The action of chloral on alkaloids in general.—When an alkaloid is dissolved in carbon disulfide and chloral or bromal added to it, a precipitate is formed which is insoluble in ether. This is true of every alkaloid soluble in carbon disulfide which we have studied. The powder formed is an additive compound of the alkaloid and the aldehyde.

The following alkaloids were studied: Cevadine, cevine, nicotine, codeine, brucine, strychnine, cocaine, conine, chinchonine and papaverine. In every case the precipitate formed was insoluble in ether.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TRIPHENYLMETHYL. XXIV. THE ADDITIVE COMPOUNDS OF TRIPHENYLMETHYL AND SOME SATURATED HYDROCARBONS.

BY M. GOMBERG AND C. S. SCHOEPFLE.

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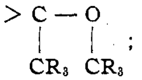
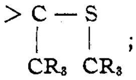
The unsaturated character of triphenylmethyl is strikingly illustrated by its tendency to unite spontaneously with compounds of various types. In fact, it is rather difficult to find solvents from which triphenylmethyl crystallizes without taking up solvent of crystallization. Triphenylmethyl has been found to unite in this manner with ethers, esters, ketones, aldehydes, and nitriles; with olefines and with aromatic hydrocarbons; with carbon disulfide, with chloroform, etc.[1]

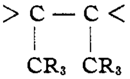
The trivalency of carbon in triphenylmethyl is sufficient in itself to account for the additive tendencies of the free radical. On the other hand, it seems rather difficult to find a plausible explanation in terms of graphic formulas for the additive compounds thus produced. In the esters, ketones, and aldehydes, we have the double linking C = O; in carbon disulfide, the corresponding C = S; while in the aromatic hydrocarbons and in the olefines, we have the grouping C = C. But it seems hardly probable that in all these instances triphenylmethyl adds itself in virtue of the double bond in the various compounds. If this were the case, we should expect the addition to result in fairly stable substances, as for example, in the addition of the Grignard reagent to aldehydes, ketones, esters, etc.



$$>\underset{\substack{|\\ CR_3}}{C}-\underset{\substack{|\\ CR_3}}{O};$$



$$>\underset{\substack{|\\ CR_3}}{C}-\underset{\substack{|\\ CR_3}}{S};$$



$$>\underset{\substack{|\\ CR_3}}{C}-\underset{\substack{|\\ CR_3}}{C}<$$

But as a matter of fact, the addition compounds in the triphenylmethyl series are extremely unstable, dissociating readily at temperatures of 50–100°, into the original components. Indeed, the stability of these additive compounds is apparently no greater than that of the additive com-

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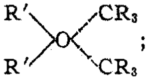
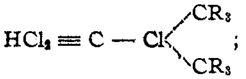
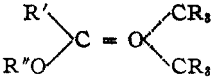
[1] THIS JOURNAL, 36, 1147 (1914).

binations that result from triphenylmethyl with ethylene oxide, with ethers, with chloroform, all of which contain no double bond of any kind whatsoever.

An explanation in terms of the valence hypothesis for the existence of all the various additive compounds might still be had, if we are willing to assume that the oxygen, the sulfur, or the chlorine atom, as the case may be, functions as having acquired a higher valence state than it ordinarily possesses. Sulfur and chlorine are known, of course, to be endowed with the capacity of variable valence, and of late, although the proof is far from satisfactory, it has become customary to consider that oxygen, too, can acquire a higher than its usual valence state.







While such an explanation might perhaps account for the addition of triphenylmethyl to ethers, esters, etc.,[1] the question still remains unanswered as to the mechanism of the addition of the free radical to the olefines.

The problem of finding a satisfactory explanation in terms of the valence hypothesis that would account for the existence and the nature of all of these additive compounds becomes still more puzzling when we take into consideration the rather unusual circumstance that triphenylmethyl unites with completely saturated hydrocarbons. In a previous paper[2] it has been shown that such additive compounds are probably formed. But since the hydrocarbons employed in those experiments consisted merely of purified samples of petroleum ethers, the alternative was not entirely excluded, that these hydrocarbons might have still retained a small amount of some member of the olefine series. Because of the theoretical interest attached to this phase of the unsaturated character of triphenylmethyl, we have repeated the experiments, employing this time individual paraffins of natural origin which were most carefully purified and fractionated, and also some synthetic aliphatic and alicyclic hydrocarbons.

The Hydrocarbons.—The hexane and heptane used were pure products obtained from petroleum, obtained from a well-known firm. They were further purified by shaking with concentrated sulfuric acid for ten hours, with concentrated nitric acid for ten hours, and with alkaline permanganate for six hours, after which they were dried and fractionated. The octane (normal) and the decane (di-isoamyl) were synthetic products, but nonetheless, these were also shaken with concentrated sulfuric acid before fractionation. The cyclohexane and methylcylochexane were carefully distilled before using. After this treatment, all the hydrocarbons men-

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[1] This Journal, **23**, 501 (1901).

[2] *Ber.*, 38, 1338 (1905).

tioned above were found to be free from olefines or other similar reducing constituents.

The Additive Compounds.—The triphenylmethyl was prepared for these experiments by the action of metallic mercury upon triphenylchloromethane, with the addition of a small amount of powdered lead, which greatly facilitates the settling of the finely divided mercurous chloride formed during the reaction. Ten grams of the chloride, 10 g. of mercury, and about 0.5 g. of lead powder are placed in a small Drexel bottle, and enough dry benzene, about 75 cc., is added to almost fill the bottle. The stopper is removed and the bottle is provided with a well fitting cork, covered with parchment paper in such a manner that none of the paper projects beyond the neck of the flask. After several hours' shaking, the reaction is complete. The mercury is now allowed to settle, the cork removed, and there is rapidly inserted the glass connection which permits the syphoning off of the clear liquid into the apparatus, which has been described in a previous paper.[1] The benzene is distilled under reduced pressure, and the product recrystallized from hot acetone. The solvent is drawn off and the beautifully crystalline triphenylmethyl is washed, and then dried in a stream of carbon dioxide and finally in vacuum, the crystals remaining all the while in the same apparatus.

The triphenylmethyl prepared in the above manner was converted into the various additive compounds as follows: About 60 cc. of the saturated hydrocarbon intended for combination were added and heated as high as its boiling point would permit. The hot solution was then filtered off from the undissolved triphenylmethyl into a second similar piece of apparatus. On cooling, the additive compound separated usually in almost colorless crystals. The mother liquid was drawn off and the crystals were dried in a stream of carbon dioxide, and finally in vacuum. In the case of the higher boiling hydrocarbon decane, the crystals before being dried were freed from the adhering mother liquid by washing with a small amount of low boiling petroleum ether. It may be said that the solubility of triphenylmethyl in the fatty hydrocarbons is but slight at room temperature, decreasing, apparently, with the increase of the molecular weight of the hydrocarbon; on the other hand, the solubility shows a marked increase with the rise of temperature of the solvent. In the alicyclic hydrocarbons triphenylmethyl is more soluble, expecially when the solvent is hot.

Dissociation of the Additive Compounds.—A sample of the additive derivative was weighed out in a porcelain boat, placed into a glass tube about 15 inches long and heated in an air bath at 80–110° for one to one and a half hours, a slow stream of dry carbon dioxide being passed at the same time through the tube. In the case of the additive derivatives with

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[1] *Ber.*, **37**, 2034 (1904).

hydrocarbons possessing a high boiling point, the tube was also connected with a suction pump, in order to facilitate the vaporization of the hydrocarbon. The loss in weight of the original sample represented in each case the amount of the hydrocarbon in combination with triphenylmethyl. The escaping vapors were condensed in a small test tube surrounded by a freezing mixture, and the distillate was examined for its identity with the solvent originally used by determining its boiling point and molecular weight, the Schleiermacher and the Bleier and Kohn methods, respectively, being employed for that purpose. The residue in the boat was identified as unchanged triphenylmethyl by conversion into the characteristic peroxide.

TABLE I.

			Loss as per cent.			Boiling points[1] (uncorrected).		Molecular wts.	
Solvent.	Wt. of additive compd.	Loss on heating.	Found.	Calc. for $[R_3C]_2.X$.	Calc. for $R_3C.X$.	Distillate.	Original solvent.	Found for dist.	Calc. for orig. solvent.
Hexane......	0.8044	0.0006	0.1	15.0	26.1	...	(66–68)	....	86.1
	0.7262	0.0022	0.3	....	....	...	......	....	.....
	0.9327	0.0011	0.1	....	....	...	......	....	.....
Heptane.....	2.2246	0.0259	1.2	17.1	29.2	...	(94–96)	....	100.1
	2.4126	0.0101	0.4	....	....	...	......	....	.....
	1.7153	0.2534	14.8	....	....	...	......	....	.....
	2.7338	0.4244	15.5	....	....	95	......	96.6	.....
	1.9181	0.2844	14.8	....	....	93	......	97.4	.....
	3.1208	0.4558	14.6	....	....	...	......	....	.....
	1.5881	0.2288	14.4	....	....	...	......	....	.....
Octane.......	2.1688	0.0409	1.9	19.0	32.0	...	(122–124)	....	114.1
	1.2609	0.0185	1.5	....	....	...	......	....	.....
	3.0028	0.2768	9.2	....	....	113	......	114.2	.....
	2.1992	0.0140	0.6	....	....	...	......	....	.....
	1.8966	0.0672	3.5	....	....	119	......	....	.....
	3.3074	0.1842	5.6	....	....	120	......	114.5	.....
Decane......	0.8626	0.0090	1.0	22.6	36.9	...	(154–157)	....	142.2
	0.8252	0.0131	1.6	....	....	...	154	....	.....
	1.6046	0.0095	0.6	....	....	...	......	....	.....
	2.6980	0.7500	27.8	....	....	153	......	141.9	.....
	4.1539	1.2310	29.6	....	....	153	......	142.1	.....
	2.0309	0.7029	34.6	....	....	154	......	144.3	.....
Cyclohexane .	....	....	....	....	....	...	......	85.4	.....
	5.6579	0.8362	14.8	14.7	25.7	76.5	(79–79.5)	83.7	84.1
	....	....	....	....	....	...	77	84.6	.....
Methyl cyclohexane.....	4.6414	0.7343	15.8	16.8	28.7	97.5	(99–101)	98.2	98.1
	4.7550	0.7200	15.1	....	....	98	98	97.9	.....

[1] The figures in parentheses indicate the range of temperature at which the whole of the liquid distilled. The figures not in parentheses were obtained by the Schleiermacher method, and consequently indicate the boiling point of the lowest fraction in the sample.

It was also found that the condensed distillate, at times, reduced a solution of potassium permangante, but only in those cases when the heating of the additive compound was carried out at 100° or above, and for a considerable length of time. Undoubtedly, this reduction is due to some product resulting from a slight decomposition of the triphenylmethyl itself. Moreover, the amount of the reducing substance present was always slight, and seldom constituted more than about 1% of the total distillate, this being determined by comparison with samples of the original solvent, to which a definite amount of hexylene had been added. In order to make still more certain that the formation of the additive compound is not due to the presence of a small amount of an unsaturated hydrocarbon in the solvents used, we have in a few instances crystallized triphenylmethyl from the solvent in question, and then used the *filtrate* for a second and a third crystallization of fresh samples of triphenylmethyl. But the additive compounds in all such instances proved to be identical.

A summary of the results obtained is given in Table I.

Discussion of the Results.

From the results given in the table it appears that the formation of an additive compound is conditioned upon several factors. The foremost factor is, undoubtedly, the temperature at which the compound dissociates into its components; the second, the relative solubility of triphenylmethyl in the hydrocarbon in question. The higher the temperature of dissociation, the more likely will triphenylmethyl crystallize out on cooling its solution as an additive compound. On the other hand, the less is the solubility of triphenylmethyl in the particular hydrocarbon, the more apt it is to commence to crystallize while the solution is still quite hot. The result under these circumstances is quite likely to be unchanged triphenylmethyl, unless perchance the solution, ere crystallization sets in, should become supercooled, at least slightly below the dissociation temperature of the presumptive additive compound. If the latter conditions prevail, the additive compound will be formed.

Thus, with hexane, the product did not crystallize out until the solution had cooled to nearly room temperature; but the dissociation temperature is evidently still lower, so that no additive compound resulted. Likewise, with heptane, in the first two experiments cited, the product crystallized out while the solution was still quite warm, and there was no additive compound present. But in the other five experiments with the same solvent, crystallization did not occur until the solution had cooled considerably, and the product consisted almost wholly of the additive derivative. With octane, due to the decreased solubility of triphenylmethyl in it, the product invariably commenced separating while the solution was very hot, and we did not succeed in inducing supercooling. In consequence thereof, the product that crystallized out consisted either wholly of unchanged triphenylmethyl or of triphenylmethyl with a variable admixture of its additive derivative.

The results with decane deserve particular mention. Here again, as with octane, it is possible to get from the hot solutions unchanged triphenylmethyl. But in several instances we have succeeded in obtaining the true additive derivative. This additive compound with decane differs, however, from all other analogous compounds in that it consists, apparently, of the *monomolecular* triphenylmethyl in combination with the solvent. Nor are we without an adequate explanation for this unusual behavior. It is now well established that the dimolecular triphenylmethyl—whatever its constitution may be—dissociates with the rise of temperature of the solvent into the monomolecular free radical, so that at 80° the dissociation may reach as high as 25%.[1] Decane boils at about 155°, and at that temperature triphenylmethyl must be monomolecular to a very large extent. Should separation of the solute occur at a temperature when the monomolecular phase predominates, then the additive compound will have the composition $R_3C.C_{10}H_{22}$, provided, of course, that the high temperature at which this crystallization occurs is still favorable for the formation of the additive derivative. This, evidently, is what happened in our experiments. It will be noticed in some of our results, that the percentage of the additive solvent falls short of that calculated for the monomolecular, but is nonetheless too high for the dimolecular triphenylmethyl. It must remain undecided whether in these cases we are dealing with a mixture of free triphenylmethyl and its additive compound, $R_3C.C_{10}H_{22}$, or with a mixture of the two additive compounds $R_3C.C_{10}H_{22}$ and $[R_3C]_2.C_{10}H_{22}$.

Of course, the high percentage of additive solvent might be explained by assuming the formation of the additive compound $[R_3C]_2(C_{10}H_{22})_2$ but the explanation here given seems to us preferable to this alternative.

With cyclohexane and methylcyclohexane, in which triphenylmethyl is quite soluble, the products crystallized at comparatively low temperatures, and the additive compounds were found to possess the normal composition.

To sum up, it has been shown in this paper that triphenylmethyl actually possesses the capacity to form additive compounds with completely saturated aliphatic and alicyclic hydrocarbons. Furthermore, it appears probable, that under certain conditions the monomolecular, instead of the dimolecular, modification of triphenylmethyl enters into these additive derivatives. No explanation based upon the valence hypothesis can satisfactorily account for the existence of such additive compounds.

ANN ARBOR, MICH.

[1] THIS JOURNAL, 36, 1166 (1914).