It is of interest to note that increasing methyl substitution in benzene affects λ_{max} of the complex as well, but in this case the shift is toward longer wave lengths. If this shift were to be employed as a qualitative criterion for the change in basicity of the electron donor molecule[12] then the low result for the equilibrium constant of the hexaethylbenzene–iodine complex could be attributed to fewer, though comparatively strongly bound, associated molecules as a consequence of unfavorable steric requirements. Consideration of molecular models, as pointed out by Andrews and Keefer,[5] indicates that an ethyl group can fold back and overlap a small area above the aromatic ring.

The investigation of steric factors in the formation of iodine complexes with polymethylbenzenes cannot be considered as confirming uniquely the Mulliken model R for the $Ar \cdot I_2$ complex. Although structures in which the iodine molecule is at a corner or edge of the benzene ring (as in models L, E and O) now appear highly improbable, structures other than R in which the iodine molecule is centrally located with respect to the benzene ring (as in model A) still remain. Comparing the possibilities R and A for the hexaethylbenzene–iodine complex, the one which would be predicted the more likely to result in steric interaction between the iodine molecule and the ethyl groups is structure R. But the fact that a steric effect is observed experimentally does not necessarily eliminate model A, although it is a point in support of the Mulliken proposal.

Experimental

Materials.—Carbon tetrachloride and the liquid hydrocarbons were purified by the distillation procedure previously described.[13] Carbon tetrachloride, $n^{20}D$ 1.4609, was purified as specified by Fieser.[14] The method of Benesi and Hildebrand,[7] except for the mercury treatment, was used to purify benzene and mesitylene, $n^{20}D$ of 1.5008 and 1.4965, respectively. Isodurene (prepared by the Organic Manufacturing Laboratory at the University of Illinois) was dried over calcium chloride and distilled, $n^{20}D$ 1.5095.

Pentamethylbenzene, hexamethylbenzene and hexaethylbenzene were made available to us by Dr. A. P. Lien. Several months of standing in capped vials did not affect the purity. Prior to use the uncorrected melting points were 52–53°, 164 and 127°, respectively.

Reagent grade iodine from the General Chemicals Company was sublimed and stored over phosphorus pentoxide in a desiccator.

Procedure.—The procedure for obtaining absorption spectra data was the same as that described by Benesi and Hildebrand.[7] The instrument employed was a Cary Recording Quartz Spectrophotometer with a matched pair of 1-cm. glass-stoppered quartz cells.

A standard iodine stock solution was prepared at room temperature by dissolving a known weight of iodine (0.3105 g.) in 100 ml. of carbon tetrachloride. More dilute solutions were prepared, as required, by taking a known aliquot of the stock solution and diluting with carbon tetrachloride in a calibrated 25-ml. volumetric flask. The concentrations of the iodine solutions were checked spectrophotometrically from time to time.

A solution of each aromatic compound was prepared by dissolving a known weight of the compound in a known weight of carbon tetrachloride. The use of solutions was necessary for the solid aromatic compounds, but solutions of the liquid aromatics in carbon tetrachloride were made also in order to study the same range of concentrations. Aliquots were taken by means of calibrated pipets and each aliquot was weighed. To each was added a known weight of iodine solution, delivered through a calibrated pipet, and the absorption measurement was then made immediately. From these data, the mole fraction of the aromatic compound and the molar concentration of iodine could be calculated. The ranges of mole fractions of the aromatic compounds in the mixtures thus prepared were: benzene 0.901–0.0239; mesitylene 0.366–0.0317; isodurene 0.216–0.0748; pentamethylbenzene 0.0770–0.0254; hexamethylbenzene 0.0594–0.0196; hexaethylbenzene 0.0805–0.0253.

Acknowledgment.—We are indebted to Dr. A. P. Lien of the Standard Oil Company of Indiana for the pentamethylbenzene, hexamethylbenzene and hexaethylbenzene which he generously provided.

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[12] The data of this investigation and that of Andrews and Keefer suggest that this may apply to closely related derivatives of a parent compound. It does not appear to apply to unrelated compounds. Note Added to Proof.—McConnell, Ham and Platt[11] have shown that there is an inverse linear relationship between the ionization potential, I_p, of the electron donor molecule and the wave length of maximum absorption, λ_{max}, of its complex with iodine. The ionization potential increases in the order: mesitylene < *o*- or *m*- xylene < toluene < benzene. This is the same order for decreasing stability of the complex. Since the magnitude of the equilibrium complex, K, is regarded as an indication of basic strength (barring steric factors) as well as a measure of stability, there is some justification for relating K with λ_{max}. A plot of ϵ_c *versus* λ_{max} for benzene and its methyl derivatives (data of Table I) gives a smooth curve except for mesitylene which, as was noted previously, does not lie on the ϵ_c *versus* $1/\sqrt[3]{K}$ graph of Fig. 1.

There is some doubt at present that the K and λ_{max} values for the iodine complexes of all electron donor molecules can be related by a single expression. Diethyl ether, which lies on the linear I_p *versus* λ_{max} plot, has an ionization potential which is considerably greater than that for benzene. If taken to mean that the equilibrium constant for the diethyl ether–iodine complex is less than that for the benzene–iodine complex, this would constitute an unusual reversal of expected basic characteristics. There is a need for additional data for the K values of iodine with other electron donors. But until such data are forthcoming, it seems best to restrict the use of λ_{max} as a qualitative measure of basicity to closely related compounds.

[13] M. Tamres, THIS JOURNAL, **74**, 3375 (1952).

[14] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1935, p. 309.

The Reaction of Trifluoroacetone with Acetylene

BY PAUL TARRANT, D. A. WARNER AND R. E. TAYLOR

RECEIVED MARCH 30, 1953

It has been claimed[1] that trifluoroacetone reacts with ethynylmagnesium bromide to give a product which was dehydrated with oxalic acid to 3-trifluoromethylbutyn-1-ene-3. The acetylenic compound was then treated with hydrogen to yield 3-trifluoromethylbutadiene-1,3. No physical constants nor analyses were given for the intermediate compounds.

As part of the program in this Laboratory on the preparation of fluoroölefins for the Arctic rubber program for the Office of Quartermaster General, it seemed desirable to repeat the experiments described in the patent to obtain trifluoromethylbutadiene. Although a number of runs were carried out with trifluoroacetone and the Grignard reagent prepared from ethylmagnesium bromide, no product which could be dehydrated with either magnesium sulfate or oxalic acid was obtained. However, there was obtained some 3-trifluoromethyl-1-butyne-3-ol and a larger amount of 2,5-

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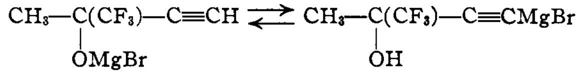
[1] H. M. Hill and E. B. Towne, U. S. Patent 2,490,753 (Dec. 6, 1949).

bis-(trifluoromethyl)-3-hexyne-2,5-diol whose properties were determined.

Since low yields of the carbinol were obtained using the Grignard reagent, a study was made of the reaction of acetylides of sodium and potassium with trifluoroacetone in various solvents. The highest yield of 3-trifluoromethyl-1-butyne-3-ol (15%) was obtained by the use of aqueous potassium hydroxide as the condensing agent; the glycol was still the chief product (37%). Apparently trifluoroacetone does not react readily in liquid ammonia since a 55% recovery was obtained when the ketone was treated with sodium acetylide in ammonia. No reaction occurred between trifluoroacetone and potassium acetylide in dibutyl cellosolve using Bergmann's procedure[2] at −40° or at −20°. The method of Smith[3] using butanol and xylene also failed to give either the alcohol or the glycol.

Evidence has been found that the formation of 3-trifluoromethyl-1-butyne-3-ol was hindered by a redistribution of the ionic charge in the salt of the alcohol which is the initial product in all of these reactions. The result of this shift is a new carbanion from the substituted acetylene. Thus in the case of the Grignard reagent, the following equilibrium may exist



$$\underset{\displaystyle \text{OMgBr}}{CH_3\text{—}C(CF_3)}\text{—}C\equiv CH \rightleftharpoons \underset{\displaystyle \text{OH}}{CH_3\text{—}C(CF_3)}\text{—}C\equiv CMgBr$$

The position of the equilibrium could not be readily determined since the new acetylenic Grignard reagent reacted immediately with a second molecule of trifluoroacetone to give the glycol, 2,5-bis-(trifluoromethyl)-3-hexyne-2,5-diol, which was the principal product in all cases. An analogous situation exists also in the case of the alkali metal acetylides.

It was found that, in the case of the Grignard reaction, the time elapsing between the addition of the trifluoroacetone to the solution of ethynylmagnesium bromide and hydrolysis of the adduct exerted a pronounced influence on the yield of the alcohol. For example, in a run standing at 20° under an inert atmosphere for 36 hours, a 7.72% conversion to the alcohol was obtained; in a run standing for two hours, a 13.8% conversion was obtained. In each case the conversion to the glycol exceeded 32%. Froning and Hennion[4] have found that increased yields of 2,5-dimethyl-3-hexyn-2,5-diol were obtained by allowing the reaction product of acetone and sodium acetylide to stand for several days; the initial product from trifluoroacetone and acetylene seems even more sensitive to aging since overnight aging gave 32% of the glycol. Since it has been established[5,6] that a quantitative yield of HC≡CNa is obtained on the reaction of sodium with excess acetylene in liquid ammonia solution, the formation of the glycol must be a consequence of the charge redistribution in the initial adduct. Since it further appears from the evidence presented above that this redistribution is quite rapid in the anion from 3-trifluoromethyl-1-butyne-3-ol it may be concluded that the same effect is present in the Grignard synthesis with the result that a low yield of the alcohol is obtained there as well.

Experimental

Source of Reagents.—Trifluoroacetone was prepared by the Claisen type condensation of ethyl trifluoroacetate with ethyl acetate followed by decomposition of the resulting ethyl trifluoroacetoacetate with 35% sulfuric acid. The crude trifluoroacetone was distilled from phosphoric oxide to obtain anhydrous material, b.p. 21–23°.

Acetylene was delivered from a tank, scrubbed with water, 95% H_2SO_4, dried over anhydrous $CaCl_2$ and Drierite.

Anhydrous methanol was prepared by distillation of the commercial material from CaO.

The Grignard Reaction.[1]—One mole of ethylmagnesium bromide was prepared under nitrogen in a 1000-ml. three neck flask fitted with a stirrer, a Y tube carrying a gas inlet tube and an ice-water cooled reflux condenser, and a jacketed dropping funnel. Acetylene was bubbled into the stirred solution at a rate of about 100 ml. per minute for four hours; the rate was then reduced to about 20 ml. per minute while 0.80 mole of trifluoroacetone was added during one hour. The addition of acetylene was stopped and the mixture refluxed for 30 minutes. It was cooled to room temperature and poured into 100 ml. of concd. hydrochloric acid and 200 g. of ice. The water layer was separated, saturated with sodium chloride and extracted with fresh ether. The ether was stripped off and the residue steam distilled.

The liquid steam distillate was dried over magnesium sulfate followed by Drierite and rectified. If the drying process had been thorough, there was obtained 10–15 g. (9–13%) of a water-white liquid of pleasant odor, b.p. 97–98°, n^{25}_D 1.3521, d^{25}_4 1.160.

Anal. Calcd. for $C_5H_5F_3O$: MR_D, 24.52; mol. wt., 138.09; F, 41.28. Found: MR_D, 25.69; mol. wt., 139; F, 40.82; AR_F, 1.39.

In all cases, if the solid residue were recrystallized from ethylene chloride, there was obtained a 30–40% yield of the glycol as white, silky needles, m.p. 108–108.5°.

Anal. Calcd. for $C_8H_9F_6O_2$: mol. wt., 250.1; F, 45.48. Found: mol. wt., 244; F, 45.4.

Sodium Acetylide in Liquid Ammonia.—One mole of sodium acetylide was prepared in 1.2 l. of liquid ammonia according to the procedure already described.[3] The flask was then partially immersed in a bath of Dry Ice and acetone, and one mole of trifluoroacetone added in one hour. Acetylene was bubbled into the solution for an additional 15 minutes before the stirrer was stopped to allow the ammonia to evaporate overnight. The residue was covered with 150 ml. of ether while iced 35% sulfuric acid was added to dissolve the solid. From this point the procedure was that described for the Grignard reaction. Distillation yielded 62 g. of trifluoroacetone (55%), 15 g. of 3-trifluoromethyl-1-butyne-3-ol (11%) and 22 g. of the glycol (18%).

A run in which the sodium was converted to sodamide before addition of the acetylene gave almost identical results.

Potassium Hydroxide in Water.—In a 200-ml. flask fitted with a stirrer, gas inlet tube and ice-water cooled reflux condenser 0.5 mole of trifluoroacetone was added to 40 ml. of 2.5% aqueous potassium hydroxide. Acetylene was bubbled into the solution for six hours. At the end of the time 1.5 g. of sodium bicarbonate was added, followed by 10 ml. of water. The layers so formed were separated; the lower layer deposited 12 g. of glycol. The liquid portion gave 10 g. (14.5%) of alcohol on drying and distillation. An additional 5 g. of glycol was obtained on acidification of the upper layer; total conversion to glycol, 36.8%.

Potassium Hydroxide in Methanol.—One fourth mole of trifluoroacetone was cooled to 0° in a 200-ml. flask and saturated with acetylene. Sixty ml. of 2% methanolic potassium hydroxide was added dropwise while the addition of acetylene was continued. After four hours the acetylene was stopped and 1.5 g. of $NaHCO_3$ was added. The liquid was filtered and dried over Drierite. After removal of the

[2] E. D. Bergmann, *Selecta Chim.*, No. 9, 24 (1950).

[3] E. F. Smith, U. S. Patent 2,385,547 (Sept. 25, 1945).

[4] J. F. Froning and G. F. Hennion, THIS JOURNAL, **62**, 653 (1940).

[5] T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

[6] K. N. Campbell, B. K. Campbell and L. T. Eby, THIS JOURNAL, **60**, 2882 (1938).

methanol, there remained 22 g. of undistillable material, presumably glycol (70.5%).

Acknowledgments.—We wish to acknowledge with thanks the help of the analytical section of the M. W. Kellogg Co., who ran the fluorine analysis on the 2,5-bis-(trifluoromethyl)-3-hexyne-2,5-diol. We appreciate the encouragement of Dr. J. C. Montermoso of the Research and Development Division of the Office of the Quartermaster General.

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Infrared Absorption of Some Steroid Digitonides

BY RICHARD B. TURNER

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Although formation of stable molecular compounds (digitonides) from the saponin, digitonin, and steroids possessing a C_3 hydroxyl group is known to be ultimately dependent upon a 3β-orientation of the latter group,[1] little information is available regarding the nature of the secondary valence forces responsible for complex formation. In particular, the extent to which, in polyfunctional molecules, groups other than the 3β-hydroxyl group may be involved, through hydrogen bonding or other associative phenomena, has not been ascertained. The work reported in this communication was undertaken in order to examine the effects of digitonide formation upon the characteristic infrared absorption frequencies of carbonyl groups located at various positions in the steroid nucleus. 3β-Hydroxy steroids possessing carbonyl functions at positions 6, 7, 11, 12, 17 and 20 were investigated in this connection. Two α,β-unsaturated ketonic derivatives were also included. Owing to insolubility of the digitonides and to the possibility of dissociation in solution, measurements were made on suspensions of the crystalline complexes in mineral oil. Absorption data for the free sterols in mineral oil and in carbon disulfide solution are listed for comparison (Table I).

TABLE I

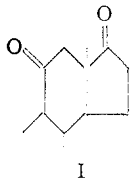
INFRARED ABSORPTION OF STEROID DIGITONIDES

No.	Compound*	Maxima, cm.$^{-1}$ (Mineral oil) Sterol	Digitonide	(CS_2 soln.) Sterol
1	6-Ketocholestanol	1692	1704	1715
2	7-Ketocholestanol[a]	1691	1700	1715
3	11-Ketoergostenol[b]	1693	1704	1709
4	Hecogenin[c]	1688	1697	1712
5	Δ^5-Androstene-3β-ol-17-one	1720	1735	1742
6	Δ^5-Pregnene-3β-ol-20-one	1673	1697	1709
7	Δ^4-Cholestene-3β-ol-6-one[a]	1666	1677	1692
8	7-Ketocholesterol[a]	1660	1675	1675

* Compounds indicated by lettered superscripts were furnished through the kindness of the following investigators: (a) L. F. Fieser, Harvard University, Cambridge, Mass. (sample no. 7 represents a highly purified preparation, m.p. 155.5–156.5°), (b) M. Tishler, Merck and Co., Rahway, N. J., (c) G. Mueller, University of Tennessee, Nashville, Tenn.

From inspection of the data (columns 1 and 2) it is clear that digitonide formation is accompanied by small, but significant, displacements (8 to 24 cm.$^{-1}$) of the carbonyl stretching maxima toward higher frequencies in all cases investigated. These displacements correspond to *increases* in the force constants of the carbon–oxygen double bonds. Since shifts to lower frequencies, associated with *decreases* in the C=O force constants, result from hydrogen bonding involving carbonyl groups,[2,3] participation of forces of this kind in stabilization of the digitonides would appear to be minimized.

High frequency displacements of the C=O stretching maxima have been observed by Jones and his collaborators[2,4] in a number of instances in which two appropriately oriented carbonyl groups occupy proximate positions in space. 11,17-Diketo steroids (I) and ketol acetates of types II and III[5] may be cited as illustrative of the several recorded examples of this phenomenon. Suppression of polar resonance structures (*cf.* IV) by mutual dipole repulsions, with consequent reinforcement of the double bond character of the respective carbonyl groups, may account for these observations.[6] However, the assumption that similar processes (for example, interactions between carbonyl groups of different molecules) are involved in the case of the digitonides, requires acceptance of a number of elaborate hypotheses.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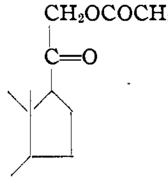

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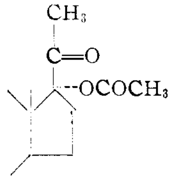

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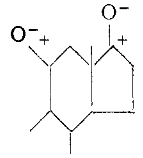

IV

A more plausible explanation for the spectral shifts encountered in the present work is based upon consideration of forces operative within the steroid crystals. The results of X-ray analyses indicate that hydrogen bonding, particularly that involving the C_3 hydroxyl group, plays an important part in determining the lattice structure of these substances.[7] Thus sterols possessing a single hydroxyl group (C_3) are doubled in the unit cell by head-to-head association of the hydroxyl functions

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[1] A discussion of digitonide formation is given by L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publ. Corp., New York, N. Y., 1949, pp. 102, 648.

[2] R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2820 (1952).

[3] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *ibid.*, **71**, 1068 (1949); M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948); M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755 (1938); W. Gordy, THIS JOURNAL, **60**, 605 (1938).

[4] R. N. Jones and K. Dobriner, *Vitamins and Hormones*, **7**, 293 (1949).

[5] R. B. Turner, THIS JOURNAL, **75**, 3489 (1953).

[6] *Cf.* A. D. Walsh, *Trans. Faraday Soc.*, **43**, 1158 (1947); R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952).

[7] D. Crowfoot, *Vitamins and Hormones*, **2**, 439 (1944).