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NMR SPECTRA OF 5-SUBSTITUTED 1,3,5-TRIPHENYL-2,4-PENTADIEN-1-ONES AND OF 1,3,5-TRIPHENYL-5-IMINO-3-PENTEN-1-ONES

MAGNETIC NON-EQUIVALENCE OF PHENACYL METHYLENE PROTONS IN 3,5-DIPHENYL-5-PHENACYL-2-PYRAZOLINES

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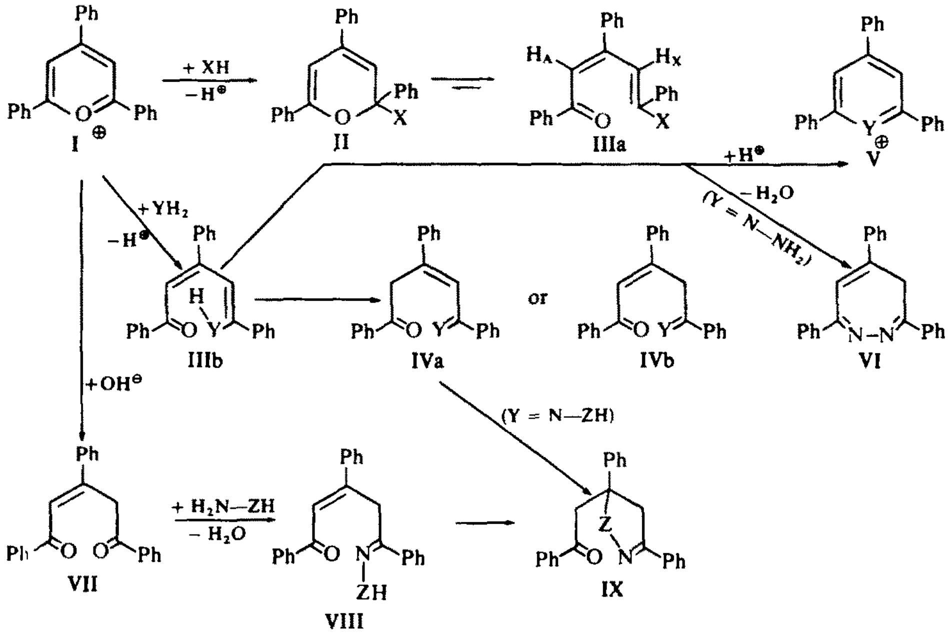
Abstract—NMR Spectra of reaction products of 2,4,6-triphenylpyrylium salts with alkali cyanides, dialkylamines or alkoxides (IIIa, X = CN, NR_2, OR), and hydroxylamine, hydrazine, phenylhydrazine, ammonia, or hydroxide (IVa, Y = NOH, NNH_2, NNHPh, NH, O) are discussed. The latter products are possibly formed by intramolecular 1,5-hydrogen transfer. Phenacyl methylene protons of 3,5-diphenyl-5-phenacyl-2-pyrazolines (IX, Z = NH or NPh) are magnetically non-equivalent, unlike those of 3,5-diphenyl-5-phenacyl-2-isoxazoline (IX, Z = O).

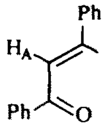
INTRODUCTION

THE primary products, α- and/or γ-pyrans[1-4], are formed in the reaction between pyrylium salts (I) and nucleophiles $X^{\ominus}$.[1-4] They may isomerize into one another, and the α-pyran (II) may valence-isomerize to a 2-*cis*-3,5-dien-1-one (IIIa). IR absorption spectra cannot distinguish between α-pyrans II and dienones IIIa, since both absorb in the 1700 cm^{-1} region, therefore a NMR study of systems II $\rightleftharpoons$ IIIa formed from the 2,4,6-triphenylpyrylium cation I and nucleophiles X = CN, NR_2, OR was undertaken.

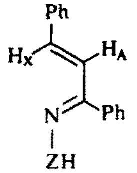
When the $X^{\ominus}$ group possesses a H atom, e.g. when X = YH, then the reaction may proceed further: the dienone IIIb can tautomerize by a 1,5-hydrogen shift into the 3-penten-1-one IVa (or by a 1,3-hydrogen shift into the isomeric 2-penten-1-one, IVb), or can undergo dehydration in acid conditions leading to 6-membered heterocycles V. In the case of hydrazino-derivatives, Y = NNH_2, the dehydration leads to 4*H*-1,2-diazepines VI.[5] NMR Data of systems IVa as well as of their 5-membered cyclic isomers IX, were also collected.

5-Substituted 1,3,5-*triphenyl*-2,4-*pentadien*-1-*ones* (IIIa). The reaction of 2,4,6-triphenylpyrylium salts (I) with alkali cyanides affords yellow 5-cyano-2,4-pentadien-1-ones[6,7] which unlike 2*H*-pyrans can give rise to various functional derivatives of the ketonic group: semicarbazone, oxime, arylhydrazones; hence a formula IIIa (X ≠ CN) is probable. Reactions of I with dimethyl- and diethylamine afford red

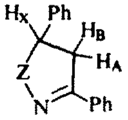




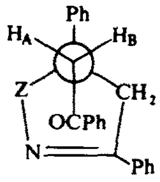
X



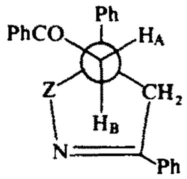
XI



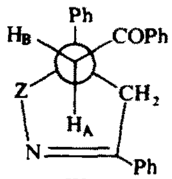
XII



IXa



IXb



IXc

compounds IIIa, $X = NR_2$ as advocated by Lombard[8] and Schroth.[9] The reaction of I with sodium alkoxides in the corresponding alkanols afford the oily methoxy and ethoxy derivatives, or the colourless crystalline isopropoxy derivative IIIa, $X = OR$ (the presumed methoxyderivative IIIa, $X = OMe$ obtained by Dilthey[10] from the pseudobase VII and methyl iodide, and quoted by Berson[11] and Farcasiu,[12] was shown by Rio and Fellion[13] to be a C-Me derivative).

Table 1 presents the NMR data of the three groups of compounds with $X = CN$, NR_2 ($R = Me$, Et) and OR ($R = Me$, iPr). As it may be seen, two doublets are obtained in all cases for the two vinylic hydrogens H_A and H_X. When, as in the case of

TABLE 1. NMR SPECTRA OF 5-SUBSTITUTED 1,3,5-TRIPHENYL-2,4-PENTADIEN-1-ONES (IIIa) (τ values, $CDCl_3$ solution, 38°)

X	H_A ppm	H_X ppm	J_{AX} cps	νCO (KBr) cm^{-1}
CN	1·63	2·69	1·4	1650
NMe_2	2·51	3·60	<0·6[a]	—
NEt_2	2·54	3·70	0·66[b]	—
OMe	3·50	4·26	1·5[c]	1647
OiPr	3·54	4·22	1·5[d]	1645

[a] Me peak at 7·16 τ

[b] Et peaks at 8·80 (Me) and 6·75τ (CH_2), $J = 7$ cs (100 MHz spectrum)

[c] Me peak at $\tau = 6{\cdot}69$.

[d] iPr peaks at 8·87 (Me) and 5·82τ(CH), $J = 6$ cs.

IIIa, X = CN or NEt_2, partial overlap with the phenyl multiplet appearing between 1·9 and 2·8 τ occurs, spin decoupling was employed to distinguish the vinylic proton(s). The doublet at the lowest field was assigned to the proton H_A adjacent to the CO group, while the other doublet was assigned to the proton H_X adjacent to the X group. The range of τ values for both vinylic protons is large and overlaps with the values found for compounds which were assigned 2*H*-pyranic[3] or -thio-pyranic structures.[14] The visible absorption of the compounds IIIa, X = NR_2 closely similar to that of the anion of the pseudobase, was interpreted by Lombard and Kress[8] in terms of a dipolar structure $^{\ominus}O{-}(C{=}C)_2{-}C{=}NR_2^{\oplus}$. This can explain the absence of IR absorption bands between 1620 and 1800 cm^{-1} as well as the relatively low-field position of the vinylic peaks in IIIa, X = NR_2 relatively to IIIa, X = OR. Compounds IIIa, X = CN and OR have the strongest IR band in the 1600–1700 cm^{-1} range at 1645–1650 cm^{-1}. *trans*-Chalcone (X) presents a similar νCO stretching frequency.[11, 15] We conclude therefore that the cyclic (II) or acyclic formulas (IIIa) are still open to discussion, especially since their mutual valence-isomerisation,[16] a symmetry-allowed thermal pericyclic process[17, 18] can have a low activation energy.[4, 19] Chemical data are in favour of acyclic structures IIIa.

1,3,5-*Triphenyl-5-imino-penten-1-ones* (IV, Y = NR). When the nucleophile possesses a primary amino group, the intermediately appearing valence-tautomers II or III immediately isomerize to the 5-imino-penten-1-one derivative IVa or IVb. As indicated in the preceding paper,[20] there exist IR and NMR data favoring structure IVa which could arise by a symmetry-allowed thermal pericyclic 1,5-hydrogen shift in IIIb. Even this intermediate compound IV is unstable because, according to the nature of the nucleophile Y, it can cyclize intramolecularly either without dehydration forming the 5-membered azoline IX, or with dehydration forming 6- (V) or 7-membered heterocycles (VI). Despite this instability, the NMR spectra of compounds IV, Y = O (pseudobase VII[11, 21]), NOH,[5a, b] NNH_2,[5a, b] and NNHPh ('α-pyranol-hydrazide'[7, 8, 22]) prepared from I and the respective nucleophiles in mild conditions could be studied. In solution, compounds IV, Y = NOH and NNH_2 cyclize slowly even at room temperature affording IX, Z = O and VI, respectively.

The NMR spectra of compounds IV are presented in Table 2. The methylene group appears as a sharp singlet at 5·16 τ when Y = O and at ca. 5·9 τ when Y = NOH

TABLE 2. NMR SPECTRA OF 1,3,5-TRIPHENYL-5-IMINO-3-PENTEN-1-ONES (IVa) IN $CDCl_3$ (τ values)

Y	—CH= ppm	—CH_2— ppm	$NH_{(2)}$ ppm	νCO, CN, CC (CCl_4) cm^{-1}
O	—[a]	5·16	—	1693, 1660
N—OH[b]	3·20	5·91[b]	—	1675, 1635[d]
N—NH_2[c]	3·40	5·90	4·12	1688, 1655
N—NHPh	3·33	5·85	1·55	1692, 1659

[a] Submerged under Ph multiplet.

[b] Gradually the NMR spectrum passes into that of IX, Z=O.

[c] Gradually the NMR spectrum passes into that of VI.

[d] In KBr pellet.

or NNHR. The vinylic proton appears in the latter case at ca. 3·3 τ. There is no indication of allylic coupling between these two groupings.

In order to be able to choose between formulas IVa and IVb, NMR spectra of model compounds X and XI were studied. *trans*-Chalcone X has both vinylic protons submerged under the phenyl multiplet, hence the vinylic proton in IVb is expected to appear below 3·0 τ. This is borne out by the NMR spectra of IIIa, X = CN or NR_2 discussed above. On the contrary, the NMR spectrum of *trans*-chalcone thiosemicarbazone (XI, Z = $NCONH_2$) presents a doublet (J = 17·0 c/s) at 3·49 τ assigned to the vinylic proton H_A, hence a formula IVa would have the vinylic proton between 3·0 and 3·5 τ, as observed in Table 2. *trans*-Chalcone thiosemicarbazone presents the NH_2 protons at 1·34 τ, with half-width 10 c/s, and the doublet corresponding to proton H_X partly overlapping with the phenyl multiplet; decoupling indicates that it occurs at 2·85 τ, J_{AX} = 17·0 c/s in agreement with the *trans* configuration. Dypnone (in $CDCl_3$ as in the preceding cases) and its semicarbazone have the vinylic proton corresponding to H_A at τ 2·91 and 3·74, respectively.

IR spectra also agree with formula IVa, with the CO group conjugated only with the phenyl and presenting νCO at 1670–1690 cm^{-1} (acetophenone has νCO at ca. 1690 cm^{-1},[23]), whereas IVb with the CO group conjugated to a phenyl and a double bond would have νCO at ca. 1640–1660 cm^{-1}.[15]

In contrast with the above compounds, the unstable intermediate product formed from I and aqueous ammonia[24] (which dehydrates easily to 2,4,6-triphenylpyridine) presents a methylene peak at 6·74 τ (doublet) and a vinylic proton peak at 3·14 τ (triplet) with a coupling constant of 1·5 c/s. These peaks decrease in time and the spectrum is replaced gradually by that of 2,4,6-triphenylpyridine. As mentioned previously, in CCl_4 this compound presents IR bands at 3595 and 1643 cm^{-1}. From the six possible formulas listed in Ref. 24, those containing an —NH_2 or a $PhCOH_2$— group are ruled out, therefore the structure of this compound is not IVa, Y = NH, but possibly IVb, Y = NH, the corresponding enol, or 2,4,6-triphenyl-2-hydroxy-2H-dihydropyridine.

Structure of chalcone (thio)semicarbazones. As mentioned above, *trans*-chalcone semicarbazone was studied as model compound. Two isomers of this compound are described in the literature.[25] Likewise two isomers are known for chalcone oxime[26,27] and thiosemicarbazones.[25] In the case of the oxime, the two isomers were assigned acyclic (XI) and cyclic 2-isoxazolinic structures (XII), respectively, but in the other two cases *cis-trans syn-anti* isomerism was advocated.[25] NMR studies have not been so far reported. Our data indicate that in all three cases the isomer formed in neutral or slightly acidic conditions has formula XI with two vinylic protons as doublets (cf. above for the semicarbazone). In alkaline conditions these compounds cyclize affording isomeric 3,5-diphenyl-2-isoxazoline or -2-pyrazoline derivatives XII with an ABX multiplet: e.g. for XII, Z = N—CS—NH_2 in deuterochloroform, H_X appears at 3·90 τ, H_A and H_B at 6·19 and 6·80 τ; J_{AX} = 11·7, J_{BX} = 3·7, J_{AB} = 18·0 c/s. Coupling constants and peak positions for H_A and H_B are almost unchanged in pyridine, but H_X appears at 3·60 τ. Details will be communicated in a subsequent paper.

3,5-Diphenyl-5-phenacyl-2-isoxazoline and -2-pyrazoline. On heating in neutral media, or on recrystallization from hot ethanol, compounds IVa, Y = NOH or NNHPh, cyclize by intramolecular Michael reaction affording compounds IX, Z = O or NPh. These same compounds are obtained from the pseudobase VII with the corresponding nucleophiles; this pathway also allows the preparation of IX, Z = NH which cannot be obtained from IVa, Y = NH, because this dehydrates to VI instead.

The NMR spectra of compounds IX, Z = O, NH and NPh, are presented in Table 3. The methylene group in the ring appears as an AB quadruplet with a geminal coupling constant of 17–18 c/s at 5·8–6·5 τ (similarly to literature data[28]). The phenacyl methylene group appears in the 2-isoxazoline derivative IX, Z = O at − 40 to + 40° as a sharp singlet; however, as already pointed out for IX, Z = NPh[5a] in the other two cases (IX, Z = NH or NPh) the phenacyl methylene protons appear as a second AB quadruplet, indicating that these protons are magnetically non-equivalent. Their coupling constant is ca. 17 cs. Temperature variations from − 40° to + 150° and solvent changes ($CDCl_3$, pyridine, *o*-dichlorobenzene) do not alter markedly the spectra. The ring methylene AB quartet of IX, X = NH has the most notable change in *o*-dichlorobenzene (J_{AB} decreases from 17 to 15·9 c/s, and $\Delta\nu$ decreases from 29 to 20 c/s on heating from 40° to 160°). On passing from deuterochloroform to *o*-dichlorobenzene, $\Delta\nu$ almost doubles for the phenacyl methylene quartet (from 6·5 to 10·5 c/s for X = NH, and from 8·9 to 17·0 for X = NPh at 40°). Pyridine shifts towards lower fields the phenacyl methylene peak(s) more than the ring methylene peaks, in all three compounds. As shown by the projections IXa–c it is easily seen that formula IX fulfills the conditions for magnetic non-equivalence.[29] The magnetical equivalence of the phenacyl methylene group in the isoxazoline IX, X = O, however, indicates that additional processes have to be considered.

TABLE 3. NMR SPECTRA OF 3,5-DIPHENYL-5-PHENACYL-2-PYRAZOLINES AND -2-ISOXAZOLINES (IX) IN $CDCl_3$ AT 38° (τ values)

		Phenacyl CH_2			Ring CH_2		νCO(CCl_4)
Z	H_A	H_B	J_{AB}	H_M	H_N	J_{MN}	cm^{-1}
NH	6·63	6·73	16·5	6·10	6·48	17·0	1690
NPh	5·90	6·05	17·2	5·83	6·43	18·0	1690
O		6·32	—	5·91	6·32	17·5	1695

EXPERIMENTAL

2,4,6-Triphenylpyrylium perchlorate (I)[30] and sodium cyanide in ethanol afford IIIa, X = CN, m.p. 106° (from EtOH),[7] yellow crystals. From I and dimethyl- or diethylamine in EtOH, red needles of III, X = NEt$_2$ are formed in an exothermal reaction after a few hours' standing at room temp m.p. 106° (from EtOH)[8].

Compound IIIa, X = OCHMe$_2$ was prepared by dissolving Na in iPrOH under reflux, and adding this soln to a suspension of I in iPrOH. A clear red soln resulted (cf. Ref. 31 for the spectrum of the similarly red anion of the pseudobase VII) which on cooling and scratching deposited white crystals m.p. 102° (from iPrOH). (Found: C, 84·50; H 6·37. $C_{26}H_{24}O_2$ requires: C, 84·75; H 6·56%). Water hydrolyzes slowly this ether under yellow coloration.

Treatment of I with hot solutions of excess NaOMe or NaOEt in the corresponding alcohols followed by cooling separates oils (IIIa, X = OMe or OEt), which are more stable towards hydrolysis than IIIa, X = OiPr. The analogous compound IIIa, X = O-tBu is hydrolyzed in 15–20 min at room temp.

The preparation of the pseudobase VII (IV, Y = O) from I and aqueous ethanolic sodium carbonate or acetate, or aqueous pyridine,[11, 21]; of IVa, Y = NOH from I and hydroxylamine in the cold;[5a] of IVa, Y = NNH$_2$[20] from I, aqueous hydrazine and ether; of IVa, Y = NNHPh from I[5a, 7, 22] and ethanolic phenylhydrazine; and of IVb, Y = NH from I, aqueous ammonia and ether[24] was described elsewhere.

The preparation of IX, Y = O by recrystallization of IV, Y = NOH from ethanol, or from the pseudobase, sodium acetate and hydroxylamine hydrochloride in hot aqueous ethanol;[20] of IX, Y = NPh by refluxation of IV, Y = NNHPh in ethanol[5a, 7, 22] or by reacting the pseudobase with phenylhydrazine in ethanol:[20] and of IX, Y = NH from the pseudobase and hydrazine in ethanol,[20] was also described elsewhere.

Chalcone X,[32] its semicarbazone and thiosemicarbazone XI, Z = NCONH$_2$ and NCSNH$_2$ and the corresponding cyclized pyrazolinic isomers XII (Z = NCONH$_2$ and NCSNH$_2$) were prepared according to literature data,[25] from chalcone and (thio)semicarbazide hydrochloride and sodium acetate, in acid (pH = 4) and alkaline (pH = 8) medium, respectively.

NMR spectra were measured with a Varian A-60A apparatus. Thanks are expressed to Prof. O. Polansky for his support, to Miss H. Martinek for technical assistance, to Drs. W. Szinowatz and E. Proksch for making the Perkin–Elmer spectrophotomer 125 available for infrared spectra, and to Dr. G. C. Mateescu for one 100-MHz NMR spectrum.

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