride and aluminium chloride or with benzoic anhydride and perchloric acid in nitromethane, the yields were too small to be of preparative interest.

Of the various reaction paths to the triacetylation product (VIII), the most likely seems to be that marked (A) on the chart because the conversions (I) → (II) are more probable than (I) → (III) since an olefinic double bond is usually more reactive towards electrophilic agents than is an aromatic ring. The process (II) → (V) is also more probable than (II) → (IV), for the same reason. Indeed, the pyrylium salt (V) is formed from (II) as the sole possibility. Further, the step (V) → (VI) is possible since a 3-phenyl group is not deactivated towards electrophilic substitution; 2- and 4-phenyl groups are not further acylated under these conditions: evidence is the *para*-orientation and the results obtained in nitration of triphenylpyrylium [7] and 2,3-diphenylbenzopyrylium perchlorate.[8]

While this work was in progress Praill and Whitear [9] showed that 1- and 3-alkylpropenes may be diacylated with anhydrides and perchloric acid, yielding 3-substituted pyrylium salts (similarly isolated as pyridines).

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* It was shown [3] that 2- and 4-phenyl groups exert a characteristic and different influence on the position and intensity of the ultraviolet absorption of pyrylium salts. A 3-phenyl group would be expected to contribute vectorially to these effects, namely, to behave like two-thirds of a phenyl group for the *y*-bands and one-third of a phenyl group for the *x*-bands.[3]

[3] Balaban, Sahini, and Keplinger, *Tetrahedron*, 1960, **9**, 163.

[4] Katritzky, *Quart. Rev.*, 1959, **13**, 353.

[5] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1958.

[6] Brügel, " Einführung in die Ultrarotspektroskopie," Steinkopff, Darmstadt, 1957, p. 333.

[7] Le Fèvre and Le Fèvre, *J.*, 1932, 2894.

[8] Shriner and Moffett, *J. Amer. Chem. Soc.*, 1944, **66**, 301.

[9] Praill and Whitear, *Proc. Chem. Soc.*, 1959, 312.

EXPERIMENTAL

Acetylation of Allylbenzene.—70% Perchloric acid (30 g., 0·2 mole) was cautiously added to a stirred solution of allylbenzene [10] (11·8 g., 0·1 mole) and acetic anhydride (102 g., 1·0 mole), without external cooling. At first only 1—2 ml. of acid were added and reaction was allowed to start (15—30 min.), otherwise reaction starts almost explosively. Later the remaining acid was added at such a rate as to keep the mixture refluxing. Then the mixture was stirred for 3 hr., until the temperature was that of the laboratory. Water (50 ml.) and then an excess of aqueous ammonia were added with stirring and cooling. The whole was shaken with ether (100 ml.) and the ether layer was separated, filtered from polymer if necessary, and washed with water. The basic products are extracted into N-hydrochloric acid, and then set free by aqueous alkali. The base was extracted with ether, dried (NaOH), and fractionated. This gave as first fraction 2,6-dimethyl-3-phenyl-pyridine (VII), b. p. 180—200°/80 mm. (3·5 g., 22%), that on redistillation had b. p. 185°/96 mm., n_D^{25} 1·5812, d_4^{25} 1·034, $[M_R]_D$ 59·07 (calc. 59·73, bond increments; 58·97, atomic increments), and gave a moderately soluble *chloroplatinate*, m. p. 212° (decomp.) (from dil. HCl.) (Found: C, 40·3; H, 3·8; N, 3·4; Cl, 27·0; Pt, 24·9. $C_{26}H_{28}Cl_6Pt$ requires C, 40·2; H, 3·6; N, 3·6; Cl, 27·4; Pt, 25·15%), *picrate*, m. p. 168° (from ethanol) (Found: C. 55·3; H, 3·9; N, 13·4. $C_{19}H_{16}N_4O_7$ requires C, 55·3; H, 3·9; N, 13·6%), and *picrolonate*, m. p. 182° (from ethanol) (Found: N, 15·9. $C_{23}H_{22}N_5O_5$ requires N, 15·6%). The second fraction was 3-*p*-acetylphenyl-2,6-dimethypyridine (VIII), b. p. 230—245°/80 mm. (2·1 g., 10%), that on redistillation had b. p. 243°/96 mm. and gave a slightly soluble *chloroplatinate*, m. p. 225° (decomp.) (from dil. HCl) (Found: C, 42·2; H, 4·0; N, 3·25; Cl, 24·6; Pt, 22·8. $C_{30}H_{32}Cl_6N_2O_2Pt$ requires C, 41·9; H, 3·75; N, 3·3; Cl, 24·7; Pt, 22·7%), *picrate*, m. p. 156° (from ethanol) (Found: C, 55·5; H, 4·0; N, 12·1. $C_{21}H_{18}N_4O_8$ requires C, 55·5; H, 4·0; N, 12·3%), and *picrolonate*, m. p. 197° (from ethanol) (Found: N, 14·2. $C_{25}H_{24}N_5O_6$ requires N, 14·3%).

The infrared absorption spectra, recorded for carbon disulphide and carbon tetrachloride solutions, with an automatic UR-lo spectrophotometer, were:

VII: 672w, 707s, 720m, 743m, 769s, 831s, 912w, 930w, 963w, 999m, 1011s, 1030m, 1075m, 1132m, 1158w, 1185w, 1238w, 1262m, 1369m, 1378m, 1392s, 1435s, 1443s, 1466vs, 1499m, 1513m, 1568s, 1584w, 1595vs, 1607s, 1634w, 1674w, 1688w, 1718w, 1747w, 1814w, 1890w, 1930w, 1955w, 2853w, 2922m, 2963m, 3026m, 3060m, 3082w, 3105vw.

VIII: 672m, 706s, 751m, 768m, 778s, 830m, 840w, 869w, 912m, 931m, 957vw, 984w, 1011w, 1030m, 1059m, 1074w, 1132w, 1159vw, 1195m, 1222s, 1257s, 1290m, 1357m, 1371m, 1394m, 1435m, 1445s, 1500m, 1543m, 1589w, 1596s, 1607s, 1670vw, 1696vs, 1744w, 1812w, 1890w, 1960w, 2852w, 2863w, 2875w, 2926m, 2960m, 2971m, 3002w, 3030m, 3062m, 3081w, 3108vw.

The analyses were by Misses Elvira Sliam, Violeta Sandulescu, and Maria Petcu.

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[10] Tiffeneau, *Compt. rend.*, 1904, **139**, 482; Hershberg, *Helv. Chim. Acta*, 1934, **17**, 352.