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SPECTROSCOPIC STUDIES OF TAUTOMERIC SYSTEMS—III

2-ARYLHYDRAZONES OF 1,2,3-TRIKETONES

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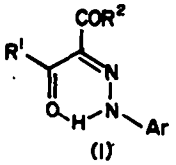
Abstract—The IR and NMR spectra of a range of 2-arylhydrazones of 1,2,3-tricarbonyl compounds have been recorded. Compounds containing different end groups in the 1,2,3-tricarbonyl system can exist in two different tautomeric forms. The influence of electronic and steric factors on the structure of the preferred tautomer is discussed.

Reactions of aryldiazonium salts with β-dicarbonyl compounds lead to 1,2,3-tricarbonyl-2-arylhydrazones.[2] Such compounds have been shown to exist as the intramolecularly H-bonded arylhydrazone tautomers (1 and/or 2) rather than in any of the other alternative



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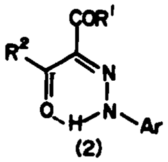

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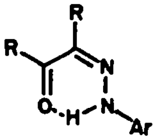
tautomeric forms. Thus the NMR spectra of these compounds are characterized by a very low-field signal diagnostic of an intramolecularly H-bonded proton.[3–7] IR studies indicate the presence of a free CO group as well as a H-bonded CO group.[3–5,8] Parallel IR studies on the structurally related 2-arylhydrazones of 1,2-diketones indicate that these compounds exist in the arylhydrazo form (3) and not the alternative tautomeric forms (4 and 5). NMR studies on Schiff bases derived from β-diketones and amines indicate they exist as the keto-amine tautomer (6) rather than the enol-imine tautomer (7), or the keto-tautomer (8), i.e. there is a preference for an N–H-----O H-bond rather than the O–H-----N H-bond.[9–12]



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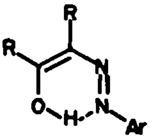

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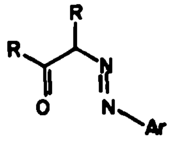
β-Diketones with different end groups and β-ketoesters could give rise to two distinct intramolecularly H-bonded hydrazone tautomers, i.e. 1 and 2. In a preliminary communication we reported the isolation of the two possible tautomeric hydrazones for the *p*-chloro-, *p*-bromo- and *p*-ethoxycarbonyl-phenylazo derivatives of 1-phenylbutan-1,3-dione.[13] The individual tautomers could be rapidly equilibrated by treatment of their deuteriochloroform solutions with a drop of conc hydrochloric acid. Equilibration of the tautomers was also base catalysed. In each case the predominant form in the equilibrated mixture was (1; R^1 = Me, R^2 = Ph) in which the acetyl rather than the benzoyl group was involved in the H-bonded system. Both possible tautomers have also been detected (but not isolated) for the phenylazo derivatives of acetoacetaldehyde[5] and methyl acetoacetate.[3] We now report a detailed spectroscopic study on 2-arylhydrazones of a number of 1,2,3-tricarbonyl compounds with particular reference to the factors which enhance the stability of one or other tautomeric form.



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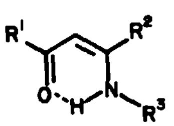

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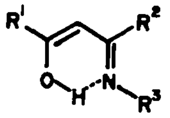

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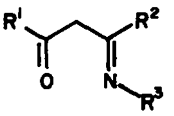

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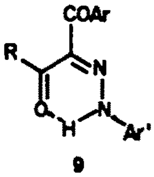
The arylhydrazones reported in this paper were all prepared by coupling the appropriate diazonium salt with a β-dicarbonyl compound.[14] The arylhydrazone isolated from reactions using acylbenzoylmethanes normally consisted of the tautomer (9; R = Alkyl, Ar = Ph) though in certain instances (Experimental) the alternative tautomer (10; R = Alkyl, Ar = Ph) was obtained. In those cases where this latter tautomer was isolated it was readily converted into the other tautomer by sublimation followed by crystallization from a hydrocarbon solvent with rigorous exclusion of traces of acid or base. It has been observed that irrespective of the nature of the substituent in the arylhydrazone a solution of either tautomer in deuteriochloroform containing a trace of acid or base equilibrated rapidly to give a mixture of the two tautomers. The composition of this mixture of tautomers was examined spectroscopically to determine the influence of electronic effects, steric effects and solvent effects on the relative proportions of the two tautomers. We have previously discussed the mechanism of interconversion of the tautomers.[13]



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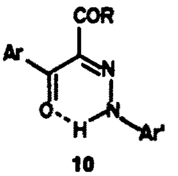

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Factors influencing the composition of the tautomeric mixture

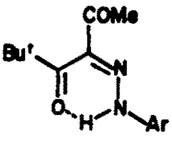
Table 1 (Compounds **16–28** and **30–38**) indicates that arylhydrazones derived from acylbenzoylmethanes preferentially exist in the tautomeric form **9** (the "lowfield" form) in which the benzoyl group rather than the acyl group is excluded from the intramolecularly H-bonded system.

The IR CO stretching frequency of a benzoyl group is lower than that of an acetyl group. Consequently the charge density would be expected to be greater on the oxygen of a benzoyl group than of an acetyl group. One might thus expect that the benzoyl group would be preferentially involved in the intramolecularly H-bonded system to give the tautomer **10** (R = Me, Et, Pr^n or Pr^i, Ar = Ph). That this is not so is attributed to steric effects as is also the case for diacetylbenzoylmethane.[15] Models indicate that the phenyl group and the H-bonded system cannot be coplanar, due to steric interaction between the phenyl group and the free acyl group. Apparently steric effects are less in the case of 2-arylhydrazones of 1,2,3-triketones than in diacetylbenzoylmethane as both tautomers are obtained whereas only a single tautomer can be detected in the case of daicetylbenzoylmethane. This is perhaps not surprising as in this latter case the free acyl group would be subject to steric interactions from the two alkyl or aryl residues of the intramolecularly H-bonded system.

The influence of electronic effects. According to the above argument the proportion of the less favoured tautomer (**10**) derived from acylaroylmethanes should be increased by electron-donating substituents in the aroyl residue as this would increase the electronegativity of the oxygen of the aroyl group. The results in Table 1 (compounds **20–28**) indicate that the proportion of the tautomer **10** is greater for a series of arylhydrazones derived from *p*-nitrobenzoylacetone. Similarly the only tautomer detected from the reaction of 1,1,1-trifluoroacetylacetone with benzene diazonium salts was (**1**; R^1 = Me, R^2 = CF_3) in which the acetyl group rather than the trifluoroacetyl group was involved in the H-bonded system. This is again consistent with the foregoing argument as the oxygen of the acetyl group is indubitably more electron rich than the oxygen of the trifluoroacetyl group. The predominant though not exclusive tautomer of 1-phenyl-4,4,4-trifluorobutane-1,2,3-trione-2-methoxyphenylhydrazone was that in which the trifluoroacetyl group was excluded from the H-bonded system IR (**10**; Ar = Ph, R = CF_3). The analogous tautomer **10** (Ar = C_4H_3S, R = CF_3) was also the major form in the case of 1-thienyl-4,4,4-trifluorobutane-1,2,3-trione-2-phenylhydrazone whereas the major tautomer from the phenylhydrazone derived from 1-thienylbutane-1,3-dione was **9** (Ar = C_4H_3S; R = Me). No clear cut effects could be obtained from phenylhydrazones of 1,3-diarylpropane-1,2,3-triones. Approximately equal proportions of the two possible tautomers were obtained from arylhydrazones derived from 4-methyl- and 4-methoxydibenzoylmethanes. The phenylhydrazone derived from benzoylfuroylmethane was tentatively assigned the structure **1** (R^1 = C_4H_3O, R^2 = Ph) in which the more electron rich furyl group was involved in the intramolecularly H-bonded system.

Similar trends also occur in arylhydrazone derivatives of β-ketoesters. Both possible tautomers are obtained from methyl and ethyl acetoacetates (**1** and **2**, R^1 = Me, R^2 = OMe or OEt) whereas the ester group seems to be more or less exclusively involved in the H-bonded system in derivatives of ethyl benzoylacetate and ethyl trifluoroacetates much as would be anticipated from the above results.

Electron-releasing substituents in the aryl group of the arylhydrazone residue increase the proportion of the low-field tautomer (**9**) in derivatives of benzoylacetone (compounds **16–22**), *p*-methoxybenzoylacetone (compounds **23–25**), and 4-methyl-1-phenylpentane-1,3-dione (compounds **32–38**). This effect is possibly related to the influence of the substituents on the strength of the H-bonds. Electron-releasing effects in the arylhydrazone residue result in increased deshielding of the hydrazone proton. This can be interpreted as indicating a more symmetrical and hence stronger H-bond (see Ref. 16).



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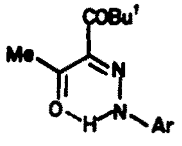

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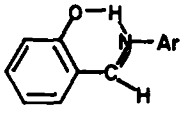
The influence of steric effects. The influence of steric effects on the equilibrium proportion of the two possible tautomers was studied by examination of the phenylhydrazones of a series of acetylacylmethanes and acylbenzoylmethanes with acyl groups of different sizes (Table 1). The results indicate that unless the two alkyl groups are of very disparate size as occurs in derivatives of acetylpivaloylmethane the two tautomers are present in approximately equal amounts. However, the preferred tautomer derived from acetylpivaloylmethane is **11**. Models indicate that steric interaction between the t-Bu group and the acetyl group is less than that between the Me group and the pivaloyl group in **12**. Similarly for arylhydrazones derived from benzoylpivaloylmethane, there is a much greater proportion of the tautomer **10** (R = Bu^t, Ar = Ph) in which the pivaloyl rather than the benzoyl group is excluded from the H-bonded system. Earlier we suggested that **9** was the preferred tautomer for arylhydrazones derived from benzoylacetone and 4-methyl-1-phenylpentane-1,3-dione because of steric interaction between the phenyl group and the acyl group in the alternative tautomer **10**. In arylhydrazones derived from benzoylpivaloylmethane there is also very significant steric interaction in the tautomer 9 (R = Bu^t, Ar = Ph). This results in both tautomers being obtained in approximately a 1:1 ratio from this diketone.

Factors influencing the chemical shift of the intramolecularly hydrogen-bonded proton

Electronic effects. The chemical shifts of the intramolecularly H-bonded proton in the phenylhydrazones derived from acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone, i.e. 1 ($R^1 = R^2$ = Me), 1 (R^1 = Me, $R^2 = CF_3$) and 1 ($R^1 = R^2 = CF_3$) are δ 14.65, 15.1 and 14.45 respectively. These results indicate that a substantial downfield shift is effected by replacement of the free acetyl group by a trifluoroacetyl group, whereas an upfield shift is brought about by increasing the electron-withdrawing character of the alkyl group attached to the CO involved in the H-bonded system (cf. the phenylhydrazones derived from trifluoroacetylacetone and hexafluoroacetylacetone. The electron-withdrawing trifluoromethyl group would make the oxygen of the adjacent CO group less electron rich and hence the H-bond to the proton of the hydrazone group would be weaker. This would have the effect of moving this proton slightly out of the deshielding environment of the CO group thus giving an upfield shift. Similar upfield shifts of the enolic proton are observed in the NMR spectra of β-diketones and β-ketoesters containing electron-withdrawing substituents.[16,17]

Comparison of the chemical shifts of the intramolecularly H-bonded protons in the lowfield tautomers of arylhydrazones derived from substituted acylbenzoylmethanes 9 indicates that a slight downfield shift is induced by electron-withdrawing substituents on the free benzoyl group (compounds 16, 20, 22–28). Similar downfield shifts have previously been reported for diacylaroylmethanes containing electron-withdrawing groups: the aroyl group is also not involved in the H-bonded system in these compounds.[15] Electron-withdrawing substituents in the benzoyl group involved in the H-bonded system however induce substantial downfield chemical shifts on the H-bonded protons. This contrasts to the effect of replacement of the Me group by the electron-withdrawing trifluoromethyl group. The reason for this difference in behaviour is not understood.

The chemical shifts of the intramolecularly H-bonded proton in both tautomers of the arylhydrazones derived from substituted benzoylacetones and from 4-methyl-1-phenylpentane-1,3-dione and also from the arylhydrazones from acetylacetone all show an upfield shift if the aryl group of the arylhydrazone moiety possesses an electron-withdrawing group. This contrasts to the situation with Schiff bases derived from aromatic amines and β-diketones: these compounds have been shown to prefer the ketoenamine tautomeric form with an N–H-----O H-bond.[9] Electron-withdrawing substituents in the aromatic amine fragment of salicylaldehyde-anils do, however, result in an upfield shift of the intramolecularly H-bonded protons. These compounds exist in the alternative enolimine form (18). In the compounds under study in this paper there seems to be no evidence whatsoever for the enolazo tautomers analogous to the enolimine form of the salicyldehyde-anils (13). A major distinction between the arylhydrazones of this study and the Schiff bases is that in the latter the lone-pair on the nitrogen attached to the aromatic ring is in direct conjugation with the CO group: this type of interaction cannot occur with the arylhydrazones because of the polarity of the C=N system. These results can be accounted for by electron-withdrawing groups resulting in shortening of the N–H bond (IR studies of aromatic amines indicate that the N–H stretching frequency is increased and hence the bond length is decreased by electron-withdrawing substituents). Shortening of the N–H bond would bring the enolic proton out of the deshielding cone of the CO group thereby resulting in an upfield shift.



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Steric effects. The chemical shift in the *p*-chlorophenylhydrazone derived from dipivaloylmethane (1; $R^1 = R^2 = Bu^t$, Ar = p-ClC_6H_4) is shifted upfield by over 4 ppm compared to the p-chlorophenylhydrazone derived from acetylacetone. This is attributed to the large steric interaction between the t-Bu and pivaloyl groups attached to the H-bonded system causing so much out of plane distortion that the chelate ring is twisted and the H-bond weakened. Models support this explanation. Previous work on tripivaloylmethane had indicated that steric interactions were so severe that this compound existed exclusively as the ketonic tautomer.[18] A substantial upfield shift was also noted for the "downfield" tautomer of arylhydrazones derived from benzoylpivaloyl-methane (9; R = Bu^t, Ar = Ph) so that the hydrazo protons in this tautomer were further upfield than in the tautomer 10. The chemical shifts of the hydrazo protons in the tautomer 10 for these compounds were, however, normal.

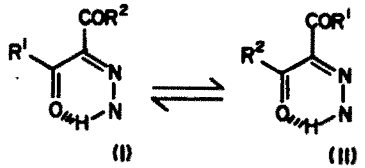
Steric effects in the aryl group of the arylhydrazone moiety seem to be unimportant as the chemical shift of the 2,4,6-trichlorophenylhydrazone of acetylacetone is as expected purely on the basis of electronic effects.

The chemical shift of the H-bonded proton of the phenylhydrazone of benzoyl-α-naphthoylmethane is at δ 14.2. This is very significantly lower than the chemical shifts of the arylhydrazones of other diaroylmethanes. This downfield effect may be a result of steric compression leading to a shorter H-bond but not of such a magnitude as to cause buckling of the enolic ring as encountered in phenylhydrazones from dipivaloylmethane.

Establishment of structures

(i) *Derivatives of acylbenzoylmethanes and diacylmethanes.* The IR spectra of arylhydrazones derived from acetylacetone (1; $R^1 = R^2$ = Me) and dibenzoylmethane (1; $R^1 = R^2$ = Ph) were characterized by CO absorption at *ca* 1680 cm^{-1} and 1640 cm^{-1} due to the free acetyl group and benzoyl groups respectively. The lowfield and highfield tautomers of benzoylacetone, substituted benzoylacetones and other acylbenzoylmethanes with the exception of benzoylpivaloylmethane were characterized by IR absorption at *ca.* 1640 and 1680 cm^{-1} respectively thus establishing that these tautomers have the structures 9 and 10. The chemical shift of the lowfield tautomers of these systems is similar to that obtained for derivatives of acetylacetone as would be expected as the H-bonded ring system is similar in both cases. From analysis of the NMR spectra of

Table 1. NMR spectra of 2-arylhydrazones of 1,2,3-tricarbonyl compounds



Compound No.	R^1	R^2	Ar	δ_{NH}(I)	δ_{NH}(II)	δ_{Me}(I)	δ_{Me}(II)	ν_{CO}(I)	ν_{CO}(II)	%I	Form Isolated
1	Me	Me	p-$NO_2C_6H_4$	14.50		2.64, 2.53		1675, 1625			
2	Me	Me	p-$EtO_2CC_6H_4$	14.50		2.58, 2.46		1675, 1625			
3	Me	Me	p-BrC_6H_4	14.65		2.60, 2.48		1680			
4	Me	Me	p-ClC_6H_4	14.60		2.57, 2.45		1680			
5	Me	Me	2,4,6-$Cl_3C_6H_2$	14.45		2.62, 2.42		1680			
6	Me	Me	Ph	14.65		2.58, 2.46		1680			
7	Me	Me	p-MeC_6H_4	14.75		2.57, 2.45		1680			
8	Me	Me	p-$MeOC_6H_4$	14.90		2.57, 2.45		1680			
9	Me	Et	p-ClC_6H_4	14.60	14.45	2.56	2.42	1675	a		II
10	Me	Pr^i	p-ClC_6H_4	14.60	14.45	2.56, 1.10^b	2.49, 1.16^b	1670	a		I
11	Me	Bu^t	p-ClC_6H_4	14.65	14.35	2.53, 1.23^c	2.47, 1.41^c	1665	a		II
12	Pr^i	Pr^i	p-ClC_6H_4	14.45		1.16^b, 1.10^b		1670			
13	Bu^t	Bu^t	p-ClC_6H_4	10.40		1.41^c, 1.20^c		1680			
14^d	Me	CF_3	Ph	15.1		2.57		1725		100	I
15^e	CF_3	CF_3	Ph	14.45				1710			
16	Me	Ph	p-$NO_2C_6H_4$	14.50	12.00	2.61	2.61	1640	f	85	I
17	Me	Ph	p-$EtO_2CC_6H_4$	14.55	12.25	2.64	2.55	1640	1675	85	I, II
18	Me	Ph	p-BrC_6H_4	14.70	12.67	2.61	2.51	1640	1675	85	I, II
19	Me	Ph	p-ClC_6H_4	14.65	12.62	2.61	2.54	1640	1675	85	I, II
20	Me	Ph	Ph	14.75	12.80	2.60	2.53	1645	f	90	I
21	Me	Ph	p-MeC_6H_4	14.90	13.10	2.60	2.55	1645	f	95	I
22	Me	Ph	p-$MeOC_6H_4$	15.10	13.50	2.60	2.55	1645	f	95	I
23	Me	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	14.60	13.00	2.66	2.52	1645	f	80	I
24	Me	p-$NO_2C_6H_4$	Ph	14.90	13.75	2.66	2.52	1645	f	88	I
25	Me	p-$NO_2C_6H_4$	p-$MeOC_6H_4$	15.20	14.20	2.66	2.52	1645	f	95	I
26	Me	p-$MeOC_6H_4$	p-$NO_2C_6H_4$	14.45	11.50	2.49	2.56	1645	f	70	I
27	Me	p-$MeOC_6H_4$	Ph	14.70	12.30	2.50	2.50	1645	f	80	I
28	Me	p-$MeOC_6H_4$	p-$MeOC_6H_4$	15.00	12.90	2.50	2.50	1645	f	88	I
29^g	CF_3	Ph	p-$MeOC_6H_4$	14.30	h			1705	f	90	II
30	Et	Ph	p-ClC_6H_4	14.55	12.58			1640	f	80	I
31	Pr^n	Ph	p-ClC_6H_4	14.55	12.55			1640	f	80	I
32	Pr^i	Ph	p-$NO_2C_6H_4$	14.40	12.00	1.20	1.30	1640	1675	75	II
33	Pr^i	p-$EtO_2CC_6H_4$	14.50	14.50	12.50	1.15	1.25	1640	f	80	I

34	Pr^i	Ph	*p*-ClC_6H_4	14.60	12.80	1.20	1.30	1640	f	80	I
35	Pr^i	Ph	*p*-BrC_6H_4	14.50	12.70	1.17	1.30	1645	f	80	I
36	Pr^i	Ph	Ph	14.60	12.80	1.20	1.30	1645	1680	80	II
37	Pr^i	Ph	*p*-MeC_6H_4	14.60	12.70	1.10	1.20	1645	f	85	I
38	Pr^i	Ph	*p*-$MeOC_6H_4$	14.95	13.50	1.10	1.20	1645	f	85	I
39	Bu^t	Ph	*p*-ClC_6H_4	12.25	12.45	1.46	1.30	1640	f	50	I
40	Bu^t	Ph	*p*-BrC_6H_4	12.25	12.45	1.46	1.29	1640	f	60	I
41	Bu^t	Ph	Ph	12.40	12.60	1.46	1.30	1640	f	50	I
42	Me	2-C_4H_3O	Ph	14.65		2.57		1680	f	100	I
43	Me	2-C_4H_3S	Ph	14.70		2.57		1680	f	100	I
44	CF_3	2-C_4H_3S	Ph	13.60	13.90			1705	f		
45	Me	2-C_5H_4N	Ph	14.70	12.85	2.61	2.54	1680	f	55	
46	Ph	Ph	Ph	13.45				1640	a		
47	*p*-MeC_6H_4	*p*-MeC_6H_4	Ph	13.35				1640	a		
48	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	Ph	13.35				1640	a		
49	*p*-MeC_6H_4	Ph	Ph	13.35	13.45			1640	a		
50	*p*-$MeOC_6H_4$	Ph	Ph	13.35	13.45			1640	a		
51	2-C_4H_3O	Ph	Ph		13.43						
52	2-C_4H_3S	Ph	Ph		13.18						
53	2-C_5H_4N	Ph	Ph	13.6	13.4						
54	1-$C_{10}H_7$	Ph	Ph	14.2							
55	Me	OMe	*p*-ClC_6H_4	14.77	12.78	2.60	2.48	f	1680	70	II
56	Me	OMe	Ph	14.80	12.77	2.62	2.52	1715	f	70	I
57	Me	OEt	*p*-$Cl_6C_6H_4$	14.70	12.70	2.55	2.45	1715	f	60	I
58	Me	OEt	Ph	14.85	12.77	2.59	2.49	1715	f	60	I
59	CF_3	OEt	Ph		13.40			1715			II
60	Ph	OEt[i]	*p*-ClC_6H_4	12.63				1700			I
61	Ph	OEt	Ph	12.70				1700			I

[a] ν_{CO} for I and II indistinguishable.

[b] Refers to CH_3 protons of isopropyl group.

[c] Refers to CH_3 protons of t-butyl group.

[d] ^{19}F NMR band at −70.74 (d, J 1 Hz) ppm.

[e] ^{19}F NMR bands at −75.14 (s) and −71.72 (d, J 1 Hz).

[f] ν_{CO} for I and II not distinguishable.

[g] ^{19}F NMR bands at −73.15 (s) and −70.75 (d, J 1 Hz) ppm in a ratio 1:9.

[h] Not observable.

[i] ^{19}F NMR bands at −73.19 (s) and −70.50 (d, J 1 Hz) ppm in a ratio 1:3.

[j] ^{19}F NMR band at −71.02 (s) ppm.

derivatives of acetylacetone and benzoylacetone it can be seen that the chemical shift of the Me of the acetyl group involved in the H-bonded system ($\delta \sim 2.6$) is slightly further downfield than the free acetyl group ($\delta \sim 2.55$). Using analogous arguments the chemical shifts of the Me protons in t-Bu and i-Pr groups in the two different environments were deduced. The values of these chemical shifts are remarkably constant between the diacylmethane and acylbenzoylmethane series. From these values the various peaks in arylhydrazones derived from diacylmethanes with two different alkyl groups can be assigned as indicated in Table 1. For these compounds IR spectra are of little assistance.

(ii) *Derivatives of β-diketones containing a trifluoroacetyl group.* The IR spectrum of the phenylhydrazone derived from hexafluoroacetylacetone shows CO absorption at 1725 cm^{-1} characteristic of a free trifluoroacetyl group. The CO absorption in the IR spectrum of the phenylhydrazone from trifluoroacetyl acetone is at 1710 cm^{-1}. This is attributed to a free trifluoroacetyl group as it is much higher than would be expected for a free acetyl group. The compound is thus assigned the structure 1 ($R^1 = Me$, $R^2 = CF_3$). Moreover the chemical shift of the H-bonded proton is more downfield than that of the phenylhydrazone from hexafluoroacetylacetone 1 ($R^1 = R^2 = CF_3$): the alter-

Table 2. New 2-arylhydrazones of 1,2,3-tricarbonyl compounds

Compound	M.p. (°C)	Crystals	Recryst. from	Found (%)			Formula	Calc. (%)		
				C	H	N		C	H	N
1	230	Orange	MeOH	53.1	3.5	16.9	$C_{11}H_{11}N_3O_4$	53.1	3.2	16.9
2	137	Yellow	MeOH	60.9	5.9	10.3	$C_{14}H_{16}N_2O_4$	61.0	5.9	10.1
3	145	Yellow	MeOH	46.5	4.0	10.1	$C_{11}H_{11}BrN_2O_2$	46.7	4.0	9.9
5	108	Yellow	Pet. (40-60°)	43.0	3.15	—	$C_{11}H_9Cl_3N_2O_2$	42.9	2.95	
9	95	Yellow	MeOH	57.1	5.3	11.2	$C_{12}H_{13}ClN_2O_2$	57.2	5.2	11.1
10	96	Yellow	MeOH	59.0	5.7	10.75	$C_{13}H_{15}ClN_2O_2$	58.4	5.7	10.5
11	78	Yellow	MeOH	60.2	5.9	10.2	$C_{14}H_{17}ClN_2O_2$	59.9	6.1	10.0
12	82	Yellow	MeOH	60.7	6.3	9.6	$C_{15}H_{19}ClN_2O_2$	61.1	6.45	9.5
13	115	Yellow	MeOH	63.3	7.05	8.6	$C_{17}H_{23}ClN_2O_2$	63.2	7.2	8.7
14	122	Yellow	Pet. (40-60°) -CH_2Cl_2	51.5	4.1		$C_{11}H_9F_3N_2O_2$	51.2	3.5	
15	83	Yellow	Pet. (40-60°)	42.3	2.4		$C_{11}H_6F_6N_2O_2$	42.3	1.9	
16	143	Yellow	MeOH	61.9	4.3	13.9	$C_{16}H_{13}N_3O_4$	61.8	4.2	13.9
21	65	Yellow	MeOH	72.7	5.6	10.1	$C_{17}H_{16}N_2O_2$	72.9	5.8	10.0
22	85	Orange	MeOH	68.9	5.0	9.4	$C_{17}H_{16}N_2O_3$	69.0	5.4	9.4
23	170	Yellow	MeOH	54.3	3.7	15.3	$C_{16}H_{12}N_4O_6$	54.0	3.4	15.7
24	150	Yellow	MeOH	61.75	4.3	13.5	$C_{16}H_{13}N_3O_4$	61.7	4.2	13.5
29	107	Orange	Pet. (40-60°) -CH_2Cl_2	58.2	3.7		$C_{17}H_{13}F_3N_2O_3$	58.3	3.7	
30	87	Yellow	MeOH	67.2	4.8	8.9	$C_{17}H_{15}ClN_2O_2$	67.2	4.8	8.9
31	94	Yellow	MeOH	66.3	5.3	8.0	$C_{18}H_{17}ClN_2O_2$	65.8	5.2	8.5
32	118	Yellow	MeOH	63.8	5.15	12.5	$C_{18}H_{17}N_3O_4$	63.8	5.0	12.4
33	93	Yellow	MeOH	69.0	6.1	7.7	$C_{21}H_{22}N_2O_4$	68.9	6.1	7.6
34	97	Yellow	MeOH	65.8	5.3	8.5	$C_{18}H_{17}ClN_2O_2$	65.8	5.2	8.5
35	98	Yellow	MeOH	57.8	4.35	7.6	$C_{18}H_{17}BrN_2O_2$	58.0	4.6	7.5
36	95	Yellow	MeOH	73.7	6.3	9.55	$C_{18}H_{18}N_2O_2$	73.5	6.2	9.5
37	110	Yellow	MeOH	74.15	6.4	9.0	$C_{19}H_{20}N_2O_2$	74.1	6.5	9.1
38	117	Orange	MeOH	70.7	6.1	8.4	$C_{19}H_{20}N_2O_3$	70.4	6.2	8.6
39	149	Yellow	MeOH	66.9	5.7	8.3	$C_{19}H_{19}ClN_2O_2$	66.6	5.55	8.2
40	127	Yellow	MeOH	58.55	4.9	7.4	$C_{19}H_{19}BrN_2O_2$	58.3	5.0	7.3
41	131	Yellow	MeOH	73.6	6.55	9.0	$C_{19}H_{20}N_2O_2$	74.0	6.5	9.1
42	112	Yellow	MeOH	66.3	4.8	10.9	$C_{14}H_{12}N_2O_3$	65.9	4.8	10.9
43	99	Yellow	MeOH	61.8	4.7	10.7	$C_{14}H_{12}N_2O_2S$	61.8	4.4	10.3
44	122	Yellow	Pet. (40-60°) -CH_2Cl_2	51.4	2.8		$C_{14}H_9F_3N_2O_2S$	51.5	2.8	
45	104	Yellow	MeOH	67.7	4.8		$C_{15}H_{13}N_3O_2$	67.4	4.9	
46	152	Yellow	MeOH	77.0	4.7	8.5	$C_{21}H_{16}N_2O_2$	76.9	5.0	8.5
47	113	Yellow	MeOH	77.6	6.0	7.6	$C_{23}H_{20}N_2O_2$	77.6	5.7	7.9
48	120	Yellow	MeOH	71.3	5.4	7.3	$C_{23}H_{20}N_2O_4$	71.2	5.2	7.2
49	114	Yellow	MeOH	77.2	5.1	8.0	$C_{22}H_{18}N_2O_2$	77.2	5.3	8.2
50	131	Yellow	MeOH	73.9	5.2	7.9	$C_{22}H_{18}N_2O_3$	73.7	5.1	7.8
51	150	Yellow	MeOH	71.9	4.5	9.0	$C_{19}H_{14}N_2O_3$	71.7	4.4	8.8
52	138	Yellow	MeOH	68.3	4.3	8.1	$C_{19}H_{14}N_2O_2S$	68.25	4.2	8.4
53	128	Yellow	MeOH	72.9	4.6	13.1	$C_{20}H_{15}N_3O_2$	72.9	4.6	12.8
54	163	Yellow	PhH	79.3	4.7	7.2	$C_{25}H_{18}N_2O_2$	79.35	4.8	7.4
55	118	Yellow	MeOH	52.4	4.5	11.0	$C_{11}H_{11}ClN_2O_3$	51.9	4.35	11.0
56	87	Yellow	MeOH	59.8	5.6	12.7	$C_{11}H_{12}N_2O_3$	60.0	5.5	12.7
57	79	Yellow	MeOH	53.6	4.7	10.5	$C_{12}H_{13}ClN_2O_3$	53.5	4.9	10.4
58	80	Yellow	MeOH	61.3	6.15	12.0	$C_{12}H_{14}N_2O_3$	61.6	6.0	12.0
59	80	Yellow	MeOH		(M^+288.07276)		$C_{12}H_{11}F_3N_2O_3$		(M^+288.07217)	
60	95	Yellow	MeOH	62.3	4.7	9.0	$C_{17}H_{15}ClN_2O_3$	61.9	4.6	9.3
61	65	Yellow	MeOH	69.2	5.65	9.6	$C_{17}H_{16}N_2O_3$	69.0	5.4	9.5

Table 3. Arylhydrazones for which both tautomers were isolated

Compound No.	M.p. (°C)	Crystals	Recryst. from	Found (%) C	H	N	Formula	Calc. (%) C	H	N
17 (I)	106	Yellow	MeOH	67.6	5.5	8.4	$C_{19}H_{18}N_2O_4$	67.4	5.4	8.3
17 (II)	120	Pale yellow	Hexane	67.4	5.3	8.5				
18 (I)	123	Yellow	MeOH	55.6	3.8	9.4	$C_{16}H_{13}BrN_2O_2$	55.7	3.8	8.1
18 (II)	143	Pale yellow	Hexane	55.7	3.9	9.2				
19 (I)	110	Yellow	MeOH	63.9	4.55	9.4	$C_{16}H_{13}ClN_2O_2$	63.9	4.4	9.3
19 (II)	148	Yellow	Hexane	64.0	4.4	9.2				

native tautomer 2 ($R^1 = Me$, $R^2 = CF_3$) would have been expected to have the hydrazo proton signal less downfield. A characteristic of the ^{19}F spectra is that the signal due to the free trifluoroacetyl group is a doublet ($J = 1$ Hz) whereas the signal due to the trifluoromethyl group attached to the CO group involved in the H-bonded system is a singlet.

Analogous arguments enable the structures of the arylhydrazones of benzoyltrifluoroacetylmethane and thienoyltrifluoroacetylmethane to be assigned. Again the ^{19}F spectra of the free trifluoroacetyl groups appear as doublets.

(iii) *Derivatives of β-ketoesters.* The free ester groups have CO absorptions at *ca.* 1715 cm^{-1} and *ca.* 1700 cm^{-1} in derivatives of methyl and ethyl acetoacetates and ethyl benzoylacetate respectively. These assignments are unequivocal. It is however, very much more difficult to make an unambiguous structural assignment to the phenylhydrazone from ethyl trifluoroacetylacetate as both a free ester and a free trifluoroacetyl group would be expected to have similar CO absorption. This compound is assigned the structure 2 ($R^1 = CF_3$, $R^2 = OEt$) rather than 1 ($R^1 = CF_3$, $R^2 = OEt$) as the chemical shift of the enolic proton is at δ13.4. This is about 0.6 ppm further downfield than the chemical shift of the analogous proton in 2 ($R^1 = Me$, $R^2 = OEt$). A similar downfield shift was encountered on replacement of a free acetyl group by a trifluoroacetyl group in other cases (*cf* compounds 29 and 22, and compounds 44 and 43). The chemical shift of the hydrazo proton in the other tautomer would be expected to be about 0.6 ppm downfield from δ 14.85-the chemical shift of the analogous proton of 1 ($R^1 = R^2 = CF_3$). One unexplained feature then remains in that though the chemical shift of the CF_3 group is what would be expected for a free trifluoroacetyl group it is a singlet and not as before a doublet.

(iv) *Derivatives of diaroylmethanes.* Assignment of structure are very uncertain in the cases of derivatives of diaroylmethanes as no information can be obtained from IR spectra and definitive information is difficult to arrive at from NMR spectra since we have already seen that electron-withdrawing substituents in derivatives of substituted benzoyl acetones exert a downfield shift whether they are attached to the H-bonded or free CO groups. The splitting pattern of the protons in the furan ring in the phenylhydrazone from benzoylfuroylmethane is a somewhat different from that of the phenylhydrazone from acetylfuroylmethane which has the structure 1 ($R^1 = Me$, $R^2 = C_4H_3O$). Consequently the phenylhydrazone from benzoylfuroylmethane is tentatively assigned the structure 1 ($R^1 = C_4H_3O$, $R^2 = Ph$). Structures of the other phenylhydrazones reported are assigned purely on the basis of analogy with the results reported: the more electron-rich carbonyl group is assumed to be involved in the enolic system.

EXPERIMENTAL

IR spectra were determined on a Perkin–Elmer 157 spectrophotometer either as solns in $CDCl_3$ or in tetrachloroethylene; NMR spectra for 10% solns in $CDCl_3$ on Perkin–Elmer R10 or R14 spectrometers operating at 40 or 100 MHz using TMS as an internal standard. The NMR spectra were not significantly dependent on the concentration of the soln used.

β-Dicarbonyl compounds. These were prepared as previously described by commercial materials or were prepared by standard literature procedures.

Preparation of the 2 - *arylhydrazones of* 1,2,3 - *tricarbonyl compound.* A soln of the appropriate amine (0.011 mol) in a soln of 1 M HCl (60 ml) was diazotized at 0–5° by addition of a sat $NaNO_2$ aq (0.011 mol). The diazonium soln was added dropwise to a stirred soln of the dicarbonyl compound (0.01 mole), NaOAc (5 g) in 1:2 MeOH–water (300 ml) at room temp. The arylhydrazone was filtered off, washed well with water and recrystallised from the appropriate solvent. NMR and IR spectra were recorded on $CDCl_3$ solns of the materials prior to crystallization. New arylhydrazones are listed in Table 2, and Table 3 reported the *p*-bromo, *p*-chloro- and *p*-ethoxycarbonyl-phenylhydrazones derived from benzoylacetone for which both tautomers were isolated pure.

REFERENCES

[1] Part II. D. C. Nonhebel, *Tetrahedron* **26**, 4443 (1970).

[2] S. M. Parmerter, *Org. Reactions* **10**, 1 (1959).

[3] J. Elguero, R. Jacquier and G. Tarrago, *Bull. Soc. chim. Fr*, 2781 (1966).

[4] H. C. Yao, *J. Org. Chem.* **29**, 2959 (1964).

[5] C. Reichardt and W. Grahn, *Tetrahedron Letters* 3745 (1971).

[6] C. Reichardt and W. Grahn, *Chem. Ber.* **103**, 1065 (1970).

[7] A. K. Bose and I. Kugajevsky, *Tetrahedron* **23**, 1489 (1967).

[8] E. M. Tanner, *Spectrochimica Acta* 20 (1959).

[9] N. M. D. Brown and D. C. Nonhebel, *Tetrahedron* **24**, 5655 (1968).

[10] G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.* **83**, 2099 (1961); **84**, 2691 (1962).

[11] G. O. Dudek and G. Volpp, *Ibid*, **85**, 2697 (1963).

[12] G. O. Dudek and E. P. Dudek, *Ibid*, **86**, 4283 (1964).

[13] A. D. Mitchell and D. C. Nonhebel, *Tetrahedron Letters* 3859 (1975).

[14] H. G. Garg and S. S. Joshi, *J. Ind. Chem. Soc.* **37**, 626 (1960).

[15] D. C. Nonhebel, *J. Chem. Soc.* 676 (1968).

[16] D. C. Nonhebel, *Tetrahedron* **24**, 1869 (1968).

[17] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.* **81**, 4682 (1959).

[18] D. C. Nonhebel, *J. Chem. Soc.* (C), 1716 (1967).