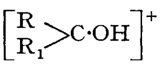
124. *Formation and Structure of Some Organic Molecular Compounds. Part II. Molecular Compounds of* s-*Trinitrobenzene with Some Unsaturated Ketones.*

By Joseph Weiss.

It is shown that a connection exists between the purely organic molecular compounds (cf. Part I; J., 1942, 245) and certain inorganic–organic molecular compounds. This has been demonstrated in the case of some ketones (dibenzylidene-, dicinnamylidene-, and di-*p*-anisylidene-acetone, etc.) in which the carbonyl group forms part of the conjugated system and which are known to form deeply coloured molecular compounds with strong acids on account of their basic properties. As this high proton affinity must be concurrent with the tendency to transfer electrons, these ketones should be capable of acting as donor molecules, *e.g.*, towards polynitro-compounds. Several new molecular compounds of these ketones with *s*-trinitrobenzene have been prepared, and their structure discussed.

The organic molecular compounds are usually classified as purely organic (*e.g.*, those of polynitro-compounds, or quinhydrones) and as organic–inorganic, the latter being largely represented by the extensive group of the " oxonium salts " of alcohol, ethers, and ketones with strong acids and certain metal salts. It is the purpose of this communication to show that there exists a close link between the two classes, as now demonstrated in the case of certain (fully conjugated) ketones.

It is well known that many unsaturated ketones dissolve in concentrated sulphuric acid with a deep colour (cf. Hammett, " Physical Organic Chemistry," McGraw Hill, 1941). All these addition products with strong acids represent salts which are easily hydrolysed, their stability depending on the strength of the acid and the basicity of the ketone under consideration. Salt formation is appreciable in those cases where the ketone represents a system of fully conjugated double bonds. The addition of the proton then results in the formation of a positive ion with a resonance structure and with a non-localised charge (I); both are essential for the appearance of the deep colour actually observed (charge resonance spectra; cf. Mulliken, *J. Chem. Physics*, 1939, **7**, 570). The binding of the proton to the conjugated system of the ketone, with a certain localisation to the oxygen of the carbonyl group, involves, at least partly, the transfer of an electron from the carbonyl group to the proton. We may conclude, therefore, that, as with increasing basicity of the ketone the proton is more strongly bound, at the same time its tendency to give off an electron increases.*



$\left[\begin{matrix}R\\R_1\end{matrix}{>}C{\cdot}OH\right]^+$

(I.)

The basic properties of these ketones must therefore be co-existent with comparatively low ionisation potentials, and these ketones should be capable of acting as electron donors towards suitable acceptor molecules, which is an essential condition for the formation of molecular compounds (Part I, *loc. cit.*). We have found that some of these fully conjugated ketones are capable of forming stable molecular compounds with *s*-trinitrobenzene.

It was known that, *e.g.*, dibenzylideneacetone forms a molecular compound with picric acid (cf. Reddelien, *J. pr. Chem.*, 1915, **91**, 239), but as picric acid is itself a strong acid, the possibility exists—it is even highly probable—that it attaches itself by virtue of the proton of its hydroxyl group. Another small group of molecular compounds of ketones with *s*-trinitrobenzene is known (Sudborough, J., 1916, **109**, 1339), but in these ketones the carbonyl group does not form part of the conjugated system. The ketones are (with the one exception of distyryl diketone, for which, however, the only molecular compound reported has the ratio 1 ketone : 2 nitro-compound) all of the type $R{\cdot}CO{\cdot}CH_3$ (with R = α-naphthyl, phenyl-α-naphthyl, etc.), and the ability of these compounds to give molecular compounds is not due to the increase in " basicity " owing to the presence of the carbonyl group, as is clearly shown by the fact that the same group R (without the CO group) is equally capable of giving stable molecular compounds with *s*-trinitrobenzene.

This is quite different in the case of the ketones now studied (see table). Whereas molecular *compounds* are easily obtained from dibenzylidene-, benzylidene-*p*-anisylidene- di-*p*-anisylidene-, and dicinnamylidene-acetone, no molecular compound formation could be obtained with benzylidene-, *p*-anisylidene-, or cinnamylidene-acetone, which are all of the type $R{\cdot}CO{\cdot}CH_3$.

This also shows that, unlike the cases investigated by Sudborough, it is not the isolated hydrocarbon group (R) which is responsible for molecular compound formation, but the completely interlinked conjugated system, the link being provided by the carbonyl group. It is also known from absorption spectra of conjugated systems that the C=O double bond acts similarly to the (CH=CH) bond, *i.e.*, the π-electrons of oxygen act similarly to those of carbon (cf. Hausser, Kuhn, Smakula, and Deutsch, *Z. physikal. Chem.*, 1935, *B*, **29**, 378). This view is further supported by the molecular ratios as summarised in the table. If the two conjugated

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* The conditions are similar to the case of ammonia and methylamine, where the stronger base methylamine has a greater proton affinity but lower ionisation potential as compared with ammonia (cf. Goeppert-Mayer and McCallum, *Rev. Mod. Physics*, 1942, **14**, 248).

Substance.	Relative basicity * (dibenzylidene-acetone = 1).	Molecular compound with *s*-trinitro-benzene.	Molecular ratio, ketone : *s*-trinitro-benzene.	M. p.
Benzylideneacetone	<1	(Not formed)	—	—
Dibenzylideneacetone	1	Light yellow	1 : 2	127°
		Light yellow	2 : 1	115
p-Anisylideneacetone	~1·5	(Not formed)	—	—
Benzylidene-*p*-anisylideneacetone	4·6	Yellow	1 : 1	114
		Yellow	1 : 2	124
Di-*p*-anisylideneacetone	6·0	Orange	1 : 1	115
		Orange	2 : 1	122
Cinnamylideneacetone	~1	(Not formed)	—	—
Dicinnamylideneacetone	4·2	Orange	1 : 1	113
		Yellow	1 : 2	110

* Measurements by Stobbe and Haertel (*Annalen*, 1909, **370**, 99), supplemented by author's measurements.

groups linked to the carbonyl group were to act independently, one should get a molecular ratio 1 ketone : 2 nitro-compound, whereas one also finds the ratio 1 : 1 or even 2 : 1.

The ionic structure of molecular compounds discussed in Part I represents a limiting case which has to be assumed, particularly in those cases where deep coloration accompanies molecular-compound formation and where the presence of ions or ion pairs is supported by other evidence. As mentioned in Part I (p. 246), the binding of the compounds may only be partly ionic, and other types of interactions may play their part under certain conditions.

A molecule of fully conjugated double bonds represents an electronic system similar to that of a metal (cf. London, *J. Physical Chem.*, 1942, **46**, 305); in general, the interaction between two such molecules could correspond to a sort of " alloy formation." As in the case of metals, if the two compounds are electronically very similar in their character we should expect only solid solutions to be formed, whereas if we have loosely bound electrons in the one component and an electron affinity in the other we should get molecular-compound formation corresponding to the intermetallic compounds in the case of metals.

Just as in the case of ordinary ionic compounds where the purely ionic character may partly disappear under certain (well-known) conditions, so the ionic molecular compounds with ions of high polarisability and great deformability of the electron clouds will show a partial redistribution of the electrons from the negative ion towards the positive ion. This amounts to a partial transfer of the electron, and in these cases the ionic compound is represented by the general formula $[A]^{\delta+}[B]^{\delta-}$ (where δ indicates as usual the fraction of the electronic charge). Molecular compounds of this type might show only a light colour not appreciably different from that of their components, and the molecular compounds discussed in this paper, for instance, belong to this group.

Experimental.—The preparation of the ketones followed the methods used by Baeyer and Villiger (*Ber.*, 1902, **35**, 1189; 1903, **36**, 2774; 1905, **38**, 582). The molecular compounds were prepared from the components in absolute alcohol and recrystallised from that solvent.

*Dibenzylideneacetone–*s*-Trinitrobenzene.*—1 : 2-*Compound*, m. p. 127° (Found: C, 52·7; H, 2·9; N, 11·9. $C_{17}H_{14}O,2C_6H_3O_6N_3$ requires C, 52·7; H, 3·0; N, 12·7%). 2 : 1-*Compound*, m. p. 115° (Found: C, 70·0; H, 4·3; N, 6·5. $2C_{17}H_{14}O,C_6H_3O_6N_3$ requires C, 70·45; H, 4·6; N, 6·2%).

*Benzylidene-*p*-anisylideneacetone–*s*-Trinitrobenzene.*—1 : 1-*Compound*, m. p. 114° (Found: C, 59·3; H, 4·2; N, 8·8. $C_{18}H_{16}O_2,C_6H_3O_6N_3$ requires C, 60·3; H, 4·0; N, 8·8%). 1 : 2-*Compound*, m. p. 124° (Found: C, 52·1; H, 3·2; N, 11·7. $C_{18}H_{16}O_2,2C_6H_3O_6N_3$ requires C, 52·1; H, 3·2; N, 12·15%).

*Dianisylideneacetone–*s*-Trinitrobenzene.*—1 : 1-*Compound*, m. p. 115° (Found: C, 59·3; H, 4·2; N, 8·8. $C_{19}H_{18}O_3,C_6H_3O_6N_3$ requires C, 59·2; H, 4·1; N, 8·3%). 2 : 1-*Compound*, m. p. 122° (Found: C, 65·5; H, 5·12; N, 5·3. $2C_{19}H_{18}O_3,C_6H_3O_6N_3$ requires C, 65·8; H, 4·9; N, 5·2%).

*Dicinnamylideneacetone–*s*-Trinitrobenzene.*—1 : 1-*Compound*, m. p. 113° (Found: C, 65·5; H, 4·2; N, 8·1. $C_{21}H_{18}O,C_6H_3O_6N_3$ requires C, 65·0; H, 4·2; N, 8·4%). 1 : 2-*Compound*, m. p. 110° (Found: C, 55·0; H, 3·3; N, 12·6. $C_{21}H_{18}O,2C_6H_3O_6N_3$ requires C, 55·7; H, 3·4; N, 11·8%).

The same procedure was adopted in the attempted preparation of the molecular compounds of benzylidene-, anisylidene-, and cinnamylidene-acetone, but no such compounds could be obtained even by varying the solvent or under different conditions.

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