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PYRYLIUM SALTS FORMED BY DIACYLATION OF OLEFINS—XV[1]

^{14}C-TRACER STUDY OF THE ACETYLATION OF 4-CHLORO-3,4-DIMETHYL-2-PENTANONE

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Abstract—One mole 4-chloro-3,4-dimethyl-2-pentanone was acetylated with two moles labeled acetyl chloride or acetic anhydride of specific activity *a* in the presence of aluminium chloride or zinc chloride, respectively. The 2,3,4,6-tetramethylpyrylium salt formed in the latter case has a specific activity *a*, as expected, but the 2,6-dimethyl-4-ethylpyrylium salt formed in the former case has a specific activity 1·33*a*, therefore in the presence of aluminium chloride the acylation of olefins to β-chloroketones is reversible.

IN PREVIOUS papers it was shown that 2-methyl-2-butene (I, R = Me) yields on acetylation two different pyrylium salts depending on the acetylation agent: acetyl chloride in the presence of aluminium chloride or antimony pentachloride[2–4] leads only to 2,6-dimethyl-4-ethylpyrylium (II, R = Me), while in the presence of beryllium chloride only 2,3,4,6-tetramethylpyrylium (III, R = Me) is obtained;[5] acetyl chloride in the presence of zinc chloride, iron trichloride or tin tetrachloride,[3,4] or acetic anhydride in the presence of boron fluoride, sulphuric acid[3,4] or perchloric acid[3,4,6] lead to mixtures in which the tetramethylpyrylium salt prevails. This behaviour is paralleled by other olefins, e.g. 2-methylpropenylbenzene (I, R = Ph), which affords 2,6-dimethyl-4-benzylpyrylium (II, R = Ph) on treatment with acetyl chloride and aluminium chloride, but 2,4,6-trimethyl-3-phenylpyrylium (III, R = Ph) on treatment with acetic anhydride and perchloric acid.[7] However, diisobutylene (I, R = tBu) yields only 2,6,-dimethyl-4-neopentylpyrylium (II, R = tBu) irrespective of the acetylating agent,[8,9] probably because the isomeric salt (III, R = tBu) would be sterically hindered. The acyl residue also influences the course of the reaction, since on propionylation or benzoylation, 2-methyl-2-butene[2,4] and 2-methylpropenyl-benzene[7] yield pyrylium salts related to III, even in the presence of aluminium chloride.

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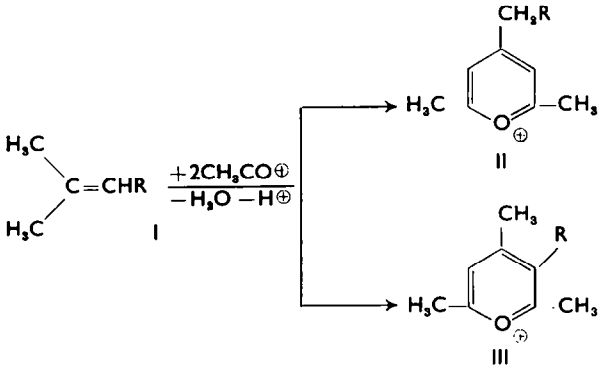
[1] Part XIV, D. Fărcaşiu, M. Fărcaşiu and A. T. Balaban, *Rev. Roumaine Chim.* **9**, 137 (1964).
[2] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann.*, **625**, 74 (1959).
[3] A. T. Balaban and C. D. Nenitzescu, *Tetrahedron Letters* No. 2, 7 (1960).
[4] A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.* 3553 (1961).
[5] A. T. Balaban, E. Barabas and M. Fărcaşiu, *Chem. & Ind.* 781 (1962).
[6] P. F. G. Praill and A. L. Whitear, *J. Chem. Soc.* 3573 (1961).
[7] A. T. Balaban, *Tetrahedron Letters* No. 91 (1963).
[8] A. T. Balaban, A. Ghenea and C. D. Nenitzescu, *Izvestia Akad. Nauk SSSR, Otdel. khim. Nauk* 1102 (1961).
[9] A. T. Balaban, G. R. Bedford and A. R. Katritzky, *J. Chem. Soc.* In press (1964).



The detailed scheme showing all possible pathways of the reaction is more complex. In this scheme the cations V and VI may add a nucleophilic reagent $X^{\ominus}$ such as $Cl^{\ominus}$ or may split a proton bonded to a carbon atom in beta position relative to the positive charge. The conjugated enones XII and XV are no longer electrophilic, but the unconjugated β,γ-enones (XIII, XIV or XVI) can undergo a second electrophilic acylation. As argued by Praill and Saville,[10] the β-proton splitting is an intramolecular process assisted by the carbonyl group, leading to ions of the enols (VIII, IX and X) and favouring the formation of β,γ-enones over that of α,β-enones (the acylation of these enols could also be involved in the reaction, i.e. pathways I → IV → VI → X → II and I → V → VIII → III, but this was not considered in the following scheme because it seems more likely that unconjugated ketones are intermediates in the reaction[2,6]).

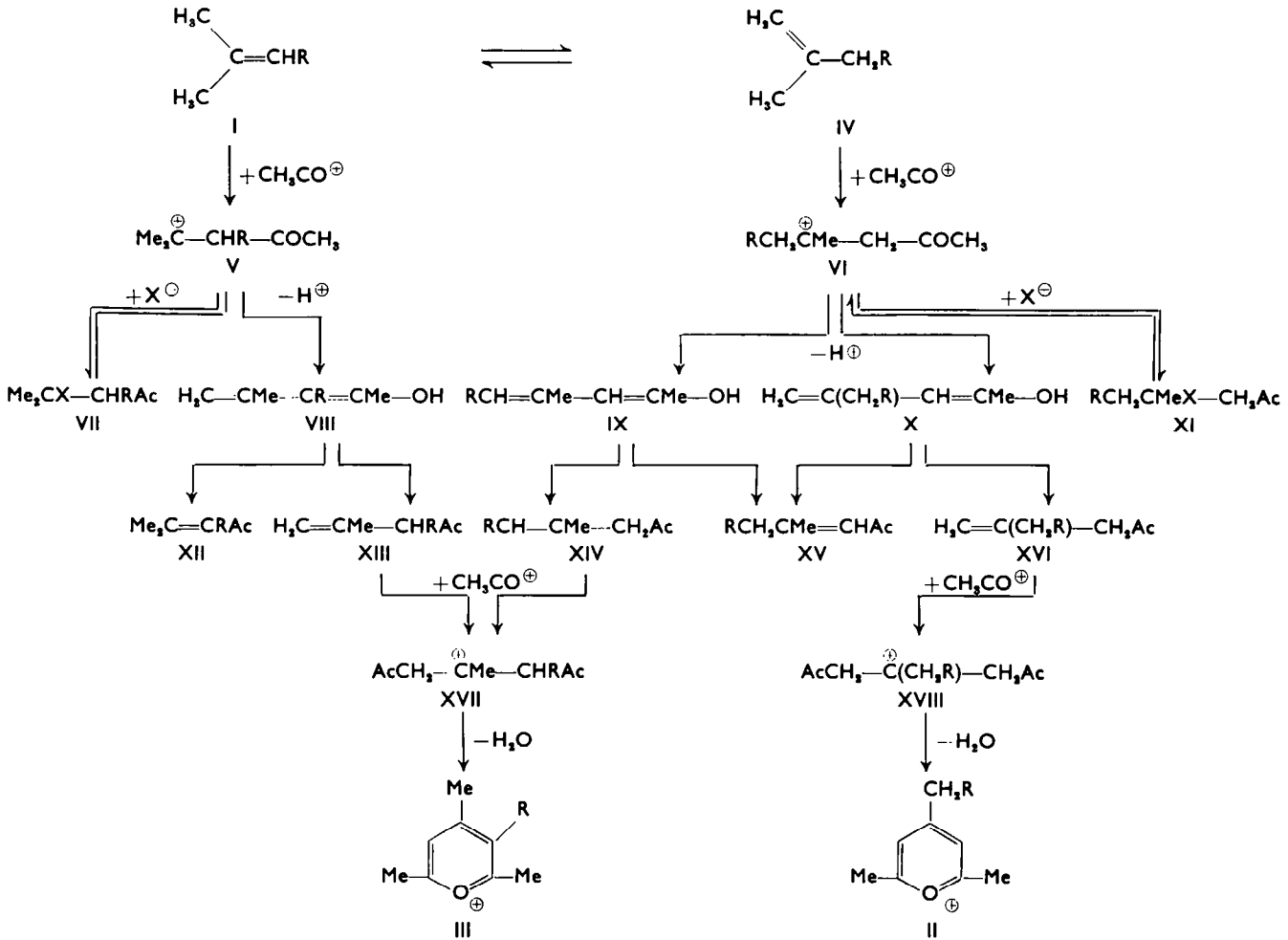
In a preliminary note, Baddeley and Khayat[11] stated that 4-chloro-3,4-dimethyl-2-pentanone (VII, R = Me, X = Cl) afforded only dimethylethylpyrylium (II, R = Me) on acetylation in the presence of $AlCl_3$, but only tetramethylpyrylium in the presence of $ZnCl_2$; and that 3,4-dimethyl-3-penten-2-one (XII, R = Me) afforded only tetramethylpyrylium in the presence of either $AlCl_3$ or $ZnCl_2$. In the preceding part of this series[1] we investigated in detail the acetylation with AcCl or Ac_2O of VII (R = Me, X = Cl), VII (R = Me, X = OH), XII (R = Me), XV (R = Me), and XI (R = Me, X = Cl) in the presence of $AlCl_3$, $ZnCl_2$ or $HClO_4$. The statements of Baddeley and Khayat are correct provided that *mostly* replaces *only*.

In order to gain more insight into the mechanism of this interesting reaction, we studied the acetylation with labeled acetylating agent, of 4-chloro-3,4-dimethyl-2-pentanone (VII, R = Me, X = Cl) in the presence of $AlCl_3$ or $ZnCl_2$. By employing an acetylating agent of known specific activity a and by measuring the specific activity of the pyrylium salts (II and III, R = Me) formed in the reaction, an information about the pathway from VII to II and III ought to be obtained.

In order to obtain the high degree of accuracy in the measurement of specific activities required by the present study, all radioactive measurements were performed in strictly similar conditions, by converting the substances to be measured into the same chemical compounds. Thus the molar specific activity a of AcCl was determined by measuring the specific activities $2a$ of the pyrylium perchlorate and tetrachloroferrate formed in the reaction with 2-methyl-2-butene in the presence of $AlCl_3$. Then

[10] P. F. G. Praill and B. Saville, *Chem. & Ind.* 45 (1960).

[11] G. Baddeley and M. A. R. Khayat, *Proc. Chem. Soc.* 382 (1961).


H3C
C=CHR
H3C
I
+CH3CO⊕
Me2C⊕—CHR—COCH3
V
+X⊖
−H⊕
Me2CX—CHRAc
VII
H2C—CMe—CR=CMe—OH
VIII
Me2C=CRAc
XII
H2C=CMe—CHRAc
XIII
+CH3CO⊕
AcCH2—C⊕Me—CHRAc
XVII
−H2O
Me
R
Me
Me
O⊕
III
H3C
C—CH2R
H3C
IV
+CH3CO⊕
RCH2C⊕Me—CH2—COCH3
VI
+X⊖
−H⊕
RCH=CMe—CH=CMe—OH
IX
H2C=C(CH2R)—CH=CMe—OH
X
RCH2CMeX—CH2Ac
XI
RCH—CMe—CH2Ac
XIV
RCH2CMe=CHAc
XV
H2C=C(CH2R)—CH2Ac
XVI
+CH3CO⊕
AcCH2—C⊕(CH2R)—CH2Ac
XVIII
−H2O
CH2R
Me
Me
O⊕
II

the corresponding salts formed in the reaction between one mole of 4-chloro-3,4-dimethyl-2-pentanone and two moles of active AcCl in the presence of $AlCl_3$ and $ZnCl_2$ were obtained, and their activities were measured in the same conditions as above. Each reaction was performed twice and the reaction product was purified separately. At least two solutions from each reaction product were prepared for radioactive measurements. As seen in the experimental part, excellent reproducibility was secured.

EXPERIMENTAL

Acetyl chloride 1-^{14}C was obtained[12,13] (first batch, specific activity a_1) by distilling a mixture of benzoyl chloride (2 moles), acetic acid 1-^{14}C (1·2 ml, specific activity 8·2 mc/ml) and unlabeled 100% acetic acid (0·5 mole), then adding a further portion of acetic acid (0·5 mole) and distilling again. The distillate was then fractionated, keeping the fraction with b.p. 51–52°. In a second batch (specific activity a_2) after the distillation, AcCl was twice added in the distillation flask and distilled over in order to make the entrainment as complete as possible.

2-Methyl-2-butene (I, R = Me) was prepared from fractionated t-pentyl alcohol (b.p. 101°) and H_2SO_4;[14] it had b.p. 38·5°.

4-Chloro-3,4-dimethyl-2-pentanone (VII, R = Me, X = Cl) was prepared by introducing at −15° 2 moles of $AlCl_3$ into a solution of 2·5 moles AcCl and 2·5 moles t-pentyl chloride (prepared from fractionated t-pentanol and HClaq).[15] The mixture was hydrolysed with ice and HCl aq, extracted with ether, dried over $MgSO_4$ and fractionated, b.p. 62°/9 Torr. The purity of the product was checked by IR spectroscopy and elementary analysis.

Acetylation of 2-methyl-2-butene in the presence of aluminium chloride. In order to measure the molar specific activity *a* of AcCl, this was converted by reaction with 2-methyl-2-butene into the pyrylium salt (II, R = Me) which irrespective of the amounts of reagents taken must possess a molar specific activity 2*a*. A procedure similar to that described previously[13] was employed.

In a flask equipped with stirrer, immersed thermometer dropping funnel, side-neck for the introduction of hygroscopic solids from a small test-tube, and exit protected by a $CaCl_2$-tube, $AlCl_3$ (13·3 g, 0·1 moles) was added gradually into 20 ml (0·28 moles) AcCl-1-^{14}C cooled at −15°, then 2-methyl-2-butene (8 ml, 71 mmole) was added dropwise at −10–0°. After stirring for 0·5 hr at 0°, and for 2 hr at room temp, the mixture was left overnight. After hydrolysis with 40 g ice and 4 ml conc. HCl, the aqueous layer was extracted with ether, treated with $HClO_4$, and kept 1 hr at 0°. The 2,6-dimethyl-4-ethylpyrylium-2,6-$^{14}C_2$ perchlorate (II, R = Me) was filtered off, washed with ether, and recrystallized twice from water acidified with $HClO_4$ in the presence of charcoal; the m.p. of the pure product is 189°.[3,4] This is the standard in radioactive measurements for acetylations in the presence of $AlCl_3$ (specific activity of the perchlorate 2*a*).

Acetylations in the presence of $ZnCl_2$ yield a mixture of pyrylium salts in which the 2,3,4,6-tetramethylpyrylium salt (III, R = Me) prevails. Since its perchlorate is too soluble in water, the chloroferrate must be employed; therefore, as a standard the chloroferrate (II, R = Me) was prepared from the previous perchlorate. The purified perchlorate (1·5 g) was dissolved in 8 ml conc. HCl at temps lower than 40°, then a saturated solution of $FeCl_3$ in conc. HCl was added. After cooling, the chloroferrate was filtered off on a sintered glass funnel and washed thoroughly with conc. HCl, and then recrystallized by dissolving it in water slightly acidified with HCl at temp lower than 40° in the presence of charcoal, filtering, and acidifying in the cold with conc. HCl; the m.p. of the pure chloroferrate (II, R = Me) is 45°[4] (specific activity of the chloroferrate 2*a*).

Acetylation of 4-chloro-3,4-dimethyl-2-pentanone in the presence of aluminium chloride. Since the specific activity of the product may depend on the amounts of reagents, these were measured precisely. Into 9·0 ml (131 mmoles) labelled AcCl, 7·6 g (66 mmoles) $AlCl_3$ was introduced at −10–0°, then 9·7 ml chloroketone (VII, R = Me, X = Cl) was added dropwise. Then the preceding procedure was followed and the perchlorate was obtained and purified for the radioactive measurement.

[12] H. C. Brown, *J. Amer. Chem. Soc.* **60**, 1325 (1938).
[13] A. T. Balaban, M. Mărculescu-Frangopol and P. T. Frangopol, *Isotopentechnik* **2**, 235 (1962).
[14] A. I. Vogel, *A Textbook of Practical Organic Chemistry* p. 239. Longmans Green, New York (1956).
[15] J. F. Norris and A. W. Olmsted, *Organic Syntheses* Coll. Vol. I, 144 (1941).

Acetylation of 4-chloro-4-methyl-2-pentanone in the presence of zinc chloride. Into 9·0 ml (131 mmoles) labelled AcCl cooled at −15°, 8·9 g (66 mmoles) anhydrous $ZnCl_2$ were added, then the chloroketone at −10°–0°. After stirring for 0·5 hr at 0°, and for 2 hr at room temp, the mixture was left overnight, and next day hydrolysed by pouring it into 60 ml conc. HCl cooled at −15°. The solution was shaken with 50 ml ether, separated after standing 1 hr in the separatory funnel, and the aqueous layer was treated with a saturated $FeCl_3$ aq in conc. HCl. The chloroferrate was filtered off and purified as above for the radioactive measurement. The m.p. of the pure 2,3,4,6-tetramethylpyrylium chloroferrate (III, R = Me) is 115°.[4*]

Radioactive measurements.[16] A windowless flowcounter of type COT-25-БФЛ[17a] working in the Geiger–Müller range was used, which allows the detection of activities as low as 10^{-10}c. A mixture of absolute ethanol (96% vol) and anhydrous ethyl ether (4% vol) kept at 0°, through which a continuous flow of He or of A passed (flow rate 5–10 bubbles per second or ca. 1 l/hr), gave the flow-gas. The starting voltage was 1500 V for He or 1800 V for A as carrier gas; a voltage of ca. 1800 and 1900 V, respectively, was employed in the measurements; the counter presents a plateau of 200–400 V with a slope of 1·5% and has a dead time of 200–400 μs.

Solid samples were measured. They were deposited on plexi trays with 18 mm diameter and 1·5 mm thickness from aqueous solutions by evaporation under IR lamps. All samples were checked visually for identity of the area and distribution of the solid deposits. The concentration of the solutions was the maximum possible so that 0·01 ml solution spread on an area with 4 mm diameter should still give very small autoabsorption, i.e.[18] less than 0·2 mg/cm^2.

Weighed amounts (m = 0·025 or 0·035 g) of carefully purified and dried pyrylium salts (chloroferrate or perchlorate, respectively) were dissolved in two calibrated flasks of V = 10 and 15 ml in distilled water acidified with 1 drop HCl aq. With a micropipette, volumes v = 0·01 ml from each of the 2 solutions were deposited in the centres of 10 plexi trays. After drying and visual inspection, 6 faultless samples were measured. The time required for measurements was determined by means of the equation[17b]

$$t = [1 + 2F/(Q - F)]/(Q - F)\varepsilon^2$$

where the standard relative error ε was taken 0·03, and the background F (ca. 40 cpm) and sample Q (ca. 800 cpm) count rates were determined by preliminary measurements.† Background count rates were measured in the presence of the clean numbered plexi trays, with counting times 5 min. Every sample was counted 10 times, and the results for one sample were screened by means of Chauvenet's criterion.[19] The remaining determinations yielded an average value for one sample. The Chauvenet criterion was again applied to the 6 samples from the same solution; the remaining data yielded an average value from which the background was subtracted, giving the average activity P (counts/min). This was converted into the specific activity A (counts/min/mole) by the equation A = MPV/mv, where M is the mol wt of the chloroferrate (335) and perchlorate (236·5), respectively.

DISCUSSION OF THE RESULTS

Results of radioactive measurements are presented in Tables 1 and 2. It may be seen from Table 1 that the results are reproducible and that autoabsorption in the samples only slightly influences the results (the specific activities of the more concentrated solutions from 10 ml-calibrated flasks are consistently a little lower than those of less concentrated solutions from 15 ml-flasks; somewhat larger differences

* In reference 4 the m.p. is erroneously printed as 155° instead of 115°.

† The abbreviations cpm (counts/min) and cpmm (counts/min. mole) will be used.

[16] A. Genunche, *Bibliography of* ^{14}C-*Measurements*, IFA/CO/21, Acad. RPR, Institute of Atomic Physics, Bucharest (1962).

[17] An. N. Nesmeyanov, V. I. Baranov, K. B. Zaborenko, N. P. Rudenko and Yu. A. Priselkov, *Prakticheskoe rukovodstvo po radiokhimii*. Goskhimizdat, Moscow, [a] Vol. 2, p. 46 (1961); [b] Vol. 1, p. 139 (1956).

[18] M. Calvin, C. Heidelberger, J. Reid and B. Tolbert, *Isotopic Carbon*, p. 31, J. Wiley, New York (1949).

[19] A. G. Worthing and J. Geffner, *Treatment of Experimental Data* p. 170, J. Wiley, New York (1948).

TABLE 1. ACTIVITY MEASUREMENTS OF 2,6-DIMETHYL-4-ETHYLPYRYLIUM PERCHLORATES*

	Standard of activity $2a_1$				Product obtained from one mole (VII, R = Me, X = Cl) and two moles AcCl in the presence of $AlCl_3$			
Preparation	1		2		1		2	
Substance dissolved m, mg	36·4	36·0	36·3	36·2	37·0	36·5	35·9	36·6
Calibrated flask V, ml	10	15	10	15	10	15	10	15
Average activity P, cpm	768	509	760	512	483	360	461	358
Error $\pm$ ΔP, cpm	28·9	23·5	28·6	24·2	23·2	20·4	22·6	20·6
Specific activity, 10^{-7} A, cpmm	499	501	495	503	308	349	304	346
Error $\pm$ 10^{-7} ΔA, cpmm	18	23	18	23	14	19	14	20
Average specific activity, 10^{-7} A, cpmm	500 $\pm$ 20		499 $\pm$ 20		328 $\pm$ 17		325 $\pm$ 17	
	$2a_1 = 499 \pm 20$				$326 \pm 17 = (1{\cdot}31 \pm 0{\cdot}07)a_1$			

* Counting time 1 min, samples of v = 0·01 ml.

TABLE 2. ACTIVITY MEASUREMENTS OF PYRYLIUM CHLOROFERRATES*

	2,6-Dimethyl-4-ethylpyrylium tetrachloroferrate, standard of activity $2a_2$†		2,3,4,6-Tetramethylpyrylium tetrachloroferrate obtained from one mole (VII, R = Me, X = Cl) and two moles AcCl in the presence of $ZnCl_2$	
Preparation	1	2	1	2
Substance dissolved m, mg	24·85	25·2	24·9	25·05
Calibrated flask V, ml	10	10	10	10
Average activity P, cpm	290·6	295	139·7	142·6
Error $\pm$ ΔP, cpm	7·96	7·99	5·80	6·04
Specific activity, 10^{-7} A, cpmm	392	392	187	191
Error $\pm$ 10^{-7} ΔA, cpmm	10	10	8	8
Average specific activity, 10^{-7} A, cpmm	$2a_2 = 392 \pm 10$		$189 \pm 8 = (0{\cdot}96 \pm 0{\cdot}05)a_2$	

* Counting time 5 min; samples of v = 0·01 ml.

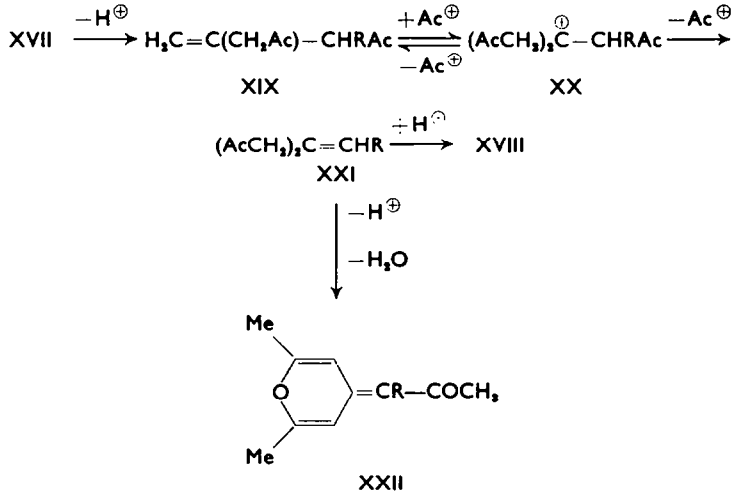
† The average specific activity of the perchlorate from which this chloroferrate was prepared was $(406 \pm 19)10^7$ cpmm.

are observed with the product than with the standard). In Table 2 only results with 10 ml-calibrated flasks are included; the average specific activity of the standard is influenced by the anion, probably also owing to autoabsorption in the sample. As seen from Table 1 perchlorate II (R = Me) formed from one mole chloroketone VII, (R = Me, X = Cl) and two moles of labeled AcCl (with specific activity a activity units per mole) in the presence of $AlCl_3$ has an average specific activity $(1{\cdot}31 \pm 0{\cdot}07)a$ (i.e. $4a/3$); hence from the two acetyl groups which lead to II, two thirds originate in the AcCl and one third in the chloroketone. On the other hand, as seen from Table 2, chloroferrate III (R = Me) formed from the same reagents in the presence of $ZnCl_2$ has an average specific activity $(0{\cdot}96 \pm 0{\cdot}05)a$ (i.e. a), showing that this salt is formed simply from the chloroketone and one mole of AcCl (pathway VII → V → VIII → XIII → III).

Three explanations have been hitherto considered for the effect of the catalyst on the structure of the pyrylium salt obtained in the diacetylation of 2-methyl-2-butene.

1. The interconversion of the cations II and III under the influence of strong Lewis acids (kinetic *versus* thermodynamic control of the reaction). Such an interconversion could not be evidenced.[4] Should such a process be involved, the specific activities of the two salts ought to be identical, and equal to *a*.

2. Since it was shown that 2-methyl-2-butene can be triacetylated in the presence of strong Friedel–Crafts catalysts such as $AlCl_3$,[20] it could be supposed that the formation of II involves triacylation to XX followed by deacylation.



Attempts to evidence deacetylation of the vinylogous pyrone XXII (R = H) or to convert pyrylium salts II and III into one another or into XXII under the influence of $AlCl_3$ and AcCl failed. Should such a process be involved, the specific activity of III should be *a*, but that of II should be 2*a*.

Since both the chemical methods, and the present tracer study disproved these two explanations, they may be rejected.

3. The explanation which is in satisfactory agreement with the known experimental data rests on the assumption that the rates of isomerization of the two olefins I and IV, and of their acylation, depend on the nature of the acylating agent, i.e. of the acyl group and catalyst. In the presence of strong catalysts the equilibrium I $\rightleftharpoons$ IV is so rapidly established that practically only IV with a more reactive marginal methylene group reacts; when R is a bulky group such as t-Bu, (I) can no longer react, but (IV) is not sterically hindered. In both these cases only II is formed. When, on the other hand, weaker catalysts are employed, the isomerization I → IV is no longer rapid relatively to the acylation so that I is being acylated. In the presence of the stronger catalysts the course of the acetylation of 2-methyl-2-butene is I → IV → X → XVI → XVIII → II, because IV reacts more rapidly than I, and XVI than XIV; in the presence of the weak catalysts the course of the reaction is I → V → VIII → XIII → XVII → III; with catalysts of intermediate strength the equilibration I $\rightleftharpoons$ IV is not rapid enough to allow the olefin IV to react exclusively, so that both pathways are involved leading to mixtures of II and III. Although in the schemes the acylating agent was represented for brevity as an acetyl cation, this is not generally true. It seems that polarized donor-acceptor complexes formed by the weaker

[20] A. T. Balaban, P. T. Frangopol, A. R. Katritzky and C. D. Nenitzescu, *J. Chem. Soc.* 3889 (1962).

catalysts or by acyl groups larger than acetyl (cf. propionyl and benzoyl hexachloroantimonates[21]) react preferentially with I leading to III, while the easier polarizable IV is more susceptible to attack by ionic complexes.

Cation V may undergo a β-splitting of the acetyl group leading to I, i.e. the acylation I $\rightleftharpoons$ V $\rightleftharpoons$ VII is *reversible* (other examples of reversible aliphatic acylation may be found in Ref. 11 and 22). By starting from VII instead of I, in the presence of weak catalysts, such as $ZnCl_2$, the reaction proceeds normally by the second pathway, i.e. VII $\rightarrow$ V $\rightarrow$ VIII $\rightarrow$ XIII $\rightarrow$ XVII $\rightarrow$ III and must lead to a specific activity a of III; however, in the presence of strong catalysts such as $AlCl_3$, the first pathway is followed; the specific activity of the product II from two moles acetyl chloride of specific activity a and one mole inactive VII must be $2(2a/3) = 4a/3$ because the acetyl group of VII becomes equivalent to the AcCl in the deacylation process. Previous studies[1,11] showed that unsaturated ketones such as XII cannot undergo deacylation as easily as haloketones VII.

The present results constitute a direct proof of the reversibility of the aliphatic acylation and imply that in the presence of $AlCl_3$ rapid equilibria VII $\rightleftharpoons$ I $\rightleftharpoons$ IV are established, while with $ZnCl_2$ the deacylation is either impossible or very slow relatively to the formation of III.

Further tracer studies concerning the reversibility of the acylation of olefins, and the investigation of the acylation of 1-phenyl-2-methyl-1-butene which may yield three different pyrylium salts are in progress. A more detailed mathematical treatment of the data from Ref. 1 and from the present paper will be published in *Rev. Roumaine Chim.*

[21] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, *J. Amer. Chem. Soc.* **84**, 2733 (1962).

[22] C. D. Nenitzescu and A. T. Balaban, in *Friedel-Crafts and Related Reactions* (Edited by G. A. Olah) Chap. 37; Vol. 3. Interscience, New York (1964).