508. *Spectroscopic Studies. Part I. 2 : 4-Dinitrophenylhydrazones in Neutral and in Alkaline Solutions.**

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The absorption spectra of numerous 2 : 4-dinitrophenylhydrazones have been studied in various neutral and alkaline solutions, and the results for all the bands have been classified. The charge-transfer spectra of the ions are complementary to the charge-resonance spectra of the neutral molecules in correlating spectra with the structures of the parent carbonyl compounds. Solvent shifts, including those due to hydrogen bonding and π-complex interaction, are discussed. Further cases are reported of the formation of 2 : 4-dinitrophenylhydrazones in pyridine solution.

2 : 4-Dinitrophenylhydrazones have been employed extensively for characterisation of carbonyl compounds, particularly in the last thirty years,[1, 2] Their utility has been considerably enhanced by detailed knowledge of the correlation between their light-absorption properties and the structures of the parent carbonyl compounds.[3-10] Although it has been known that 2 : 4-dinitrophenylhydrazones give red to blue colours with

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[1] (*a*) Curtius and Dedichen, *J. prakt. Chem.*, 1894, **50**, 241; Purgotti, *Gazzetta*, 1894, **24**, 554; (*b*) Brady and Elsmie, *Analyst*, 1926, **51**, 77; Brady, *J.*, 1931, 757.

[2] Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955.

[3] Braude and Jones, *J.*, 1945, 498.

[4] Roberts and Green, *J. Amer. Chem. Soc.*, 1946, **68**, 214.

[5] Ramirez and Kirby, *ibid.*, 1952, **74**, 4331; 1953, **75**, 6026; 1954, **76**, 1037.

[6] Bohlmann, *Chem. Ber.*, 1951, **84**, 490.

[7] Fleisher and Kendall, *J. Org. Chem.*, 1951, **16**, 556.

[8] Djerassi and Ryan, *J. Amer. Chem. Soc.*, 1949, **71**, 1000; Johnson, *ibid.*, 1953, **75**, 2720; Reich, Crane, and Sanfilippo, *J. Org. Chem.*, 1953, **18**, 822; Reich and Samuels, *ibid.*, 1954, **19**, 1040: Barany and Pianka, *J.*, 1953, 2217; Heilmann, Gaudemaris, and Arnaut, *Compt. rend.*, 1952, **234**, 1177; Heilmann, Gaudemaris, and Noack, *Bull. Soc. chim. France*, 1954, 990, 992; Pestemer and Brück in "Methoden der Organischen Chemie (Houben-Weyl)," 4th edn., Ed. Müller, 1955, Vol. III, Part 2, p. 675.

[9] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890.

[10] Braude and Timmons. *J.*. 1953, 3144.

TABLE 1. *Absorption bands of representative* 2 : 4-*dinitrophenylhydrazones and related compounds in neutral and alkaline* (N/100) *ethanol.*†

The first figure in each column is the wavelength of the maximum in mμ and the second figure the extinction coefficient ($10^{-3}\varepsilon$). Figures in italics denote submerged bands estimated graphically (see Experimental section).

		Neutral								Alkaline							
No.	Compound	E_0 band		E_1 band		E_2 band		B band		E_0^- band		E_1^- band		E_2^- band		NO_2^- band	
1	C_6H_6 [a]	150	—	184	46	203	7 [e]	255	0·2 [e]	—	—	—	—	—	—	—	—
2	$Ph\cdot NH_2$ [b]	—	—	198	20	235	7	280	1·3	—	—	—	—	—	—	—	—
3	$Ph\cdot NO_2$ [f]	200	20	213	15	259	7·5	*294*	*2·0*	—	—	—	—	—	—	—	—
4	o-$NO_2\cdot C_6H_4\cdot NH_2$ [c]	—	—	231	17	276	5	402	5·5	—	—	—	—	490	>3	—	—
5	p-$NO_2\cdot C_6H_4\cdot NH_2$	—	—	229	7	371	15·5	—	—	—	—	—	—	—	—	—	—
6	p-$NO_2\cdot C_6H_4\cdot NH\cdot N:CMe_2$ [c]	—	—	249	10·5	390	23	—	—	—	—	319	4·5	510	33·5 *	—	—
7	m-$(NO_2)_2C_6H_4$ [c,f]	—	—	234	18	—	—	285	0·9 [e]	—	—	—	—	—	—	536	15 [i]
8	2 : 4-$(NO_2)_2C_6H_3\cdot NH_2$ [c]	223	11·5	257	10·5	336	16	*388*	*7*	*280*	*6*	386	19·5	*412*	*4·5*	531	14
9	2 : 4-$(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ [c,d]	219	12	258	9·5	350	14·5	*410*	*5·5*	—	—	—	—	526	17	*590*	*3·5**
10	2 : 4-$(NO_2)_2C_6H_3\cdot NH\cdot NHAc$ [g]	209	12	256	10	332	14	*380*	*3*	*280*	*6*	—	—	424	18·5	*530*	*4·5*
	Dinitrophenylhydrazones of :																
11	$Me\cdot CHO$ (m. p. 168°)	—	—	—	—	357	21	*424*	*5*	—	—	—	—	424	18·5	506	9
12	Me_2CO	227	18·5	*265*	9·5	357	20·5	*430*	*5*	*260*	*10*	—	—	431	19·5	520	11·5
13	n-$C_5H_{11}\cdot C:C\cdot CHO$ [c,d]	—	—	—	—	357	23·5	*415*	*4*	—	—	345	6	498	27·5	*575*	*6·5*
14	$Me_2C:CH\cdot COMe$	248	14	*279*	*9*	379	24	*450*	*7*	—	—	*360*	*6·5*	451	20·5	*555*	*11·5*
15	$Me_2C:CH\cdot CO\cdot CH:CMe_2$ [c]	*257*	*16*	*291*	*7·5*	385	29	*459*	*6*	—	—	360	4	492	28·5	*586*	*13·5*
16	$Me_2C:CH\cdot CH:CH\cdot COMe$	268	17	303	18·5	390	35	*463*	*8·5*	284	22	*360*	*6·5*	479	31	*575*	*13·5*
17	$CH_2:CH\cdot CMe:CH\cdot CH:CH\cdot COMe$	—	—	314	20·5	398	38·5	*475*	*10*	300	20·5	—	—	497	35·5	*605*	*10*
18	Retinene$_1$	—	—	*354*	*23*	437	59·5	*507*	*14·5*	*330*	*14·5*	371	26	518	62·5	—	—
19	$Ph\cdot COMe$	*262*	*12·5*	*288*	*8*	373	27·5	*434*	*7*	—	—	*356*	*6*	462	24·5	*550*	*15*
20	$Ph\cdot CH:CH\cdot COMe$	*271*	*13*	303	15·5	391	35	*465*	*8*	—	—	—	—	488	34	*583*	*12·5*
21	2-Cinnamylidene*cyclo*hexanone	—	—	327	22·5	408	30·5	*480*	*11*	319	20	—	—	488	30	592	11·5
22	$Et\cdot CO\cdot COPr$ (mono)	—	—	—	—	351	23·5	*404*	*7·6*	—	—	—	—	512	34	—	—
23	$Et\cdot CO\cdot COPr$ (bis)	—	—	—	—	392	38	*451*	*28*	—	—	354	11	558	44·5	—	—

* Unstable.

† In some cases 10% $CHCl_3$–EtOH (v/v) was used which obscured shorter-wavelength bands.

[a] In heptane; Platt and Klevens, *Chem. Rev.*, 1947, **41**, 301. [b] In MeOH; Ley and Specker, *Ber.*, 1939, **72**, 192. [c] Alkaline spectra in $H\cdot CO\cdot NMe_2$. [d] N/50-NaOH. [e] In hexane; fine structure also present. [f] Wenzel, *J. Chem. Phys.*, 1954, **22**, 1623. [g] Ref. 1*a*. [h] Table 2, ref. *t*. [i] 0·1N-NaOH.
References to other compounds are given in Table 2.

alkali,[1a, 4, 7, 11, 12] until recently no detailed spectroscopic studies of these colours had been reported. Since this work began two groups [13] have deduced correlations between the spectra in alkaline solution and the structure of the parent carbonyl compound for a limited range of carbonyl compounds. The results now described permit more detailed correlations for a wider range of saturated, variously unsaturated, and substituted carbonyl compounds, similar in general to the correlations in neutral solution. There are however some important differences between the two series, which give additional information about the carbonyl compound.

The spectra in various neutral solvents have also been studied and these permit an explanation of the varied solvent and substituent effects previously noted [3, 5, 7, 10] for the main absorption band, as well as allowing the other bands to be classified.

Neutral Solvents.—In general 2 : 4-dinitrophenylhydrazones show four absorption bands, two at shorter wavelengths than the main maximum and one at longer wavelengths, but these are not always all resolved as discrete bands, owing to considerable overlap. In most cases, it is possible to estimate the majority of the submerged bands graphically and these are included in Table 1 in italics. Each of these bands shifts to longer wavelengths as the number of conjugated double bonds in the carbonyl compound increases, as has been shown previously for the main band.[3] The dependence of the wavelengths of the maxima of all four bands on the number of double bonds (n) in aliphatic or mainly aliphatic compounds is illustrated in Fig. 1, where the squares of the wavelengths are plotted against the number of double bonds. The behaviour of the three subsidiary bands (E_0, E_1, B) parallels that of the main band (E_2) in conforming reasonably well to a linear relation $\lambda^2 \propto n$. The range of n studied is too small for a rigorous test of this relation and in fact the simpler relation $\lambda \propto n$ fits only slightly less accurately (particularly over the range $0 \leqslant n \leqslant 3$). By analogy with other polyene systems the λ^2 relation would be expected.

Comparison of the four bands in the 2 : 4-dinitrophenylhydrazones with those for related aromatic compounds and for benzene itself as indicated in Table 1, suggests that they may be displaced benzene absorption bands, as argued by Doub and Vandenbelt [14] for other substituted aromatic systems. For this reason, the three long-wavelength bands in the 2 : 4-dinitrophenylhydrazones have been designated E_1, E_2, and B bands [15] and the short-wavelength band, which may correspond to a band at 150 mμ in benzene, is now called the E_0 band. In the 2 : 4-dinitrophenylhydrazones, the intensity of the E_0 band shows only small variations, in contrast to the intensities of the E_1, E_2, and B bands, which increase regularly with n.

For diagnostic purposes the E_2 band is the most useful, and for this reason the other bands have received scant attention in the past. In general, bands below 270 mμ are of little use as most dinitrophenylhydrazones are difficultly soluble in solvents transparent below 270 mμ. However, the position of the E_1 band distinguishes fully conjugated from cross-conjugated dienone derivatives. Cinnamylidene*cyclo*hexanones are unusual in having a particularly intense E_1 band (nos. 21 and 83).

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[11] Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 758.

[12] Lappin and Clark, *Analyt. Chem.*, 1951, **23**, 541; Gornall and Macdonald, *J. Biol. Chem.*, 1953, **201**, 279; Hadley, Hall, Heap, and Jacobs, *J.*, 1954, 1421; Isherwood and Cruickshank, *Nature*, 1954, **173**, 121; Isherwood and Jones, *ibid.*, 1955, **175**, 419; Barrenscheen and Dreguss, *Biochem. Z.*, 1931, **233**, 305; Neuberg and Kobel, *ibid.*, 1928, **203**, 463: Raistrick and Rudman, *Biochem. J.*, 1956, **63**, 395; Schepartz and Daubert, *J. Amer. Oil Chemists' Soc.*, 1950, **27**, 267: Cavallini and Frontali, *Ricerca sci.*, 1953, **23**, 807; Pesez and Poirier, "Méthodes et Réactions de l'Analyse organique," Masson, Paris, 1954, Vol. III, p. 124; Pucher, Vickery, and Wakeman, *Ind. Eng. Chem. Anal.*, 1934, **6**, 288: Wolf, *Z. analyt. Chem.*, 1952, **136**, 401: Daniels, Scholes, and Weiss, *J.*, 1956, 832: Mendelowitz and Riley, *Analyst*, 1953, **78**, 704; Banks, Vaughn, and Marshall, *Analyt. Chem.*, 1955, **27**, 1348.

[13] Yamaguchi, Fukushima, Tabata, and Ito, *J. Pharm. Soc. Japan*, 1954, **74**, 1335; Jones, Holmes, and Seligman, *Analyt. Chem.*, 1956, **28**, 191.

[14] Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414; 1955, **77**, 4535.

[15] Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, p. 150.

Considering now only the E_2 band, the majority of 2 : 4-dinitrophenylhydrazones show a hypsochromic shift in hydroxylic solvents compared with chloroform solutions (see Table 2 and Fig. 2). The minority that show bathochromic shifts are derivatives of aldehydes and of carbonyl compounds with α-hydroxy(but not alkoxy)-substituents, and the related compounds 2 : 4-dinitroaniline (no. 8), 2 : 4-dinitrophenylhydrazine (no. 9), 2 : 4-dinitrophenylacethydrazide (no. 10), and acetone *p*-nitrophenylhydrazone (no. 6) (λ in $CHCl_3$ — λ in EtOH = —4, —7, —6, and —7 respectively). A study of solvent shifts with a typical example of the major group, acetone dinitrophenylhydrazone, summarised in Fig. 2 for a wider range of solvents, shows that the solvents fall into three

FIG. 1. *Plot of squares of the wavelengths of various absorption bands of 2 : 4-dinitrophenylhydrazones of polyene carbonyl compounds against the number of double bonds in the parent carbonyl compounds.*

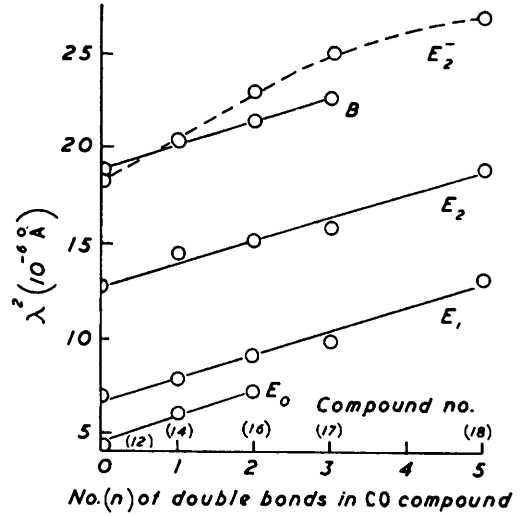
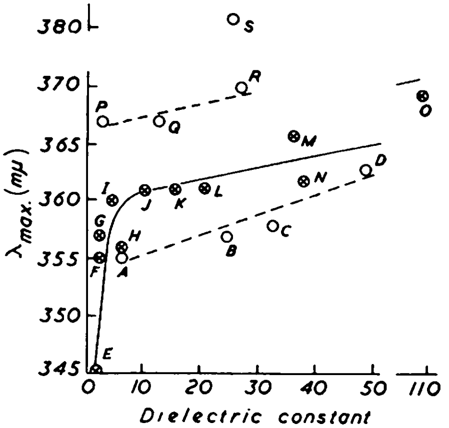


FIG. 2. *Plot of wavelength of main band of acetone 2 : 4-dinitrophenylhydrazone in various solvents against dielectric constant of solvent* (cf. *Weissberger, Proskauer, Riddick, and Toops, "Technique of Organic Chemistry,"* 1955, *Vol. VII, Interscience Pub. Inc., New York*).



A, Acetic acid; *B*, ethanol; *C*, methanol; *D*, 80% v/v aqueous methanol; *E*, *cyclo*hexane; *F*, dioxan; *G*, benzene; *H*, ethyl acetate; *I*, chloroform; *J*, methylene dichloride; *K*, pentan-2-one; *L*, acetone; *M*, nitromethane; *N*, acetonitrile; *O*, formamide; *P*, carbon disulphide; *Q*, pyridine; *R*, dimethylformamide; *S*, benzonitrile.

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* Unstable. † In $CHCl_3$

[redacted]

TABLE 2. *Main maxima* (mμ) *and* pK_a' *of dinitrophenylhydrazones of various carbonyl compounds.*

No.	Carbonyl compound	Neutral solvent			Solvent 0·01N in NaOH					Ref. (see p. 2616)
		10% $CHCl_3$ in EtOH		λ ($CHCl_3$) − λ (EtOH)	10% $CHCl_3$ in EtOH		H·CO·NMe_2		− pK_a'	
		λ	$10^{-3}\varepsilon$		λ	$10^{-3}\varepsilon$	λ	$10^{-3}\varepsilon$		
24	CH_2O	348	19·5	−1	428	18 *	—	—	3·2	2
25	Me·CHO (m. p. 147°)	357	20	−1	426	17	—	—	—	2
11	Me·CHO (m. p. 168°)	357	21	−2	424	18	439	20·5	3·0	*a*
26	Pr^n·CHO	356	20·5	0	431	19·5	—	—	—	2
27	Bu^t·CHMe·CH_2·CHO	358	21	−1	434	21	—	—	—	
28	HO·$[CH_2]_4$·CHO	358	22·5	0	428	19 *	—	—	—	*b*
29	HO·CMe_2·CHO	354	24	−5	429	19	—	—	2·8	*c*
30	EtO_2C·$[CH_2]_4$·CHO (m. p. 73°)	357	23	2	431	21	—	—	—	*d*
31	EtO_2C·$[CH_2]_4$·CHO (m. p. 54°)	357	22	—	431	20	—	—	—	*d*
32	2 : 6 : 6-Trimethyl*cyclo*hex-2-ene-1-aldehyde	360	24·5	1	435	24·5	—	—	—	*e*
33	Pyran-2-aldehyde	356	23	5	436	18	—	—	—	*f*
12	Me_2CO	358	21	5	432	19	446	22	2·8	2
34	Bu^i·COEt	361	22·5	3	435	18	—	—	—	2
35	*n*-C_5H_{11}·COMe	361	22·5	5	435	21	—	—	—	2
36	Bu^t·COMe	359	23	5	432	19	—	—	—	2
37	2-Methyl*cyclo*pentanone	364	22	1	434	19	—	—	2·6	*g*
38	*cyclo*Hexanone	362	22·5	2	435	19	—	—	—	11
39	2 : 2 : 6-Trimethyl*cyclo*hexanone	360	22	5	432	16	—	—	2·8	*h*
40	HO·CMe_2·COMe (m. p. 71—72°)	357	21	−2	436	19·5	—	—	—	*c*
41	HO·CMe_2·COMe (m. p. 148°)	357	23	−2	437	22	—	—	—	*i*
42	CMe_2:CH·CMe(OH)·COMe	359	22·5	−3	436	22	—	—	—	*c*
43	Pr^n·CH(OH)·COEt	362	20	−1	436	20	—	—	—	10
44	Pr^i·CH(OH)·$COPr^i$ (m. p. 101°)	356	21	0	442	20·5	—	—	—	10
45	Pr^i·CH(OH)·$COPr^i$ (m. p. 147°)	371	27	3	438	25	—	—	—	10
46	EtO·CMe_2·COMe	357	23·5	4	439	19·5	—	—	—	
47	HO_2C·COMe	356	22	−5	442	17	—	—	—	2
48	HO_2C·$[CH_2]_2$·COMe	358	16·5	5	432	17	—	—	—	2
49	NC·CHMe·CH_2·COMe	355	21·5	−2	436	20·5	—	—	—	*j*
50	Me·CH:CH·CHO	374	27·5	—	456	29·5	464	30·5	—	3
51	*cyclo*Hex-1-enealdehyde	376	28·5	—	458	28·5	—	—	—	*k*
52	2 : 6 : 6-Trimethyl*cyclo*hex-1-enealdehyde	382	28·5	—	458	28·5	—	—	—	*l*
13	*n*-C_5H_{11}·C⋮C·CHO	357	22·5	—	451	6	498	27·5	—	*m*
53	CH_2:CMe·COMe	367	26	8	456	22·5	—	—	—	*n*
54	Me·CH:CH·COMe	375	25	8	453	24	476	27·5	—	*o*
14	Me_2C:CH·COMe	381	24		452	21	476	27	2·5	2
55	Bu^t·CH:CH·COMe	373	27·5	—	456	25	—	—	—	
56	1-Acetyl-4 : 4-dimethyl*cyclo*hexene	376	25	—	452	21·5	—	—	—	*p*
57	2-Ethylidene*cyclo*hexanone	378	23·5	5	445	21	476	26	—	*q*
58	Cholest-4-en-3-one	384	31	—	462	25·5	—	—	—	*r*
59	Me·CH:CH·CO·Bu^t	366	22·5	—	—	—	478	23	1·7	
60	Me_2C:CH·$COPr^i$	369	26·5	—	462	19·5	—	—	—	
61	1-Acetyl-2-methyl*cyclo*hexene	372	23·5	—	442	21	468	24	—	*s*
62	CH_2:C(OMe)·COMe (m. p. 173—175°)	366	19·5	—	454	22·5	—	—	—	
63	CH_2:C(OMe)·COMe (m. p. 147—149°)	363	23·5	3	490	24	—	—	3·3	
64	3-*iso*Propoxy*cyclo*hex-2-enone	395	26·5	3	456	24	—	—	—	
65	5-Chloro-3 : 3 : 6-trimethyl*cyclo*hexanone	374	28	—	468	26	—	—	—	*t*
66	Me·CH:CH·CH:CH·CHO	390	32·5	—	480	34·5	494	39	—	3

TABLE 2. (*Continued.*)

		Neutral solvent			Solvent 0·01N in NaOH					
		10% $CHCl_3$ in EtOH		λ ($CHCl_3$) − λ (EtOH)	10% $CHCl_3$ in EtOH		H·CO·NMe_2			Ref. (see p. 2616)
No.	Carbonyl compound	λ	$10^{-3}\varepsilon$		λ	$10^{-3}\varepsilon$	λ	$10^{-3}\varepsilon$	− pK_a'	
67	Me·CH:CH·CH:CH·COMe	390	36·5	6	480	30·5	496	38	3·0	*u*
16	Me_2C:CH·CH:CH·COMe	392	36	—	478	33	—	—	—	*v*
68	Me·CH:CMe·CH:CH·COBu^t	371	24	—	—	—	502	24·5	—	*u*
69	4-(2 : 6 : 6-Trimethyl*cyclo*hex-1-enyl)but-3-en-2-one	384	29·5	—	468	28	—	—	—	3
70	2-(1 : 3-Dimethylbut-2-enylidene)*cyclo*hexanone	406	26·5	—	476	26	—	—	—	*w*
71	2-(2-*cyclo*Hexylidene-ethylidene)*cyclo*hexanone	408	22	—	464	21·5	—	—	—	*x*
72	CH_2:CH·CMe:CH·CH:CH·COMe	398	38·5	—	497	35·5	—	—	—	*y*
18	Retinene$_1$	437	59·5	7	518	62·5	548	61·5	3·4	*z*
73	Ph·CHO	379	28	−4	464	30	488	34·5	3·3	*g*
19	Ph·COMe	376	26	—	460	24	482	30	—	2
74	Ph·COBu^t	376	26	—	463	22·5	—	—	—	*aa*
75	*p*-MeO·C_6H_4·CHO	390	25	—	466	26·5	—	—	—	*g*
76	3 : 4 : 1-MeO·C_6H_3(OH)·CHO	393	27	—	478	27·5	—	—	—	*g*
77	Furfuraldehyde (m. p. 223—225°)	388	26	1	470	30·5	—	—	3·7	*bb*
78	Furfuraldehyde (m. p. 194—196°)	375	28	5	476	28·5	—	—	3·2	*bb*
79	Ph·CH:CH·CHO	391	37	−1	488	41·5	508	44	3·5	*r*
80	Ph·CH:CMe·CHO	384	36·5	—	470	36·5	—	—	—	*r*
81	Ph_2C:CMe·CHO	386	36	—	478	36·5	—	—	—	*r*
20	Ph·CH:CH·COMe	391	35	—	488	34	508	42	—	*r*
82	4-Methyl-3-phenyl*cyclo*hex-2-enone	389	33·5	—	480	31	—	—	—	*cc*
83	1-Cinnamylidene-6 : 6 : 10-trimethyl-2-decalone	412	27	8	488	24	—	—	—	*t*
84	1-(*cyclo*Hexylideneacetyl)*cyclo*hexene (m. p. 150—155°)	373	25	6	—	—	464	23·5	2·5	*dd*
85	Di(*cyclo*hex-1-enyl) ketone	380	27·5	—	—	—	476	28	—	*ee*
15	Me_2C:CH·CO·CH:CMe_2	386	26·5	10	—	—	492	28·5	1·3	*ff*
86	Ph·CO·CH:CH_2	378	24	—	458	20·5	—	—	—	*r*
87	Ph_2CO	379	29	8	—	—	502	32	2·0	*r*
88	Ph·C⋮C·CO·CH:CHPh	397	37·5	—	510	~31 *	—	—	—	*r*
89	Ph·C⋮C·COPh	390	30·5	—	498	~21 *	—	—	—	*r*
90	3-Cyano-2-phenylinden-1-one	*375*	*9*	—	—	—	*535*	*15*	—	*gg*
		430	28·5	0	—	—	594	66·5	4·3	
91	3-Carbamoyl-2-phenylinden-1-one	387	27 †	—	—	—	*501*	*13*	—	*gg*
		432	*20 †*	—	—	—	576	50·5	—	

		Neutral solvents				Solvents 0·01N in NaOH					
	Polycarbonyl compounds	10% $CHCl_3$ in EtOH		H·CO·NMe_2		10% $CHCl_3$ in EtOH		H·CO·NMe_2		− pK_a'	Ref.
	Mono-derivatives										
92	Me·CO·COPr	351	16·5	—	—	500	23·5	—	—	—	*hh*
22	Et·CO·COPr	351	23·5	—	—	512	34	—	—	—	
93	2-Methylnaphtha-1 : 4-quinone	457	38	460	42	635	70	635	83	4·1	*ii*
	Bis-derivatives :										
94	OHC·CHO	—	—	*385*	*20·5*	—	—	588	59	—	*jj*
				448	42·5						
95	Me·CO·COMe	—	—	412	38	—	—	572	48·5	—	*c*
				478	*20·5*						
23	Et·CO·COPr	392	38	409	40·5	558	44·5	570	34	—	10
		451	*28*	*472*	*24·5*						
96	3 : 4 : 1-MeO·C_6H_3(OEt)·CO·COMe	399	43	413	47	556	49	576	59·5	3·7	*kk*
		458	*23·5*								

classes, hydroxylic, non-hydroxylic, and a third group giving much larger bathochromic shifts. Within each class the position of the absorption maximum increases with increasing dielectric constant of the solvent. In benzonitrile an exceptionally large bathochromic shift is observed

Simple alkyl substitution produces bathochromic shifts (see, *e.g.*, nos. 24, 25, 12, and 34) but in more complex examples hypsochromic shifts are found (*e.g.*, nos. 38 and 39; 73 and 19; 79 and 80) particularly when the substituent is near the dinitrophenylhydrazone residue. Hydroxy- and alkoxy-substituents give variously both bathochromic and hypsochromic shifts, probably depending on the configuration of the derivative (cf., *e.g.*, nos. 44 and 45). Several pairs of derivatives from particular carbonyl compounds have been studied; in some cases they have different spectra (*e.g.*, nos. 44 and 45; 77 and 78) but in the absence of substituents other than alkyl, no appreciable differences in spectra were observed (*e.g.*, nos. 25 and 11; 30 and 31).

The bis-derivatives of α-dicarbonyl compounds are distinguished by the increased intensities of the E_2 and more particularly of the B bands. With the glyoxal derivative (no. 94), the B band is the most intense, but alkyl substitution enhances the E_2 band relatively to the B band (cf., *e.g.*, nos. 95 and 23).

Alkaline Solutions.—In the presence of alkali the four bands are all shifted towards longer wavelengths in both the 2 : 4-dinitrophenylhydrazones and related aromatic compounds (Table 1). By analogy with the bands in neutral solutions, the first three bands will be termed E_0^-, E_1^-, and E_2^- bands. The longest-wavelength band for reasons stated in the discussion is called the NO_2^- band. For most derivatives the solvent mixture, 10%(v/v) $CHCl_3$ in EtOH, is suitable; the alkali bands were fully produced by addition of aqueous sodium hydroxide to make the solutions N/100 in sodium hydroxide. With less soluble compounds (*e.g.*, bis-derivatives) and with less acidic derivatives (*e.g.*, no. 15) N/100-alkali in dimethylformamide was necessary, the latter being a more powerful solvent and having greater ionising properties.[16] For comparison of derivatives in either solvent a number of spectra are recorded in Table 2 in both solvents.

The NO_2^- band is resolved as a discrete but broad band with derivatives of saturated aldehydes and ketones and is of value for distinguishing the two (498—512 mμ for aldehydes and 515—540 mμ for ketones in 10% $CHCl_3$–EtOH). Of more general application is the E_2^- band, the wavelength of which increases with increasing number of conjugated double bonds in the carbonyl compound. Whilst a linear relation between the square of the wavelength and the number of double bonds holds up to $n = 3$, the curve then starts to converge with the compounds studied (Fig. 1). An acetylenic bond gives a smaller increment than an ethylenic bond as in the spectra of the neutral derivatives [17] (*e.g.*, 13). Phenyl groups are equivalent to about 1·2 double bonds. The derivatives of cross-conjugated ketones absorb at shorter wavelengths than those of comparable linear conjugated ketones (cf. nos. 15 and 67) in the same solvent. Saturated substituents produce only small effects on the spectra of the ions, so that the spectra in alkaline solution are more characteristic of the extent of conjugation than the spectra in neutral solution. In contrast, substituents which can readily accommodate a negative charge (*e.g.*, $C{=}O$) produce large bathochromic shifts with the ions, but only small changes with the neutral molecules (*e.g.*, nos. 22, 23, 92—96). Hypsochromic shifts resulting from steric hindrance by substituents are less pronounced in the spectra of the ions than of the neutral molecules when the steric hindrance is small (cf., *e.g.*, nos. 59, 60), but larger shifts are found in alkaline than in neutral solution when the hindrance is great (*e.g.*, no. 69).

Qualitatively the colour in alkaline solution gives a rough indication of the extent of the conjugation present, although it is now apparent that a blue colour is not specific [11] for bis-derivatives of α-diketones, but is shown by all derivatives giving particularly stable anions (*e.g.*, nos. 90, 91, and 93).

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[16] Porter, *Analyt. Chem.*, 1955, **27**, 805.

[17] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

Acid Strengths.—A large variation in the acid strengths, conveniently measured spectrophotometrically, was encountered (pK_a varying from −1·3 to −3·4; see Table 2). Particularly weak acids were the derivatives of cross-conjugated ketones and sterically hindered ketones.

Preparation of 2 : 4-Dinitrophenylhydrazones.—Most of the derivatives studied had been prepared earlier for other work. The new compounds, described in detail in the Experimental section, include examples of acid-sensitive compounds (nos. 62, 63, 64) which were conveniently prepared in pyridine solution.[18]

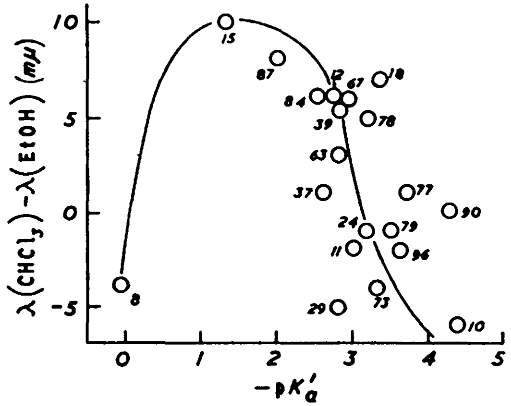

FIG. 3. *Plot of solvent shifts of main bands of various 2 : 4-dinitrophenylhydrazones and related compounds against apparent* pK_a' *values.*

DISCUSSION

Neutral Solvents.—In the absence of hydrogen bonding, $\lambda(CHCl_3) - \lambda(EtOH)$ would be expected to be negative, on account of the larger dielectric constant of ethanol. This is found with 2 : 4-dinitroaniline (no. 8) (Fig. 3) which is a very weak acid so that the amino-hydrogen atom is not available for hydrogen bonding. With stronger acids such as 2 : 4-dinitrophenylacethydrazide (no. 10), an internal hydrogen bond is present: since it is present in both solvents, $\lambda(CHCl_3) - \lambda(EtOH)$ is also negative. With intermediate acid strengths external hydrogen bonding with the solvent and internal bonding are both possible. The ratio of the two will be influenced by several factors, such as the extent of conjugation and steric effects in these 2 : 4-dinitrophenylhydrazones. Thus there is little correlation between solvent shifts and acid strengths, when pK' is between −2·6 and −3·4, as shown in Fig. 3. However, in general, at acid strengths greater than pK_a' −1·2, as the acidity of the amino-hydrogen increases, the value of $\lambda(CHCl_3) - \lambda(EtOH)$ decreases. The different behaviour of acetone *p*-nitrophenylhydrazone (no. 6) (see p. 2616) confirms that the internal hydrogen bonding involves the *o*-nitro-group.

The group of solvents giving the bathochromic solvent shifts out of proportion to their dielectric constant is unexpected, but these shifts probably arise from π-complex formation between the solvent and solute.[19] In the polyene field the hitherto unexplained bathochromic solvent effects with carbon disulphide[20] may be attributed to the same cause.

Alkaline Solutions.—That dinitrophenylhydrazones ionise by loss of a proton from the amino-nitrogen atom[14] is shown by the stability of the *N*-alkyl derivatives[21] to alkali.[6] Thus light absorption by dinitrophenylhydrazones in alkaline solution involves the ion (A) and other canonical forms such as (B), (C), and (D).

The E_2^- and NO_2^- bands may be ascribed to two separate transitions: the E_2^- band to a transition of the type C $\longleftrightarrow$ A $\longleftrightarrow$ B, and the NO_2^- band to a transition of the type C $\longleftrightarrow$ D. The latter would be expected to give the longer-wavelength band, when *n* is

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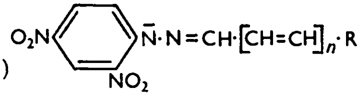
[18] Table 2, Refs. *c* and *g*.

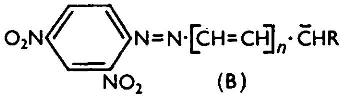
[19] For review see Orgel, *Quart. Rev.*, 1954, **8**, 422.

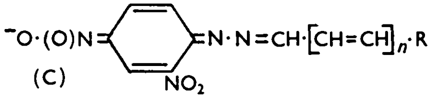
[20] Karrer and Jucker, "Carotenoids," Elsevier, Amsterdam, 1950.

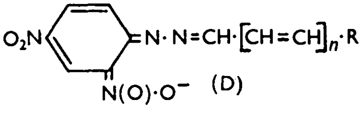
[21] Ragno, *Gazzetta*, 1945, **75**, 193, 200.

small, because the energy difference between (C) and (D), with a negative charge readily accommodated on any one of the four oxygen atoms, will be only the difference between the *o*- and *p*-quinonoid resonance energies, which will be smaller than the difference in energy between forms such as (B) and (C) where the negative charge is accommodated on the less electronegative carbon atom. Support for this assignment of the long-wavelength band is provided by the spectra in alkali of various 2 : 4-dinitrobenzene derivatives[16] (Table 1) which show bands of comparable intensities in the 500 mμ region, almost independently of the substituent in the 1-position provided it allows the formation of the ion.

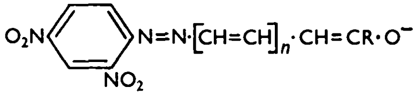

(A)

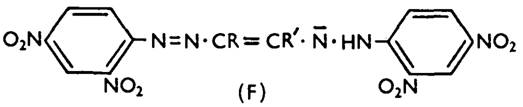

(B)

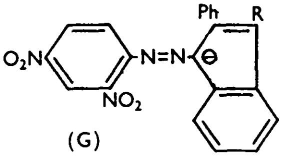

(C)


(D)

The E_2^- band is of interest as it appears to be the first example studied in detail of charge-resonance spectra in a vinylogous series of anions, although numerous cationic series have been investigated.[22, 23] Isolated examples of charge-resonance spectra involving vinylogous anions reported include 1 : 3-diketones, glutaconic derivatives and its vinylogues,[24] and the oxonols.[25] With the dinitrophenylhydrazone anions the convergence of wavelength of the maxima with increase of *n* is expected for a series in which the two extreme structures, *i.e.*, B and C, have different energies.[23]


(E)


(F)


(G)

Saturated substituents have little effect, since both ground and excited states are ionic, and will be affected similarly, so that the energy difference between the two states is unchanged, in contrast to the greater effect with the neutral molecules where only the excited state is ionic. Covalently unsaturated substituents may provide an alternative extreme structure, *e.g.*, (E), the energy of which will be lowered with respect to (B) by accommodation of the charge on the more electronegative oxygen instead of on a carbon atom. With bis-derivatives of α-dicarbonyl compounds similar but greater bathochromic shifts arise from contributions of structures such as (F). In the indenone derivatives (nos. 90 and 91), the high-intensity long-wavelength band results from the high stability[26] of the substituted *cyclo*pentadienyl anion (G).

[22] Thomas and Branch, *J. Amer. Chem. Soc.*, 1953, **75**, 4793; Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703; Beilenson, Fisher, and Hamer, *ibid.*, 1937, *A*, **163**, 138; Wizinger and Sontag, *Helv. Chim. Acta*, 1955, **38**, 363; Wizinger and Kölliker, *ibid.*, p. 372.

[23] Brooker and his co-workers, *Rev. Mod. Phys.*, 1942, **14**, 275, and numerous later papers; Herzfeld and Sklar, *ibid.*, p. 294.

[24] Schwarzenbach, Lutz, and Felder, *Helv. Chim. Acta*, 1944, **27**, 576; Bateman and Koch, *J.*, 1945, 216: Stobbe and Wildensee, *J. prakt. Chem.*, 1927, **115**, 163.

[25] Sveschnikov and Levkoev, *Zhur. obshchei Khim.*, 1940, **10**, 274; Hamer and Winton, *J.*, 1949, 1126; Knott, *J.*, 1952, 2399.

[26] Armit and Robinson, *J.*, 1922, 827; 1925, 1604: E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, p. 71.

EXPERIMENTAL

Heptane-3 : 4-*dione* 2 - 4-*Dinitrophenylhydrazone* (*no.* 22).—This compound was originally assigned the alternative structure 4-hydroxyhept-5-en-3-one 2 : 4-dinitrophenylhydrazone,[10] but the present spectroscopic results indicate the correct structure.

2 : 4-*Dinitrophenylhydrazone* of *Pyran*-2-*aldehyde* (*no.* 33).—This compound was obtained by Owen and Peto,[27] who suggested alternative structures. The above constitution was later suggested by Professor D. H. R. Barton [28] and is supported by the light absorption.

2 : 4-*Dinitrophenylhydrazones of* βγγ-*Trimethylvaleraldehyde* (*no.* 27), 5 : 5-*dimethylhex*-3-*en*-2-*one* (*no.* 55) *and* 2 : 2-*dimethylhex*-4-*en*-3-*one* (*no.* 59).—Reaction of *tert.*-butylmagnesium chloride with crotonaldehyde in ether,[29] followed by addition of aqueous ammonium chloride solution and ether-extraction, afforded a mixture which on fractionation gave βγγ-trimethylvaleraldehyde (40%), b. p. 96—101°/114 mm., n_D^{25} 1·4260 (cf. ref. 29, b. p. 56—57°/19 mm.), $\lambda_{max.}$ 280 and 290 mμ (ε 17, ε 17, in hexane) [2 : 4-*dinitrophenylhydrazone* (no. 27), m. p. 96—98°, light orange needles from methanol (Found : C, 54·9; H, 6·7; N, 17·6. $C_{14}H_{20}O_4N_4$ requires C, 54·9; H, 6·6; N, 17·6%)], and higher-boiling material. Further fractionation of the latter gave 2 : 2-dimethylhex-4-en-3-ol (15%), b. p. 110—114°/183 mm., n_D^{20} 1·4418 (cf. ref. 29, b. p. 75—76°/36 mm., n_D^{25} 1·4369). The 3 : 5-*dinitrobenzoate* crystallised from aqueous ethanol with m. p. 92—94° (Found : C, 55·6; H, 5·7; N, 9·2. $C_{15}H_{18}O_6N_2$ requires C, 55·9; H, 5·6; N, 8·7%). The 2 : 4-*dinitrophenylhydrazone* (no. 59) of 2 : 2-dimethylhex-4-en-3-one was formed directly from the unsaturated alcohol [30] in the cold and crystallised from methanol in orange needles, m. p. 132—136° (Found : C, 55·3; H, 6·1; N, 18·0. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9; N, 18·3%).

When the products from the Grignard reaction were washed in ether with aqueous sodium hydrogen sulphite, fractionation gave also the rearrangement product 5 : 5-*dimethylhex*-3-*en*-2-*ol*, b. p. 91—93°/52 mm., n_D^{23} 1·4360 (Found : C, 75·2; H, 12·6. $C_8H_{16}O$ requires C, 75·0; H, 12·6%), the 3 : 5-*dinitrobenzoate* of which crystallised from methanol with m. p. 130—134° (Found : N, 9·3. $C_{15}H_{18}O_6N_2$ requires N, 8·7%), and 5 : 5-*dimethylhexa*-1 : 3-*diene*, b. p. 41°/52 mm., n_D^{23} 1·4411, $\lambda_{max.}$ in EtOH 224 mμ (ε 25,000) (Found : C, 86·5; H, 13·1. C_8H_{14} requires C, 87·2; H, 12·8%). Oxidation of the alcohol with manganese dioxide [31] gave 5 : 5-dimethylhex-3-en-2-one, b. p. 99—105°/74 mm., n_D^{26} 1·4380, $\lambda_{max.}$ in EtOH 218, 234, and 314 mμ (ε 10,000, 9000, and 30 respectively) (cf. ref. 32, b. p. 78—80°/40 mm., n_D^{20} 1·4430). The 2 : 4-dinitrophenylhydrazone (no. 55) crystallised from ethanol in light red needles, m. p. 175° (cf. ref. 32, m. p. 159—161°).

2 : 4-*Dinitrophenylhydrazones of* 3-*Hydroxy*- (*nos.* 40 *and* 41) *and* 3-*Ethoxy*-3-*methylbutan*-2-*one* (*no.* 46) *and* 3-*Methylbut*-3-*en*-2-*one* (*no.* 53).—From 3-hydroxy-3-methylbutan-2-one in ethanol was obtained a mixture which was separated by chromatography into the *derivatives* of 3-ethoxy-3-methylbutan-2-one (no. 46), yellow needles (from methanol), m. p. 113—114° (Found : C, 50·1; H, 5·8; N, 18·3; OEt, 11·3. $C_{13}H_{18}O_5N_4$ requires C, 50·3; H, 5·8; N, 18·1; OEt, 14·5%), and of 3-methylbut-3-en-2-one (no. 53), m. p. 194—195° (cf. ref. 33, m. p. 192°). The latter was undepressed on admixture with a sample, kindly provided by Dr. N. Thorne, reported [34] as the derivative of 3-hydroxy-3-methylbutan-2-one. The revised structure is confirmed by the light absorption, behaviour on paper chromatography, and analysis (Found : C, 50·2; H, 4·5; N, 20·6. Calc. for $C_{11}H_{12}O_4N_4$: C, 50·0; H, 4·6; N, 21·2%).

From 3-hydroxy-3-methylbutan-2-one in water was obtained the corresponding 2 : 4-dinitrophenylhydrazone (no. 41), m. p. 145—147° after chromatography on alumina and crystallisation successively from benzene–light petroleum (b. p. 60—80°) and aqueous methanol (cf. ref. 35, m. p. 148°). The isomeric derivative (no. 40), unaffected by crystallisation from aqueous methanol, was converted into the high-melting derivative (no. 41) by chromatography on alumina.

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[27] Owen and Peto, *J.*, 1956, 1146.
[28] Barton, personal communication to Dr. L. N. Owen.
[29] Stevens, *J. Amer. Chem. Soc.*, 1935, **57**, 1112.
[30] Braude and Forbes, *J.*, 1951, 1762.
[31] Cf. Weedon, *Ann. Reports*, 1953, **50**, 169.
[32] Campbell, *J. Amer. Chem. Soc.*, 1937, **59**, 1980.
[33] Table 2, ref. *n*.
[34] Thorne, *J.*, 1956, 2587.
[35] Table 2, ref. i.

2 : 4-*Dinitrophenylhydrazone of* 2 : 5-*Dimethylhex*-4-*en*-3-*one* (*no.* 60).—*iso*Butyroin [10] (10 g.) and phosphorus oxychloride (5 g.) were heated in pyridine (20 ml.) for 3 hr. on the steam-bath. The cold, partly solidified product was dissolved in pentane and washed successively with dilute hydrochloric acid and sodium hydrogen carbonate solution. Distillation of the dried (Na_2CO_3) pentane solution afforded crude 4-chloro-2 : 5-dimethylhexan-3-one (2·5 g.) which with 2 : 4-dinitrophenylhydrazine in boiling glacial acetic acid [36] afforded the *derivative* (no. 60) of 2 : 5-dimethylhex-4-en-3-one which crystallised from hexane in orange leaves, m. p. 115—116° (Found: C, 54·6; H, 6·0; N, 18·1. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9; N, 18·3%).

2 : 4-*Dinitrophenylhydrazones of* 3-*Methoxybut*-3-*en*-2-*one* (*nos.* 62 *and* 63).—3 : 3-Dimethoxybutan-2-one [37] (1 g.) and 2 : 4-dinitrophenylhydrazine (2 g.) in pyridine [18] (10 ml.) were heated almost to the b. p. for several minutes. The product, on dilution with benzene and chromatography on alumina, afforded the isomeric *derivatives* of 3-methoxybut-3-en-2-one, m. p. 173—175° (no. 62), which crystallised from benzene–hexane in orange needles (0·25 g.) (Found: C, 47·6; H, 4·4; N, 19·9. $C_{11}H_{12}O_5N_4$ requires C, 47·2; H, 4·3; N, 20·0%), and m. p. 147—149° (no. 63), which crystallised from the mother-liquors in orange prisms (0·30 g.) (Found: C, 47·3; H, 4·5; N, 20·7%).

2 : 4-*Dinitrophenylhydrazone of* 3-iso*Propoxyhex*-2-*enone* (*no.* 64).—This *derivative*, prepared in pyridine as above from 3-*iso*propoxyhex-2-enone, crystallised from benzene–light petroleum (b. p. 40—60°) in crimson needles, m. p. 151—152° (Found: C, 54·3; H, 5·4; N, 16·5; OPr^i, 19·1. $C_{15}H_{18}O_5N_4$ requires C, 53·9; H, 5·4; N, 16·8; OPr^i, 17·7%).

Spectroscopic Measurements.—The spectra were determined by Miss D. Green using a Unicam S.P.500 spectrophotometer. Dimethylformamide was purified by drying over CaO and vacuum-distillation. Any resulting excess of base was neutralised by addition of 98—100% formic acid. Small amounts of acidic and basic impurities were determined by titration with aqueous standard acid and alkali, the bis-2 : 4-dinitrophenylhydrazone of diacetyl (no. 95) being used as indicator. The dimethylformamide used for determining the spectra of the un-ionised molecules was between 0·01N and 0·005N in formic acid. Submerged bands were resolved graphically, by assuming that the resolved bands were symmetrical about their maximum on a wavelength scale. The components were then evaluated so that their summation fitted the experimental absorption curve. The apparent pK_a' values in 10% v/v chloroform–ethanol were obtained graphically by plotting the extinction coefficient at the wavelength of the E_2^- (or in some cases the NO_2^-) band maximum against alkali concentration and taking the pK_a' value as equal to the logarithm of the alkali concentration when equal amounts of ionised and un-ionised dinitrophenylhydrazone were present.

We thank numerous colleagues who generously made samples of 2 : 4-dinitrophenylhydrazones available for this work, particularly the late Professor E. A. Braude (nos. 70, 71, 84, and 85), Dr. L. Crombie (no. 13), Dr. W. J. Hickinbottom (no. 41), Dr. L. N. Owen (no. 33), Dr. H. J. Vipond (no. 57), Dr. B. C. L. Weedon (nos. 66—68, 72) and Dr. K. R. H. Wooldridge (nos. 20, 30, 31, 58, 79—82, 86—89).

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[36] Djerassi, *J. Amer. Chem. Soc.*, 1949, **71**, 1003.

[37] Table 2, ref. *c*.