The erlenmeyer flask was attached to the cobalt hydrocarbonyl generator, and cobalt hydrocarbonyl diluted with synthesis gas was bubbled through the flask for about 5 minutes. The flask was removed from the generator and the solution transferred to a buret in an atmosphere of nitrogen. The solution was titrated in a 100-ml. beaker fitted with a stopper provided with holes for two electrodes, a buret and an inlet and an outlet tube. The inlet tube was connected to a nitrogen cylinder, the outlet tube to a mercury valve. By means of this arrangement, an inert atmosphere could be maintained during the titration. The aqueous cobalt hydrocarbonyl solution (25.00 ml.) was measured into the beaker and a buret containing 0.1 *N* sodium hydroxide inserted in the stopper. The following data were obtained at 26° with a Beckman *p*H meter (model H2).

0.1 *N* NaOH, ml.	*p*H	0.1 *N* NaOH, ml.	*p*H	0.1 *N* NaOH, ml.	*p*H
0.00	1.65	4.50	2.69	4.90	8.29
1.00	1.71	4.60	2.99	5.00	8.85
3.50	1.81	4.70	5.45	5.11	9.30
4.00	2.05	4.80	7.61	5.20	9.60

According to these data, the cobalt hydrocarbonyl solution was 0.0192 *M*. The *p*H of 1.65 indicates that the cobalt hydrocarbonyl is completely dissociated. (The *p*H of a completely dissociated 0.0192 *M* solution would be 1.72.) After standing for 14 days at room temperature, the solution was titrated again and found to be 0.0148 *M*.

Neither methyl orange nor methyl red could be used as indicators. They were discolored within a few seconds by both alkaline and acid solutions of cobalt hydrocarbonyl, possibly by reduction of the azo to a hydrazo group. A good indicator is phenolphthalein: Fifty ml. of an aqueous solution of cobalt hydrocarbonyl was titrated with 0.1 *N* sodium hydroxide in the presence of phenolphthalein. After titration, cobalt was determined by addition of ammonia and hydrogen peroxide, followed by treatment with concentrated sulfuric acid and electrolysis of the acid solution. The amount of cobalt determined by titration was 0.1656 g.; that by electrolysis was 0.1665.

The solubility of cobalt hydrocarbonyl in water was determined as follows: an erlenmeyer flask containing 50.0 ml. of distilled oxygen-free water and phenolphthalein indicator was fitted with a buret and an inlet and an outlet tube and attached to the cobalt hydrocarbonyl generator described above. A current of carbon monoxide containing approximately 1 millimole of $HCo(CO)_4$ per liter was bubbled through the water at 25° and a rate of 300 ml. per minute. Cobalt hydrocarbonyl could be detected in the gas stream leaving the erlenmeyer flask 5 minutes after the start of the experiment, and the experiment was continued for 15 minutes after this point had been reached. The flask was detached and the solution titrated with a 0.1 *N* NaOH solution; 28.0 ml. was required for neutralization. Thus the saturated aqueous solution was 5.6×10^{-2} *M* with respect to cobalt hydrocarbonyl.

Preparation of Cobalt Deuterocarbonyl.—One ml. of a pyridine solution containing 0.15 g. of dicobalt octacarbonyl was slowly added to dilute deuterium sulfate (prepared from 2 g. of sulfur trioxide and 4 g. of heavy water)[13] in a microversion of the apparatus described above for the generation of cobalt hydrocarbonyl. The cobalt deuterocarbonyl was swept out with helium and collected in a 500-ml. evacuated flask from which a gas sample was transferred to the gas cell. Mass spectrometric analysis of a similar preparation, in which argon was used instead of helium as the diluent gas, showed that the carbonyl gas consisted of about 35% of hydrocarbonyl and 65% of deuterocarbonyl. Since pure D_2SO_4 was used for the preparation, the presence of $HCo(CO)_4$ in $DCo(CO)_4$ is probably due to exchange reactions with pyridine, but this point was not investigated.

Infrared Spectra.—To obtain the spectra of $HCo(CO)_4$ and $DCo(CO)_4$ in the gas phase, two 10-cm. gas cells were filled at atmospheric pressure with helium containing approximately 0.5 millimole/liter of $DCo(CO)_4$ and $HCo(CO)_4$.

Determination of the spectra of cobalt hydrocarbonyl in hexane was carried out in a 0.1-mm. cell at a concentration of approximately 0.1 *M*. The spectrum of dicobalt octacarbonyl was carried out in a 0.014-mm. cell at a concentration of approximately 0.6 *M*. The spectrum of this solution in a 0.07-mm. cell revealed no additional bands.

The spectra were determined on a Perkin–Elmer Model 21 spectrophotometer.

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[13] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, THIS JOURNAL, **73**, 5741 (1951).

BRUCETON, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF KANSAS STATE COLLEGE]

Correlation of Color and Constitution. I. 2,4-Dinitrophenylhydrazones

BY G. DANA JOHNSON[1]

RECEIVED NOVEMBER 3, 1952

A method is described whereby $\lambda_{max.}$ of the ultraviolet absorption spectrum may be calculated from the structure of a 2,4-dinitrophenylhydrazone. The method is applicable to D.N.P.'s of all types of aldehydes and ketones, except cyclic ketones.

With reference to the formula of a 2,4-dinitrophenylhydrazone (Fig. 1), it is possible to express $\lambda_{max.}$ as the sum of three quantities: a constant quantity attributed to the central, recurring dinitrophenylhydrazone moiety, and two other quantities attributed to the groups R_1 and R_2. Thus, if the dinitrophenylhydrazone moiety is indicated by *N*, a series of equations of the form

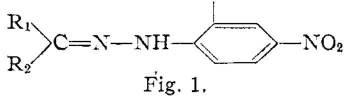

Fig. 1.

$$\lambda R_1 + \lambda R_2 + \lambda N = \lambda_{max.}$$

can be set up. Further, if attention is directed to those D.N.P.'s in which each R group is repeated in at least two compounds, it is possible by the least squares method to obtain a unique solution for each quantity in the above equation.

A first trial with 104 D.N.P.'s of aromatic, aliphatic and unsaturated aldehydes and ketones gave only fair results. Eighteen per cent. of the compounds gave deviations (obsd. − calcd.) of more than 4 mμ.

Better results came about through a division of the D.N.P.'s into three groups: group 1, diaryl ketones or vinylogs of these; group 2, aryl aliphatic ketones and aromatic aldehydes; group 3, aliphatic ketones and aldehydes. In this manner, values for the various R groups making up the D.N.P.'s and

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[1] Some of this work was carried out at Indiana University.

three different values of N were obtained which gave calculated values of $\lambda_{\max.}$ not differing from the observed values by more than 3 mμ.

Tables I, II and III give the melting points, log $\epsilon_{\max.}$ and the observed and calculated values of $\lambda_{\max.}$ for the compounds used in this work. The values for the various R groups are given in Table IV together with the number of compounds used to obtain the indicated value. Values in parentheses have been obtained from single compounds by difference. Thus, the value for *p*-chlorophenyl in group 1 is obtained from $\lambda_{\max.}$ (386 mμ) for the D.N.-P. of 4-chlorobenzophenone by subtracting the value for λ_{N_I} (199.3) and for phenyl (94.4), giving the value 92.3 for this group.

TABLE I

2,4-Dinitrophenylhydrazone of	M.p., °C.	log $\epsilon_{\max.}$	$\lambda_{\max.}$, mμ Obsd.	Calcd.
4,4′-Dichlorobenzophenone	240–241	4.49	385	385
4-Chlorobenzophenone	197–198	4.51	386	386
Benzophenone	240–241	4.51	387	387
3-Methoxybenzophenone[a]	233–234	4.47	387[b]	
2-Hydroxybenzophenone	250–251	4.44	389[b]	
4-Methylbenzophenone	231–233	4.47	390	390
4-Hydroxybenzophenone	226–227	4.47	390	393
4,4′-Dimethylbenzophenone	218–219	4.51	393	393
Phorone	108[c]	4.39[c]	395[c]	395
2-Hydroxy-5-methylbenzophenone	244–245	4.44	395[b]	
4-Methoxybenzophenone	228–229	4.47	396	394
Chalcone	248–249	4.58	398	397
4-Aminobenzophenone	189–191[d]	4.22	398[b]	
4,4′-Dimethoxybenzophenone	200–201	4.46	400	401
4,4′-Dihydroxybenzophenone	190–192[e]	4.45	401	399
1,5-Diphenyl-3-pentadienone	179–180	4.55	406	407
1,5-Diphenyl-2,4-pentadien-1-one	230–231	4.59	407	406
1,7-Diphenyl-1,4,6-heptatrien-3-one	179–180	4.57	418	416
1,9-Diphenyl-1,3,6,8-nonatetraen-5-one	199–200	4.61	424	425
4,4′-Bis-(dimethylamino)-benzophenone	273–274	4.44	440	440

[a] This compound furnished by Dr. L. H. Klemm of the University of Oregon. [b] These compounds were used to obtain values for groups based on single compounds. [c] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945). [d] Calcd. for $C_{19}H_{15}O_4N_5$: N, 18.56. Found: N, 18.82. [e] Calcd. for $C_{19}H_{14}O_6N_4$: N, 14.21. Found: N, 14.29.

TABLE II

2,4-Dinitrophenylhydrazone of	M.p., °C.	log $\epsilon_{\max.}$	$\lambda_{\max.}$, mμ Obsd.	Calcd.
Pivalophenone	192–193	4.38	366–367[a]	
Isobutyrophenone	161–162	4.40	368[a]	
m-Nitrobenzaldehyde	289–290	4.50	370	370
m-Nitroacetophenone	232–233	4.45	371	371
2-Naphthoylacetonitrile	232–233[b]	4.40	372–373[a]	
α-Chloroacetophenone	218–219	4.44	373–374[a]	
3,4-Dichlorobenzaldehyde	300–301[c]	4.51	375[a]	
2,4-Dichlorobenzaldehyde	226–227[d]	4.51	376[a]	
Benzaldehyde	239–240	4.48	377[e]	377
p-Chlorobenzaldehyde	269–270	4.50	377	377
α-Bromoacetophenone	220–221	4.42	377	378
o-Chlorobenzaldehyde	209–210	4.52	377[a]	
β-Benzoylpropionic acid	190–191	4.37	377[a]	
p-Chloroacetophenone	236–237	4.46	377–378	378
p-Bromoacetophenone	234–235	4.47	377–378	378
Acetophenone	247–248	4.40	378	378
m-Hydroxybenzaldehyde	260–261	4.47	378	378
Isovalerophenone	123–124	4.42	379[a]	
Benzoylacetic acid, ethyl ester	246–247[f]	4.52	379[a]	
Propiophenone	193–194	4.43	380	379
p-Chloropropiophenone	222–223[g]	4.46	380	379
p,α-Dibromoacetophenone	218–219	4.48	380	379
m-Hydroxyacetophenone	256–257[h]	4.44	380	380
Laurophenone	93–94[i]	4.43	380[a]	
Salicylaldehyde	254–255	4.44	381	382
Desoxybenzoin	200–201	4.46	381[a]	
m-Tolualdehyde	194–195	4.47	381[a]	
o-Nitrobenzaldehyde	250–251	4.46	381[a]	
p-Nitrobenzaldehyde	321–322	4.56	382[a]	
Butyrophenone	191–192	4.46	383[a]	
Valerophenone	167–168	4.46	383[a]	
Caprophenone	167–168	4.46	383[a]	
Methyl 3-thienyl ketone[j]	265–266	4.42	383[a]	
o-Veratraldehyde	223–224	4.49	383[a]	
o-Hydroxyacetophenone	213–214	4.41	384	383
p-Isopropylacetophenone	182–183	4.45	384[a]	
p-Methylacetophenone	259–260	4.45	384–385[a]	
2-Naphthaldehyde	270–271	4.56	386	386
2-Acetonaphthone	261–262	4.50	386	387
Benzoin	235–236	4.49	386[a]	
Mesityl oxide	205–206	4.39	386[a]	
β-Benzoylacrylic acid	229–230	4.45	386–387[a]	
p-Phenylacetophenone	241–242	4.50	387	387
o-Methoxybenzaldehyde	248–249	4.49	387[a]	
2-Furaldehyde	222–223	4.49	387[a]	
α-Bromo-*p*-phenylacetophenone	228–229	4.48	387–388	387
2-Hydroxy-5-methylacetophenone	273–274	4.38	388[a]	
α-Amylcinnamaldehyde	174–175	4.59	389[a]	
Anisaldehyde	253–254	4.49	390	390
p-Hydroxybenzaldehyde	270–271	4.40	391	390
p-Methoxyacetophenone	227–228	4.44	391	391
Cinnamaldehyde	254–255	4.59	391	392
p-Hydroxypropiophenone	240–241[k]	4.43	391–392	392
Veratraldehyde	261–262	4.49	392	391
3,4-Dimethoxypropiophenone	178–179	4.42	392	393
Methyl 2-thienyl ketone	243–244	4.46	393[a]	
Vanillin	271–272	4.48	393[a]	
3-Benzyloxy-4-methoxybenzaldehyde	196–197	4.49	394[a]	
4-Phenyl-3-buten-2-one	225–226	4.56	395[l]	394
β-Resorcylaldehyde	302–303	4.41	395[a]	
3,4-Diethoxybenzaldehyde	219–220	4.51	396[a]	
2,4-Dimethoxybenzaldehyde	257–258	4.50	400[a]	

TABLE II (*Continued*)

2,4-Dinitrophenylhydrazone of	M.p., °C.	log $\epsilon_{\max.}$	$\lambda_{\max.}$, mμ	
			Obsd.	Calcd.
p-Aminoacetophenone	266–267	4.42	403[a]	
6-Phenyl-3,5-hexadien-2-one	224–225	4.62	407[a]	
4-(4-Hydroxy-3-methoxyphenyl)-3-buten-2-one	234–235	4.54	416[a]	
p-Dimethylaminobenzaldehyde	236–237	4.48	432[a]	
p-Diethylaminobenzaldehyde	206–207	4.50	442[a]	

[a] These compounds were used to obtain values for groups based on single compounds. [b] Calcd. for $C_{19}H_{13}O_4N_5$: N, 18.66. Found: N, 18.96. [c] Calcd. for $C_{13}H_8O_4N_4Cl_2$: N, 15.78. Found: N, 16.02. [d] Calcd. for $C_{13}H_8O_4N_4Cl_2$: N, 15.78. Found: N, 15.92. [e] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945). [f] Calcd. for $C_{17}H_{16}O_6N_4$: N, 15.05. Found: N, 15.26. [g] Calcd. for $C_{15}H_{13}O_4N_4Cl$: N, 16.07. Found: N, 16.15. [h] Calcd. for $C_{14}H_{12}O_5N_4$: N, 17.72. Found: N, 17.65. [i] Calcd. for $C_{24}H_{32}O_4N_4$: N, 12.72. Found: N, 12.66. [j] The carbonyl compound was furnished by Dr. E. E. Campaigne of Indiana University. [k] Calcd. for $C_{15}H_{14}O_5N_4$: N, 16.96. Found: N, 17.29. [l] H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *J. Chem. Soc.*, 2696 (1949).

TABLE III

2,4-Dinitrophenylhydrazone of	M.p., °C.	log $\epsilon_{\max.}$	$\lambda_{\max.}$, mμ	
			Obsd.	Calcd.
Formaldehyde	164–165	4.31	346	349
1,3-Dichloro-2-propanone	132–133[a]	4.38	348	347
Malonaldehydic acid	150[b]	4.29[b]	351[b]	352
Chloro-2-propanone	125–126	4.36	354	355
β-Oxoglutaric acid, diethyl ester	86–87[c]	4.37	356	355
Acetaldehyde	160–161	4.34	356	356
α-Tolualdehyde	121–122	4.37	357	356
Propionaldehyde	154–155	4.36	357	357
Hydrocinnamaldehyde	142–144	4.35	357	357
Caproaldehyde	107–108	4.36	357–358	358
Butyraldehyde	120–121	4.34[b]	358[b]	358
Isobutyraldehyde	184–185	4.35	358	358
Isovaleraldehyde	116–117	4.35	358	358
Lauraldehyde	104–105	4.36	358	358
Acetoacetic acid, ethyl ester	93–94	4.35	358	359
Acetoacetic acid, methyl ester	119–120	4.35	358[d]	
Enanthaldehyde	107[b]	4.30[b]	358[b]	359
Valeraldehyde	104–105	4.35	359	358
Acetoacetic acid	125[b]	4.31[b]	360[b]	359
Phenyl-2-propanone	154–155	4.37	363	363
1,3-Diphenyl-2-propanone	108–109	4.39	363	363
Acetone	125–126	4.35	363–364	363
3 Methyl-2-butanone	124–125	4.35	364	365
2-Butanone	115[b]	4.34[b]	365[b]	364
3-Butyn-2-one	181[b]	4.41[e]	365[e]	364
2-Pentanone	142–143	4.37	365	365
4-Methyl-2-pentanone	80–81	4.36	365	365
4-Phenyl-2-butanone	128–129	4.38	365	365
α-Oxobutyric acid	191[b]	4.41[b]	365[b]	365
2-Hexanone	108[b]	4.29[b]	365[b]	366
Levulinic acid	205[b]	4.36[b]	365[b,d]	
1-Hexyn-3-one	136–137[e]	4.42[e]	365[e]	366
2-Heptanone	73–74	4.36	366	365
2-Tridecanone	70–71	4.35	366	366
3-Pentanone	156–157	4.40[b]	366[b]	366
2-Octanone	59–60	4.34	366	366
α-Oxoisovaleric acid	194[b]	4.40[b]	366[b]	367
3-Heptanone	80–81[f]	4.37	366–367	367
2,4-Dimethyl-3-pentanone	92–94	4.37	367	367
3-Tetradecanone	45–47[g]	4.36	367	367
Butyrone	71–73	4.38	368	368
Isovalerone	94–95	4.37	368	368
1-Hydroxy-1-phenyl-2-propanone	174[b]	4.34[b]	370[b,d]	
Crotonaldehyde	196–197	4.46	373[d]	

[a] Calcd. for $C_9H_8O_4N_4Cl_2$: N, 11.73. Found: N, 11.81. [b] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945). [c] Calcd. for $C_{15}H_{18}O_8N_4$: N, 14.92. Found: N, 14.80. [d] These compounds were used to obtain values for groups based on single compounds. [e] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946). [f] Calcd. for $C_{13}H_{18}O_4N_4$: N, 19.04. Found: N, 19.26. [g] Calcd. for $C_{20}H_{32}O_4N_4$: N, 14.28. Found: N, 14.39.

The data of Table IV are divided in two parts. The first part contains the values for aromatic groups and vinylogs of these for use with compounds in groups 1 and 2. The second part consists of the values for aliphatic and related groups for use with compounds in groups 2 and 3. To illustrate the use of Table IV in predicting $\lambda_{\max.}$, two examples are given.

The D.N.P. of *p*-phenylbenzaldehyde is in group 2. The value of $\lambda_{\max.}$ (calcd.) is $\lambda N_2 + \lambda p\text{-}C_6H_5\text{-}C_6H_4\text{–} + \lambda H\text{–} = 198.4 + 104.5 + 83.0 = 385.9$ mμ.

Propargylaldehyde D.N.P. is a group 3 compound. The value of $\lambda_{\max.}$ (calcd.) is $\lambda N_3 + \lambda CH{\equiv}C\text{–} + \lambda H\text{–} = 198.2 + 83.8 + 75.2 = 357.2$ mμ.

Inspection of the data of Table IV reveals that the order given roughly parallels the order of the electronegativities of these groups (*cf.* M. S. Kharasch[2]). The *o*- and *p*-nitrophenyl groups are prominent exceptions.

It is interesting to note that in all cases of substituted phenyls in Table IV, the magnitude of the values of the various isomers lies in the order para > ortho > meta. The value for the 2-thienyl group is greater than that of the 3-, as would be expected from the commonly accepted view that the 2-thienyl group is like the ortho isomer, while the 3- is like the meta isomer. The 2-furyl group has a value between the values for the isomeric thienyl groups.

It will be noticed that, with two exceptions, saturated aliphatic hydrocarbon radicals of group 2 lie in the range 85–89; those of group 3, 84–85. The isopropyl and *t*-butyl groups have much lower values (73–74) than other members of the group 2 series. The tentative values for these groups were obtained from $\lambda_{\max.}$ of the D. N. P.'s of isobutyrophenone and pivalophenone. On the other hand, the value for the isopropyl radical in group 3 has the normal value (84) of other hydrocarbon radicals in this group.

The cause of the additivity of the R group values

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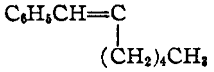
(2) M. S. Kharasch and R. E. Marker, THIS JOURNAL, **48**, 3130 (1926); M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

to give $\lambda_{max.}$ is not known, and there does not appear to be any precedent by which their physical significance can be assessed. Wave lengths are not additive, but an actual trial using frequencies was not successful, nor would it be expected since the method works so well with wave lengths.

TABLE IV

R GROUP VALUES

Group $2,4-(NO_2)_2C_6H_2NHN{=}C{=}$	Group 1 $N_1 = 199.4$	No. of comp. used 16	Group 2 $N_2 = 198.4$	No. of comp. used 27
Aromatic groups				
p-$(C_2H_5)_2NC_6H_4$			$(160.6)^a$	
p-$(CH_3)_2NC_6H_4$	120.3	2	(150.6)	
3-CH_3O-4-$HOC_6H_3CH{=}CH$			(133.5)	
$C_6H_5CH{=}CH{-}CH{=}CH$	112.9	3	(124.5)	
p-$H_2NC_6H_4$	(104.7)		(120.5)	
2,4-$(CH_3O)_2C_6H_3$			(118.6)	
3,4-$(C_2H_5O)_2C_6H_3$			(114.6)	
2,4-$(HO)_2C_6H_3$			(113.6)	
3-$C_6H_5CH_2O$-4-$CH_3OC_6H_3$			(112.6)	
3-CH_3O-4-HOC_6H_3			(111.6)	
$C_6H_5CH{=}CH$	103.9	3	111.1	2
2-C_4H_3S (2-thienyl)			(110.5)	
3,4-$(CH_3O)_2C_6H_3$			109.5	2
p-HOC_6H_4	100.0	2	108.7	2
p-$CH_3OC_6H_4$	100.8	2	108.6	2
 $C_6H_5CH{=}C{-}(CH_2)_4CH_3$			(107.6)	
2-C_4H_3O (2-furyl)			(105.6)	
o-$CH_3OC_6H_4$			(105.6)	
2-HO-5-$CH_3C_6H_3$	(101.7)		(105.5)	
p-$C_6H_5C_6H_4$			104.5	2
2-$C_{10}H_7$			104.1	2
$(CH_3)_2C{=}CH$	97.8	2	(103.5)	
p-$CH_3C_6H_4$	96.8	2	(102.0)	
2,3-$(CH_3O)_2C_6H_3$			(101.6)	
p-$(CH_3)_2CHC_6H_4$			(101.5)	
o-HOC_6H_4	(95.7)		100.6	2
p-$O_2NC_6H_4$			(100.6)	
3-C_4H_3S (3-thienyl)			(100.5)	
o-$O_2NC_6H_4$			(99.6)	
m-$CH_3C_6H_4$			(99.6)	
m-HOC_6H_4			97.1	2
p-BrC_6H_4			96.0	2
p-ClC_6H_4	92.8	2	95.7	3
o-ClC_6H_4			(95.6)	
C_6H_5	93.9	7	95.1	4
m-$CH_3OC_6H_4$	(93.7)			
2,4-$Cl_2C_6H_3$			(94.6)	
3,4-$Cl_2C_6H_3$			(93.6)	
m-$O_2NC_6H_4$			88.6	2

$2,4-(NO_2)_2C_6H_2NHN{=}C{=}$	Group 2 $N_2 = 198.4$	27	Group 3 $N_3 = 198.2$	39
Aliphatic groups				
$CH_3CH{=}CH$			(99.6)	
$HOOC{-}CH{=}CH$	(93.0)			
$C_6H_5CH(OH)$	(92.5)		(89.5)	
$CH_3(CH_2)_5$			85.3	2
$CH_3(CH_2)_3$	(89.5)		85.1	3
$CH_3(CH_2)_{10}$	(86.5)		85.0	3
$CH_3(CH_2)_2$	(89.5)		84.8	4
$CH_3(CH_2)_4$	(89.5)		84.8	2
$(CH_3)_2CHCH_2$	(85.5)		84.8	3
$HOOC{-}CH_2CH_2$	(83.5)		(84.5)	
$(CH_3)_2CH$	(74.5)		84.3	3
$(CH_3)_3C$	(73.0)			
$C_6H_5CH_2CH_2$			84.1	2
CH_3CH_2	85.2	4	83.8	6
$CH{\equiv}C$			83.5	2
HOOC			83.2	2
$BrCH_2$	84.6	3		
$C_6H_5CH_2$	(87.5)		82.6	3
CH_3	84.1	10	82.3	16
$C_2H_5OOC{-}CH_2$	(85.5)		78.6	2
$HOOC{-}CH_2$			78.5	2
H	83.0	10	75.2	12
$ClCH_2$	(80.0)		74.6	2
$NC{-}CH_2$	(70.0)			

[a] Values in parentheses were obtained from single compounds by difference (see text).

Experimental

The D.N.P.'s were made by a method earlier described.[3] The ultraviolet absorption spectra were determined with a Beckman model DU spectrophotometer whose wave length scale had been calibrated at the hydrogen alpha line (656.3 mμ). Merck and Co. reagent grade chloroform was the solvent throughout the investigation.

A number of investigators[4] have reported ultraviolet absorption data for some 2,4-dinitrophenylhydrazones in alcohol and in chloroform solution. Early in this work, several compounds were checked with previous data and some were found to give slightly different values. It was found that the deviations were random in character, and were probably due to impurities in the samples or the solvents used. As a result, all previous data were checked, insofar as possible. Where significant differences occurred, the D.N.P. was remade using a pure sample of the aldehyde or ketone. The derivative was crystallized several times from at least three different solvents, the last solvent used being alcohol or chloroform. Where the D.N.P.'s were not available for checking earlier work, the values were used as reported if the data were internally consistent.

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