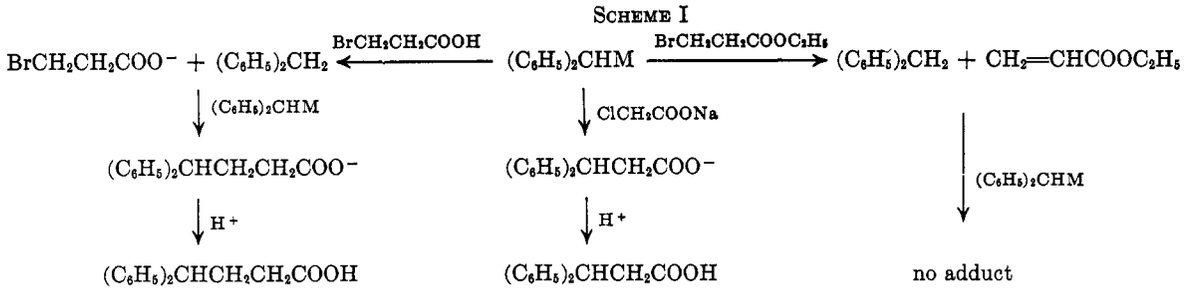
SCHEME I



sium diphenylmethide. Attempts to isolate an adduct of diphenylmethide and ethyl acrylate failed;[3] starting material was isolated when diphenylmethane and either an equivalent or a catalytic amount of potassium amide in liquid ammonia was treated with ethyl acrylate, using either direct or inverse neutralization.[4]

The alkylation of potassium diphenylmethide with the bromopropionate anion offers considerable advantage over the previous preparation of 4,4-diphenylbutyric acid derivatives by condensation of benzophenone with ethyl succinate[5] followed by decarboxylation and hydrogenation of the resulting itaconic acid derivative.[6] Thus, using the alkylation procedure, large quantities of the parent acid could be conveniently prepared in one step from commercially available materials. The synthesis of 3,3-diphenylpropionic acid from sodium or potassium diphenylmethide and commercial sodium chloroacetate offers some advantage over the alkylation of benzene with cinnamic acid, in that the product is more easily separated from starting materials, and further reaction, for example, cyclization to 3-phenyl-1-indanone, does not take place.[7] Scheme I summarizes these reactions.

Experimental Section

4,4-Diphenylbutyric Acid.—To a solution of 0.2 mole of potassium diphenylmethide[8] in 500 ml of liquid ammonia was added an ethereal solution of 15.3 g (0.1 mole) of bromopropionic acid. The orange color of the base was discharged by the last of the halo acid. The ammonia was evaporated and the residue was stirred with ether and water. The aqueous solution was separated, extracted with ether, and neutralized with hydrochloric acid. After recrystallization from ethanol there was obtained 21 g (85%) of 4,4-diphenylbutyric acid, mp 104°, undepressed by authentic 4,4-diphenylbutyric acid.[6] Evaporation of the ethereal solution gave, after distillation, 16 g of diphenylmethane. Repetition of the procedure as above, except using commercial sodium amide, afforded larger quantities of the acid in comparable yield.[9]

When ethyl acrylate was added to 1 molar equiv of potassium diphenylmethide in liquid ammonia, the orange color of the diphenylmethide ion was slowly discharged. After either direct or inverse[4] neutralization with ammonium chloride approximately 97% of the diphenylmethane was recovered, and a high-boiling ester fraction (ν 1750–1715 cm^{-1}) was obtained.

Addition of 1 molar equiv of ethyl 3-bromopropionate also decolorized an ammoniacal solution of potassium diphenylmethide; on work-up the acidic fraction yielded acrylic acid, identified by comparison of the index of refraction with that of an authentic sample (n^{20}D 1.4223), and the neutral fraction contained essentially all of the diphenylmethane (identified and analyzed by vapor phase chromatography).

3,3-Diphenylpropionic Acid.—To a solution of 0.1 mole of potassium diphenylmethide in 250 ml of liquid ammonia was added 11.7 g (0.1 mole) of solid sodium chloroacetate. The orange color of the base was discharged by the last of the salt. The ammonia was evaporated and the residue was dissolved in water. The aqueous solution was extracted with ether and acidified with hydrochloric acid. After recrystallization from aqueous ethanol there was obtained 18 g (80%) of 3,3-diphenylpropionic acid, mp 154°, undepressed by authentic 3,3-diphenylpropionic acid.

(3) See M. T. Tetenbaum and C. R. Hauser, *J. Org. Chem.*, **23**, 229 (1958).
(4) P. J. Hamrick and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 2096 (1959).
(5) G. H. Daub and W. S. Johnson, *ibid.*, **72**, 501 (1950).
(6) S. Wawzonek and J. Kozikowski, *ibid.*, **76**, 1641 (1954).
(7) See C. F. Koelsch, H. Hochmann, and C. D. LeClaire, *ibid.*, **65**, 59 (1943).
(8) C. R. Hauser and P. J. Hamrick, *ibid.*, **79**, 3142 (1957).
(9) This experiment was performed by Eric Roskin.

Synthesis of Tetrakis(dimethylamino)ethylene

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Presented is a report of an alternate synthesis of tetrakis(dimethylamino)ethylene, $[(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2$. This compound, interesting because of its chemiluminescence and its ability to form charge-transfer complexes, is generally prepared by the method of Pruett, *et al.*[1]

Tetrakis(dimethylamino)ethylene can be prepared in good yield by pyrolysis of the recently reported[2,3] tris(dimethylamino)methane, $HC[N(CH_3)_2]_3$. This method is analogous to the one reported by Winberg,

$$2HC[N(CH_3)_2]_3 \xrightarrow{\Delta} [(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2 + 2HN(CH_3)_2$$

et al.,[4] in which $HCX(NR_2)_2$ is pyrolyzed to yield the corresponding tetraaminoethylene (X = OR, CN). The X in our example is $N(CH_3)_2$, thus avoiding the possibility of contamination due to substituent scrambling.[5] Other amino substituents can, of course, be used, those from volatile amines being of particular interest.

Experimental Section

Preparation of Tetrakis(dimethylamino)ethylene.—A 2.20-g (0.0152-mole) sample of tris(dimethylamino)methane was placed in a 10-ml, round-bottom flask equipped with a reflux condenser and the system was kept under a small pressure of dry nitrogen. The reaction flask was immersed in an oil bath and the reaction was kept at reflux by adjusting the temperature upward between 150 and 190° as the reaction proceeded. The appearance of product was monitored by taking nmr spectra of aliquots [τ 7.42 (s), benzene solvent, TMS internal standard]. The

(1) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Am. Chem. Soc.*, **72**, 3646 (1950).
(2) H. Weingarten and W. A. White, *ibid.*, **88**, 850 (1966).
(3) H. Brederick, F. Effenberger, and T. Brendle, *Angew. Chem.*, **78**, 147 (1966).
(4) H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Am. Chem. Soc.*, **87**, 2055 (1965).
(5) That substituent scrambling occurs in $HC(OCH_3)[N(CH_3)_2]_3$ was privately communicated to us by E. C. Taylor and R. Buntrock.

conversion required approximately 72 hr. When the reaction was over the condenser was exchanged for a small distilling head and the product was distilled yielding 1.25 g (82%) of tetrakis-(dimethylamino)ethylene, bp 50° (1 mm), $n^{25}D$ 1.4806, mol wt 200 (mass spectrum), showing no significant impurities in the nmr.

The dibromide derivative was prepared according to Wiberg and Buchler,[6] mp 253°, infrared spectrum identical with that of authentic sample.

(6) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963).

The Reaction of Phenyl(trichloromethyl)mercury with Diiodoacetylene

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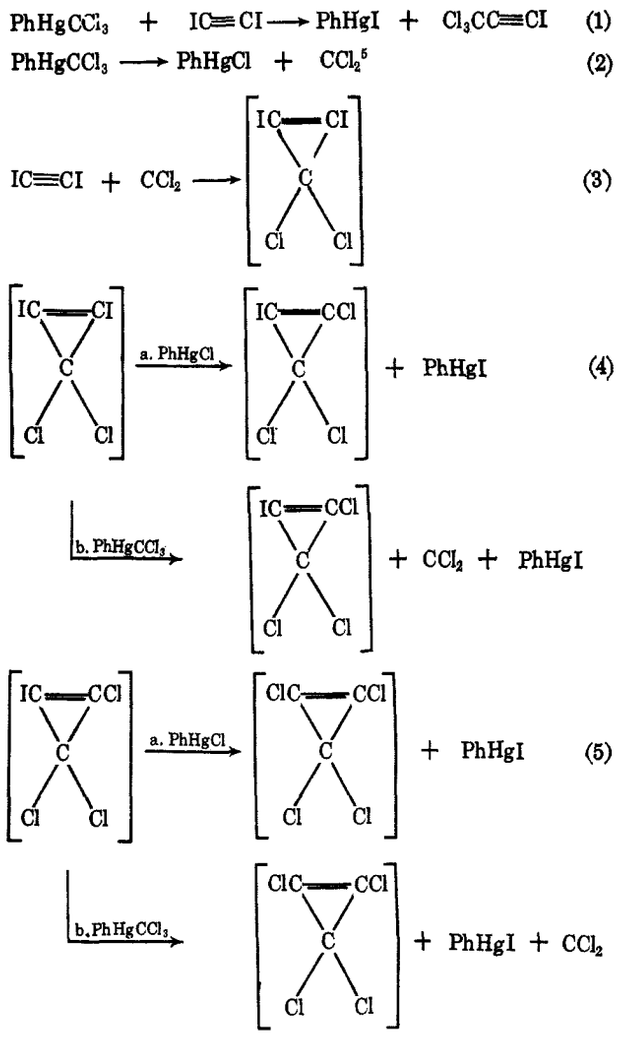
The reaction of phenyl(trihalomethyl)mercurials with a number of olefins has been shown to proceed in good yield even with olefins of low reactivity to carbene reagents.[1] Since a number of acetylenes have been shown to react with carbenes to form cyclopropenes,[2] it appeared likely that phenyl(trichloromethyl)mercury would give a dichlorocarbene adduct with a dihaloacetylene, the simplest type of nonterminal acetylene available. Accordingly, the reaction of phenyl(trichloromethyl)mercury with diiodoacetylene in benzene was studied. No reaction was found to occur at room temperature and little reaction at a temperature less than 80°. However, decomposition of phenyl(trichloromethyl)mercury was complete within 4 hr in refluxing benzene solution in the presence of diiodoacetylene. In the absence of diiodoacetylene, phenyl(trichloromethyl)mercury required 36–48 hr for complete decomposition.[3]

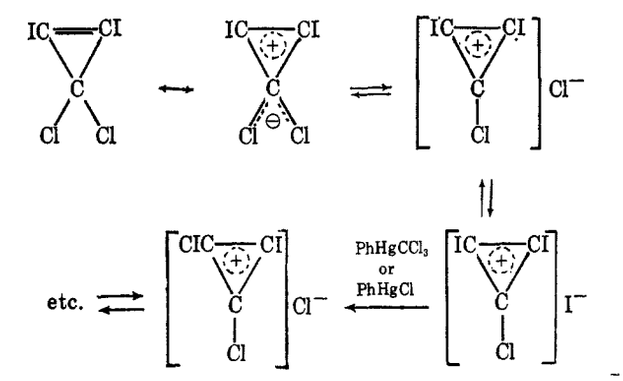
The major products isolated were tetrachlorocyclopropene (13.4%) and 1-iodo-3,3,3-trichloropropyne (12.9%). Also recovered from the reaction mixture were tetrachloroethylene (1.9%), diiodoacetylene (18.7%), and iodobenzene (4.2%). When a 2:1 ratio of phenyl(trichloromethyl)mercury–diiodoacetylene was used, diiodoacetylene was completely consumed. In addition to the products noted above, small amounts of phenyl-substituted cyclopropenes were probably present as indicated by a weak band at 1820 cm^{-1} [4] in the infrared spectrum of each of two constituents. The infrared spectrum of each constituent was otherwise almost identical with that of iodobenzene.

The results can be interpreted by considering the simultaneous reactions (eq 1–5).

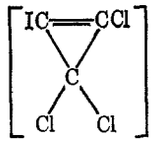
Reactions 4 and 5 may be facilitated by halogen scrambling *via* a cyclopropenium cation. The proposed mechanism for reactions 4 and 5 would account for the catalytic effect of diiodoacetylene on the thermal decomposition of phenyl(trichloromethyl)-



mercury since iodide ion is known[6] to effect the complete decomposition of phenyl(trichloromethyl)mercury within 4 hr at 80°. The reaction sequence would also



account for the lack of reaction below 80°, since reaction 2 will not occur to any appreciable extent much below this temperature. Reaction 1 may proceed by direct reaction, or reactions 1 and 4 may proceed *via* a common intermediate as shown below.



(1) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

(2) F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

(3) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(4) R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367, 2375 (1961).

(5) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

(6) D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *ibid.*, **87**, 681 (1965).