232. Tritylation and Detritylation of Active Methylene Compounds. Part IV.[1] Formation and Reactions of Some Hexasubstituted Ethanes.

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Attempts were made by various methods to prepare hexasubstituted ethanes $Ph_3C{\cdot}CXYZ$, where X and Y are strongly electron-attracting groups and Z is alkyl or aryl. Use of different active methine compounds gave the desired products in only a few cases. Heterolysis of these compounds was much more difficult than when Z = H.

In previous papers,[2] some methods for tritylation of active methylene compounds were described. No case of trityl substitution of the active methine compounds HCXYZ has been reported, although diarylmethylations are known.[3]

Attempts in our laboratory to prepare compounds of the type $Ar_3C{\cdot}CXYZ$, with three strongly electronegative substituents, failed.[4] Successful syntheses were then carried out of similar compounds in which Z was an alkyl or an aryl group. Diethyl phenyltriphenylmethylmalonate was obtained in good yield from diethyl sodiophenylmalonate and triphenylmethyl bromide in ether. Some acid-catalysed condensations of triphenylmethanol or of triphenylmethyl chloride with compounds of the type HCX_2Z, when X was carboxy, carbamoyl, or cyano, and Z was ethyl or phenyl, were successful but the yields were generally low. In some of these cases the products isolated were those of partial hydrolysis and decarboxylation of the primary condensation products.

The formation of hexasubstituted ethanes was generally more difficult than that of the corresponding pentasubstituted derivatives $Ph_3C{\cdot}CHXY$ and the yields in parallel methods were lower. Different preparative methods had to be used for different cases and no generally useful method could be found.

It could be assumed from steric considerations, and indeed observed on molecular models, that compounds of the type $Ph_3C{\cdot}CXYZ$ should be highly strained and, therefore, difficult to prepare unless X, Y, or Z is hydrogen. Nevertheless, our results show that steric factors cannot be solely governing the ease of the formation of the products: as shown by the failure of the reaction with diethyl sodio-*p*-tolyl- or benzyl-malonate, neither of which is more space demanding than the phenyl-substituted malonate, which reacts easily.

The difficulties in the preparation of highly unsymmetrical hexasubstituted ethanes have been noted [4,5] and ascribed to the ease of various reactions which may lead to side products. In our case the main identifiable interference was the formation, in most of the methods tried, of large amounts of bistriphenylmethyl peroxide. This was not observed when working with triphenylmethyl derivatives and active methylene compounds [2] and is, therefore, due not to the sensitivity of the triphenylmethyl group, itself, but probably to the tendency of the intermediates or products in the present experiments to give free radicals on decomposition.

In the previous paper,[1] the *C*-triphenylmethyl-substituted active methylene compounds were found to form triphenylmethyl ions in sulphuric–acetic acid. Diethyl phenyltriphenylmethylmalonate proved to be relatively stable and was recovered unchanged after some hours in sulphuric–acetic acid mixtures, in conditions in which diethyl

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[1] Part III, *J.*, 1962, 726.

[2] Patai and Dayagi, *J.*, 1962, 716; Patai, Dayagi, and Friedlander, *J.*, 1962, 723.

[3] Fosse, *Compt. rend.*, 1908, **146**, 1277; Vanags, Platpiere, and Matskanova, *Zhur. obshchei Khim.*, 1949, **19**, 1535; Vanags and Geita, *Latv. P.S.R. Zinatnu Akad. Vestis*, 1952, No. 10; Vanags and Romadane, *ibid.*, 1955, No. 6 (cf. *Chem. Abs.*, 1955, **49**, 307; 1956, **50**, 7095); Eckstein, Fluksik, and Sobotka, *Bull. Akad. polon. Sci., Ser. Sci. chim., geol., geog.*, 1959, **7**, 803; Byrdy, Eckstein, Sobotka, and Winsztal, *Przemysl Chem.*, 1957, **36**, 540.

[4] Z. Rappoport, M.Sc. Thesis, Hebrew University, Jerusalem, Israel, 1959.

[5] Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publ., Inc., New York, 1956, p. 17.

triphenylmethylmalonate was completely cleaved. Even in 100% sulphuric acid the initial spectrum of the former showed the presence of only about 1% of triphenylmethyl ions. The compound is slowly sulphonated, giving a deep red colour which is not discharged on dilution with water or with ethanol but changes to blue in basic solutions.

EXPERIMENTAL

Materials.—Triphenylmethanol,[6] triphenylmethyl chloride [7] and bromide,[8] diethyl *p*-tolylmalonate,[9] diethyl 2,4-dinitrophenylmalonate,[10] diethyl benzylmalonate,[11] diethyl triphenylmethylmalonate,[12] phenylmalonamide,[13] ethylmalonamide,[14] phenylmalonic acid,[15] ethylmalonic acid,[16] and ethylmalononitrile [17] were prepared according to known procedures. Other reactants, solvents, and catalysts were purified commercial products.

Phenyltriphenylmethylmalonic Acid.—Triphenylmethanol (3 g.) and phenylmalonic acid (5 g.) were refluxed for 4 hr. in acetic acid (50 ml.) and acetic anhydride (10 ml.). After cooling, the solution was poured into water (300 ml.); a yellow oil separated, which solidified overnight. This was extracted with warm (50—60°) aqueous 5% potassium hydroxide. The residue (2 g.) was triphenylmethanol (67%), m. p. 162°. The white *acid* (0·6 g., 12%) obtained by acidification of the alkaline solution crystallized from ethanol as plates, melting at 195° with sublimation (Found: C, 79·7; H, 5·8. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2%).

Phenyltriphenylmethylmalonamide.—Triphenylmethyl chloride (2 g.) and phenylmalonamide (2 g.) were refluxed for 5 hr. in nitromethane (50 ml.) containing dichloroacetic acid (5 ml.). Most of the solvent was evaporated *in vacuo*, and 10 ml. of 1 : 1 aqueous methanol were added. The white precipitate was filtered off and extracted with boiling ethanol, from which the *diamide* (1 g., 30%), m. p. 219°, was obtained (Found: C, 80·0; H, 5·7; N, 6·7. $C_{28}H_{24}N_2O_2$ requires C, 80·0; H, 5·7; N, 6·7%). The fraction insoluble in ethanol (0·1 g., 2·7%; m. p. 257° after crystallization from acetic acid) had the correct analysis for αβββ-*tetraphenylpropionamide* (Found: C, 85·7; H, 6·1. $C_{27}H_{23}NO$ requires C, 85·9; H, 6·1%).

α-*Triphenylmethylbutyramide.*—(*A*) Triphenylmethyl chloride (2 g.), ethylmalonamide (2 g.), and dichloroacetic acid (0·8 g.) were refluxed for 10 hr. in nitromethane (50 ml.). After cooling, part of the starting amide was recovered by filtration, and the mother-liquor was evaporated *in vacuo*. The unchanged starting materials were removed by extraction with boiling ethanol. The residue (0·12 g., 4·8%) crystallized from dioxan–water to give α-*triphenylmethylbutyramide monohydrate*, m. p. 292° (Found: C, 79·9; H, 6·7; N, 4·2. $C_{23}H_{23}NO,H_2O$ requires C, 79·5; H, 7·2; N, 4·0%).

(*B*) Triphenylmethyl chloride (2 g.) and ethylmalononitrile (1 g.) were refluxed for 14 hr. in acetic acid (50 ml.). The solvent was evaporated and, after addition of water, a precipitate was formed of which 0·45 g. (18%) was insoluble in boiling ethanol. After crystallization from dioxan–water, it was found to be the product prepared by method (*A*).

Diethyl Phenyltriphenylmethylmalonate.—A suspension of diethyl sodiophenylmalonate in ether was prepared by refluxing diethyl phenylmalonate (15 g.) with sodium wire (1·5 g.) in anhydrous ether (75 ml.) for 2 hr. The suspension was added in small portions to triphenylmethyl bromide (20 g.) in dry ether (500 ml.). After 24 hr. at room temperature, this mixture was refluxed for 2 hr. and filtered. Most of the ether was removed, a pale yellow solid (m. p. 90—92°; 23 g., 76%) being precipitated slowly. After crystallization from light petroleum (b. p. 60—80°), colourless crystals of *diethyl phenyltriphenylmethylmalonate*, m. p. 94°, were obtained (Found: C, 80·6; H, 6·6. $C_{32}H_{30}O_4$ requires C, 80·5; H, 6·3%).

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[6] Bachmann and Hetzner, *Org. Synth.*, 1943, **23**, 98.

[7] Bachmann, *Org. Synth.*, 1943, **23**, 100.

[8] Allen and Kolliker, *Annalen*, 1885, **227**, 110.

[9] Wallingford, Homeyer, and Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 2056.

[10] von Richter, *Ber.*, 1888, **21**, 2473; Zaheer and Sidhu, *J. Indian Chem. Soc.*, 1947, **24**, 134.

[11] Marvel, *Org. Synth.*, 1941, **21**, 99.

[12] Lund, Hansen, and Voigt, *Kgl. danske Videnskab. Selskab., Mat.-fiz. Medd.*, 1933, **12**, No. 9; Lund, *Ber.*, 1934, **67**, 636; Holmberg, *Acta Acad. Aboensis., Math. Phys.*, 1949, **16**, No. 6.

[13] Dox and Yoder, *J. Amer. Chem. Soc.*, 1922, **44**, 1564.

[14] Russell, *J. Amer. Chem. Soc.*, 1950, **72**, 1853.

[15] Wislicensus, *Ber.*, 1894, **27**, 1093.

[16] Schey, *Rec. Trav. chim.*, 1897, **16**, 356.

[17] Henry, *J.*, 1889, **55**, 639.

The ester was refluxed for 2 hr. in a 20% solution of potassium hydroxide in 3 : 1 ethanol-water and underwent hydrolysis and partial decarboxylation, to give 60% of αβββ-*tetraphenylpropionic acid*, m. p. 200° (from ethanol) (Found: C, 84·6; H, 5·7%; equiv., 395. $C_{27}H_{22}O_2$ requires C, 85·6; H, 5·8%; *M*, 379).

Unsuccessful Experiments.—Reaction of triphenylmethyl bromide with diethyl sodiobenzylmalonate gave only bistriphenylmethyl peroxide, m. p. 184° (lit.,[18] 186—187°; identified by m. p., mixed m. p., and infrared spectrum) in yields up to 70%. When the reaction was carried out under dry nitrogen, a viscous oil was obtained, which gradually gave this peroxide in air. Similarly, only oils and the peroxide were obtained by reaction of triphenylmethyl chloride or bromide with diethyl ethylmalonate, *p*-tolylmalonate, or ethoxymagnesiophenylmalonate [12] in ether or tetrahydrofuran.

The starting materials or their hydrolysis products were recovered from the reactions, in various conditions, of triphenylmethanol with phenylmalonamide, ethylmalonamide, or ethylmalonic acid; of triphenylmethyl chloride with diethyl phenylmalonate, phenylmalonic acid, diethyl ethylmalonate, or ethylmalonic acid; of triphenylmethyl bromide with diethyl sodio-2,4-dinitrophenylmalonate; of diethyl triphenylmethylmalonate with *p*-bromonitrobenzene in the presence of sodium ethoxide or in a suspension of sodium methoxide in dimethyl sulphoxide.

Attempts (by bromination of diethyl triphenylmethylmalonate by *N*-bromosuccinimide or by bromine solutions) to prepare diethyl bromotriphenylmethylmalonate as a starting material for alkylation or arylation with alkyl- or aryl-lithium compounds failed.

Cleavage Experiments.—Diethyl phenyltriphenylmethylmalonate (20 mg.) was dissolved in 100% sulphuric acid (25 ml.). The spectrum of the orange solution was identical with that of triphenylmethyl ions.[19] The concentration of the ion was calculated from the optical density, by using the value of 36,900 for ε at 406 mμ; [1] cleavage was found to amount to about 1%. The colour of the solution gradually changed to deep red, with disappearance of the absorption corresponding to the triphenylmethyl ions and appearance of new peaks at 280, 320—340, and ~520 mμ. No precipitate was formed when the red solution was poured into water or ethanol. In acetic acid containing 5—30% (v/v) of sulphuric aid, no triphenylmethyl ion absorption could be detected and the material was recovered unchanged after dilution with water.

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[18] Wieland, Hintermaier, and Dennstedt, *Annalen*, 1927, **452**, 9.

[19] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900; Gold and Howes, *J.*, 1951, 2102.