697. *Pyrylium Salts obtained by Diacylation of Olefins. Part III.* Diacylation of Cyclic Olefins and a Novel Synthesis of Isoquinoline Derivatives.*

By A. T. Balaban and C. D. Nenitzescu.

Methylenecycloalkanes (I; $n = 3$ and 4) are readily bisacylated, yielding pyrylium salts (IX) which may be converted into pyridines (X). The endocyclic isomers, 1-methylcycloalkenes (V; $n = 3$ and 4), give poor results. The pyridines thus prepared are either tetrahydroisoquinolines (X; $n = 4$) which may be dehydrogenated to 1,3-disubstituted isoquinolines, or are cyclopenta[*c*]pyridines (X; $n = 3$) which can be used as intermediates in the preparation of pseudoazulenes (XI).

In Part I[1] it was mentioned that the cyclic olefins 1-methylcyclohexene, 1-methylcyclopentene, and methylenecyclopentene, as well as methylenecyclohexane, failed to yield pyrylium salts on diacetylation with acetyl chloride in the presence of aluminium chloride. We now report that this failure was due to the small yield and the high solubility of the pyrylium perchlorate. We have now obtained sparingly soluble phenyl-substituted pyrylium perchlorates by dibenzoylation of cyclic olefins with benzoyl chloride and aluminium chloride. Pyrylium salts formed by diacetylation or dipropionylation can be identified by conversion into the corresponding pyridines.

Higher yields are obtained when acid anhydrides and perchloric acid are used in place of acid chlorides and aluminium chloride. Methylenecycloalkanes (I) give far higher yields than their endocyclic isomers, 1-methylcycloalkenes (V), which react more violently and yield polymers almost exclusively; the cyclopentene derivatives react more rapidly and yield more polymer than do the cyclohexene derivatives.

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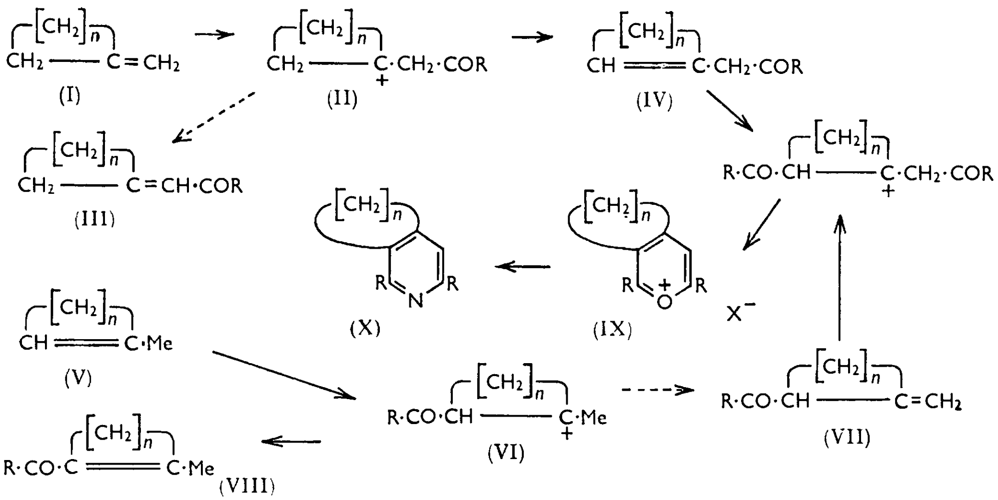
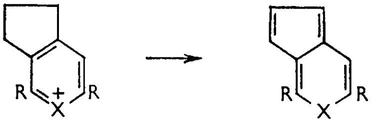
* Part II, preceding paper. Part I is considered to be a paper by Balaban and Nenitzescu, *Annalen*, 1959, **625**, 74.

[1] Turner and Garner, *J. Amer. Chem. Soc.*, 1957, **79**, 253, and references therein.

The superiority of methylenecycloalkenes over 1-methylcycloalkenes may depend on the relative stability of the endocyclic and exocyclic double bonds.[1] It is evident from the reaction scheme ($n = 3$ or 4) that the compound (IV) will be preferentially formed from the ion (II), and the isomer (VIII) from the ion (VI). The former product can be acylated further, but not the latter, which has a double bond conjugated to a ketone group. This explains why methylenecycloalkenes give far higher yields than 1-methylcycloalkenes. Of course, the conjugated ketones (III) and (VIII) will be more stable than their unconjugated isomers (IV) and (VII), but the rate of formation of the βγ-olefinic ketones can be high owing to intramolecular hydrogen transfer through a cyclic transition state of the ions (II) and (VI), as shown by Praill and Saville.[2]



The greater reactivity of cyclopentane than of cyclohexane derivatives is explained by the conformation change in passing from the olefin (I) to the ion (II) or from (V) to (VI). In these processes eclipsing is enhanced for cyclohexane derivatives and reduced for cyclopentane derivatives. This should lead to a smaller activation energy for the cyclopentane derivatives.


(XI) (X=O or N·Alk)

The pyrylium salts (IX; R = Ph, $n = 3$ and 4) and pyridines (X; R = Me and Et, $n = 3$ and 4) were thus prepared. The cyclohexane derivatives ($n = 4$) are the previously unknown *Bz*-tetrahydro-2-benzopyrylium salts, or the otherwise difficultly accessible *Bz*-tetrahydroisoquinolines. The compound (X; R = Me, $n = 4$) was catalytically dehydrogenated to the known 1,3-dimethylisoquinoline. The cyclopentane derivatives also are otherwise difficultly accessible, and the respective pyrylium or *N*-alkylpyridinium salts may be dehydrogenated [4] to pseudoazulenes [3] (XI).

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[2] Praill and Saville, *Chem. and Ind.*, 1960, 495.

[3] Boyd, *J.*, 1958, 1978; 1959, 55; Treibs and Kempter, *Chem. Ber.*, 1959, **92**, 601; Treibs and Schroth, *Angew. Chem.*, 1959, **71**, 71; Anderson, Harrison, Anderson, and Osborne, *J. Amer. Chem. Soc.*, 1959, **81**, 1255; Mayer, *Naturwiss.*, 1956, **13**, 312; *Angew. Chem.*, 1957, **69**, 481.

[4] Shemyakin and Trakhtenberg, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 763; Trakhtenberg and Shemyakin, *J. Gen. Chem.* (*U.R.S.S.*), 1943, **13**, 477.

EXPERIMENTAL

(A) *General Procedure for Diacylation with Carboxylic Anhydrides and Perchloric Acid.*—To a solution of olefin (1 mol.) in the anhydride (10 mol.), perchloric acid (70%) (2 mol.) was added drop-wise, without cooling, at *ca.* 100° with stirring and use of a large-bore condenser. The initial reaction is very vigorous and may be slow in starting. The mixture was stirred for a further 3 hr., then chilled and treated successively with water, an excess of ammonia, and ether. The ether layer (filtered if necessary) was washed with water and extracted with 2N-hydrochloric acid. Non-basic products from the aqueous acid layer were extracted with ether, and an excess of aqueous alkali then added. The pyridine was isolated by means of ether, dried (NaOH), and distilled.

(B) *General Procedure for Diacylation with Acid Chlorides and Aluminium Chloride.*—The complex $R{\cdot}COCl,AlCl_3$ was prepared by addition, with cooling and stirring, of aluminium chloride (2 mol.) to the acid chloride (3—5 mol.). Then the olefin (1 mol.) was gradually introduced at 0—5°; the mixture was stirred for 5 hr. and left overnight. After hydrolysis with ice and hydrochloric acid and extraction with ether, the aqueous layer was treated with perchloric acid, the pyrylium perchlorate crystallizing.

M. p.s and analyses of *salts* of the pyridine derivatives are presented in Tables 1 and 2.

TABLE 1. *Melting points and analyses of chloroplatinates.*[a]

				Found (%), above. Required (%)				
No.	Compound	M. p.	Formula	C	H	N	Cl	Pt
1	5,6,7,8-Tetrahydro-1,3-dimethylisoquinoline	225°	$C_{22}H_{32}Cl_6N_2Pt$	36·4	4·2	3·8	28·5	26·7
				36·1	4·4	3·8	29·1	26·7
2	1,3-Dimethylisoquinoline[b]	255	$C_{22}H_{24}Cl_6N_2Pt$	35·4	3·7	4·1	29·0	25·8
				36·5	3·3	3·9	29·4	26·9
3	1,3-Diethyl-5,6,7,8-tetrahydroisoquinoline	200	$C_{26}H_{40}Cl_6N_2Pt$	39·9	5·3	3·8	27·3	24·6
				39·6	5·1	3·6	27·0	24·8
4	6,7-Dihydro-1,3-dimethyl-5*H*-cyclopenta-[c]-pyridine	211	$C_{20}H_{28}Cl_6N_2Pt$	34·0	4·2	4·2	29·4	27·6
				34·1	4·0	4·0	30·2	27·7
5	1,3-Diethyl-6,7-dihydro-5*H*-cyclopenta-[c]pyridine	197—198	$C_{24}H_{36}Cl_6N_2Pt$	38·1	4·8	3·9	28·2	25·7
				37·9	4·8	3·7	28·0	25·7

[a] Recrystallized from 1% hydrochloric acid. [b] All the derivatives were less soluble than the corresponding tetrahydro-derivatives.

5,6,7,8-*Tetrahydro*-1,3-*dimethylisoquinoline.*—Methylenecyclohexane, prepared from cyclohexanone, cyanoacetic acid, and piperidine,[4] with subsequent alkaline hydrolysis,[5] and thermal decarboxylation,[5,6] with acetic anhydride and perchloric acid (method A) yielded the pyridine smoothly (25% yield), b. p. 170—174°/40 mm., 248—249°/760 mm. By method B the yield was only 10%. 1-Methylcyclohexene yielded the same product (method A) in a yield of only 3%. The *methiodide* had m. p. 145—147° (from ethanol–ether) (Found: N, 4·7. $C_{12}H_{18}IN$ requires N, 4·6%).

1,3-Dimethylisoquinoline was prepared by dehydrogenation at the b. p. for 5 hr. in the presence of 30% palladium–charcoal. The sulphate had m. p. 241° (from ethanol) [lit.,[7] m. p. 242—243° (corr.)] (Found: N, 5·2. Calc. for $C_{11}H_{13}NO_4S$: N, 5·5%), the *methiodide* m. p. 246° (from ethanol) (Found: N, 4·9. $C_{12}H_{14}IN$ requires N, 4·7%), and the *methoperchlorate* m. p. 232° (decomp.) (from water) (Found: C, 52·9; H, 5·2; N, 5·2. $C_{12}H_{14}ClNO_4$ requires C, 53·0; H, 5·2; N, 5·2%).

5,6,7,8-Tetrahydro-1,3-diethylisoquinoline, b. p. 189°/100 mm., was prepared analogously from methylenecyclohexane and propionic anhydride (procedure A) in 22% yield.

5,6,7,8-*Tetrahydro*-1,3-*diphenyl*-2-*benzopyrylium Perchlorate.*—This *salt* was prepared from methylenecyclohexane and benzoyl chloride in the presence of aluminium chloride (procedure B) in 2% yield and had m. p. 215° (from acetic acid) (Found: C, 65·3; H, 5·1. $C_{20}H_{19}ClO_5$ requires C, 65·2; H, 4·95%), $\lambda_{max.}$ (in 10^{-4}M-solution in acetic acid) 248 mμ (ε 19,600), $\lambda_{min.}$ 333 mμ (ε 2900), $\lambda_{max.}$ 391 mμ (ε 5350), and a flat broad maximum at *ca.* 695 mμ (ε 1000) due either to fluorescence or to solvolysis products.

6,7-*Dihydro*-1,3-*dimethyl*-5H-*cyclopenta*[*c*]*pyridine* (X; R = Me, $n = 3$).—Methylenecyclopentane was prepared from cyclopentanone by the same reactions as methylenecyclohexane.

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[5] Arnold, Amidon, and Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 2871.

[6] Šorm and Beranek, *Chem. Listy*, 1953, **47**, 708.

[7] Jantzen, *Dechema Monograph*, No. 48, Berlin, 1932, p. 135.

Its diacetylation (procedure A) proceeds more readily than that of methylenecyclohexane, though smoothly (reaction of 1-methylcyclopentene is extremely violent and leads only to polymers). After 1 hr. the mixture was diluted with twice its volume of water, the polymer filtered off, and the aqueous solution treated with an excess of ammonia. The yield of product (X) was 18%. The *methiodide* has m. p. 195—196° (from absolute ethanol) (Found: N, 4·8. $C_{11}H_{16}IN$ requires N, 5·0%).

TABLE 2. *Melting points and analyses of picrates and picrolonates.*[a]

	Picrate		Found (%)			Required (%)		
No.*	M. p.	Formula	C	H	N	C	H	N
1	124—125°	$C_{17}H_{18}N_4O_7$	52·2	4·7	14·2	52·3	4·7	14·4
2	181—182 [c]	$C_{17}H_{14}N_4O_7$	53·1	4·1	14·6	52·9	3·7	14·5
3	127	$C_{19}H_{22}N_4O_7$	54·5	5·3	13·6	54·5	5·3	13·4
4	121—122	$C_{16}H_{16}N_4O_7$	51·3	4·4	14·8	51·1	4·3	14·9
5	129—130	$C_{18}H_{20}N_4O_7$	53·5	5·0	14·1	53·5	5·0	13·9

	Picrolonate		N (%)	
No.*	M. p.	Formula	Found	Required
1	230—231°	$C_{21}H_{23}N_5O_5$ [b]	16·2	16·4
2	253	$C_{21}H_{19}N_5O_5$	16·5	16·6
3	215	$C_{23}H_{27}N_5O_5$	15·7	15·4
4	212	$C_{20}H_{21}N_5O_5$	16·7	17·0
5	222	$C_{22}H_{25}N_5O_5$	16·0	15·9

* See Table 1. [a] Recrystallized from ethanol. [b] Found: C, 52·2; H, 4·75. Reqd.: C, 52·3; H, 4·65. [c] Witkop (*J. Amer. Chem. Soc.*, 1948, **70**, 1424) gives m. p. 180°.

The 1,3-diethyl analogue, obtained (10% yield) from methylenecyclopentane, propionic anhydride, and perchloric acid by procedure A, had b. p. 171°/100 mm.

1,3-*Diphenyl*-2-*cyclopenta*[*c*]*pyrylium Perchlorate* (IX; R = Ph, n = 3).—This *salt* was obtained from methylenecyclopentane and benzoyl chloride in the presence of aluminium chloride (procedure B) in 2% yield; it had m. p. 257° (decomp.) (from acetic acid) (Found: C, 64·4; H, 4·6. $C_{20}H_{17}ClO_5$ requires C, 64·3; H, 4·5%), $\lambda_{max.}$ (in 10^{-4}M-solution in acetic acid) 257, 275, 389 (ε 16,500, 15,800, 12,850) $\lambda_{min.}$ 266, 330 mμ (ε 14,950, 4100), and two flat broad maxima at 670 (ε 1750) and 730 mμ (ε 3650) due to fluorescence or solvolysis products.

Analyses were by Misses Elvira Sliam and Violeta Săndulescu. The ultraviolet absorption spectra of the pyrylium perchlorates were recorded by Miss Elena Keplinger with a SF_4 spectrophotometer.

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[*Received, August* 11*th*, 1960.]