Notes

Stereoisomers of Trimethyl Methanetri(α-bromoacetate)

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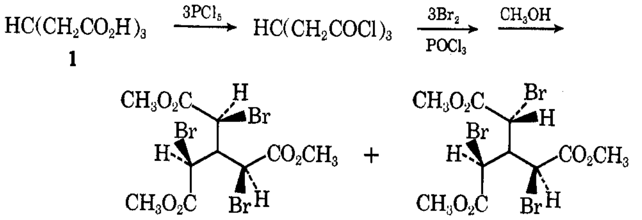
We have prepared two esters derived from methanetriacetic acid (**1**) which exhibit a novel diastereoisomerism as revealed by nmr spectroscopy. Vigorous bromination of the acid chloride of **1** in phosphorus oxychloride followed by quenching in methanol gave a mixture of esters. Separation into the components, mp 97 and 113°, could readily be effected by crystallization from methylcyclohexane. Both substances possessed the same composition ($C_{10}H_{13}Br_3O_6$) and had similar spectroscopic properties, indicating that they had the same general structure. We propose that they are the tribromides **2** and **3**, respectively.



2 **3**

The nmr spectra of the two esters demonstrated that they were indeed stereoisomeric. In deuteriochloroform both compounds exhibit only one methoxyl resonance at δ 3.82 ppm (intensity 9 H). The lower melting tribromide possessed a sharp doublet at δ 5.02 ppm (J = 4.8 Hz, intensity 3 H), corresponding to the three bromomethinyl protons adjacent to the carbomethoxy functions. The only other nmr absorption, a quartet at δ 3.64 ppm (J = 4.8 Hz, intensity 1 H), could be assigned to the remaining methinyl proton, which should be equivalently coupled to the three bromomethinyl protons in **2**. In contrast to **2**, the other tribromide **3** possessed complex absorption near δ 5 ppm. In the region where bromomethinyl resonances occur, six sharp irregularly spaced peaks of equal intensity were observed (total intensity 3 H). By examination of the spectrum at different field strengths this was interpreted as three doublets arising from *nonequivalent* bromomethinyl protons: δ 4.88 (J = 7.8 Hz), 4.94 (J = 4.2 Hz), and 5.07 ppm (J = 4.2 Hz). Such a pattern should arise from **3**, in which each of these protons would be coupled to the central proton (δ ~3.78 ppm, multiplet) but should otherwise differ with respect to the time-averaged magnetic environment, since no rotational processes can occur to bring about exchange between these three environments.[1] Therefore, the two structures may be identified as trimethyl *rac,rac*-methanetri(α-bromoacetate) (**2**) and trimethyl *meso,rac*-methanetri(α-bromoacetate) (**3**).

Some time ago Beesley and Thorpe[2] reported a triester related to **2** and **3** (from bromination of 1,1,1-ethanetriacetic acid) as an intermediate in some synthetic studies of unlikely veracity.[3] While the latter[2] workers' preparations have been claimed not to be reproducible,[4] the conditions of our synthesis of **2** and **3** are quite similar to those in the original report. Consequently, Thorpe's work[2] perhaps ought not to be discounted in its entirety. However, in contrast with his alleged findings our triester gave uncharacterizable tars with even mildly basic reagents (sodium azide or pyridine).

Experimental Section

Bromination of Methanetriacetic Acid Chloride.—A mixture of 10.0 g (0.053 mol) of methanetriacetic acid[5] (1) and 31 g of phosphorus pentachloride was heated until a homogeneous solution was obtained and gaseous hydrogen chloride evolution had ceased. To the resulting solution 30 g of bromine was added and heating was continued as hydrogen bromide was evolved. After 42 hr on a steam bath, excess bromine and phosphorus oxychloride were removed under aspirator pressure with heating. The residue was poured into 150 ml of methanol. After several hours the solution was concentrated under vacuum until a quantity of solid had separated, whereupon the mixture was chilled to 0° and the precipitate was collected and washed with a little cold methanol. The material thus obtained weighed 14.4 g and was a crude mixture of approximately equal amounts of **2** and **3**. Upon recrystallization from methylcyclohexane, **3** was observed characteristically to form clones of prisms adhering to the walls of the flask, whereas **2** formed rosettes of needles, more easily dispersed through the solvent; seed crystals could thereby be obtained; and the following separation procedure was devised. The solid mixture of isomers was dissolved in 200 ml of hot methylcyclohexane. The solution was filtered and allowed to cool to 50–60°, a seed of **3** was added, and the solution was allowed to cool to room temperature and stand undisturbed for 2 hr. The solution was then decanted from the mass of prismatic crystals coating the walls of the container and boiled down to a volume of 100 ml. The solution was cooled as before and seeded with **2**. Upon standing at room temperature, rosettes of needles grew. The solution was again decanted, boiled down to a volume of 50 ml, cooled and seeded with **3**, and allowed to crystallize. After decanting, the solution was concentrated to a volume of 25 ml and seeded with **2**. After the crystals had formed, the mother liquor was discarded.

The second and fourth fractions from the separation procedure were combined and recrystallized from 50 ml of methylcyclohexane to give 4.8 g (19.3% from 1) of trimethyl *rac,rac*-methanetri(α-bromoacetate) (**2**): mp 97–98°; ir $\nu_{\max}^{\mathrm{KBr}}$ 1755, 1740 cm^{-1}; nmr (10% $CDCl_3$) see text.

Anal. Calcd for $C_{10}H_{13}Br_3O_6$: C, 25.61; H, 2.79; Br, 51.12. Found: C, 25.78; H, 2.79; Br, 50.94.

The first and third fractions from the separation procedure were combined and recrystallized from 50 ml of methylcyclohexane to give 7.5 g (30.5% from 1) of trimethyl *meso,rac*-methanetri(α-

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[1] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966. See also J. McKenna, J. M. McKenna, and B. A. Wesby, *Chem. Commun.*, 867 (1970).

[2] R. M. Beesley and J. F. Thorpe, *Proc. Chem. Soc.*, **29**, 346 (1913); *J. Chem. Soc.*, **117**, 591 (1920).

[3] It was reported[2] that strong base coverted the tribromide to methyltricyclobutanetricarboxylic acid, the properties of which were not consistent with what is currently known of this ring system: P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 406, 3523, 5291 (1970).

[4] H. O. Larson and R. B. Woodward, *Chem. Ind.* (*London*), 193 (1959).

[5] D. D. Philips, M. A. Acitelli, and J. Meinwald, *J. Amer. Chem Soc.*, **79**, 3517 (1957); H. Stetter and H. Stark, *Chem. Ber.*, **92**, 732 (1959).

bromoacetate) (3): mp 113-114°; ir ν_{max}^{KBr} 1740 cm^{-1}; nmr (10% $CDCl_3$) see text.

Anal. Calcd for $C_{10}H_{13}Br_3O_6$: C, 25.61; H, 2.79; Br, 51.12. Found: C, 25.54; H, 2.83; Br, 50.96.

Registry No.—**2**, 31446-54-5; **3**, 31446-55-6.

Protonation and Alkylation of Dianions Derived from 1,4-Diphenyl-1,4-di(1-naphthyl)butatriene, 2,5-Diphenyl-2,3,4-hexatriene, 1,1,4-Triphenyl-1,2,3-pentatriene, and 1,1-Diphenyl-4-methyl-1,2,3-pentatriene

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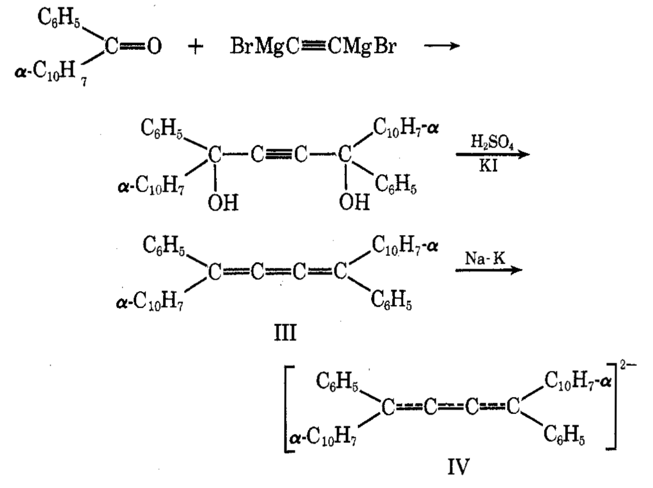
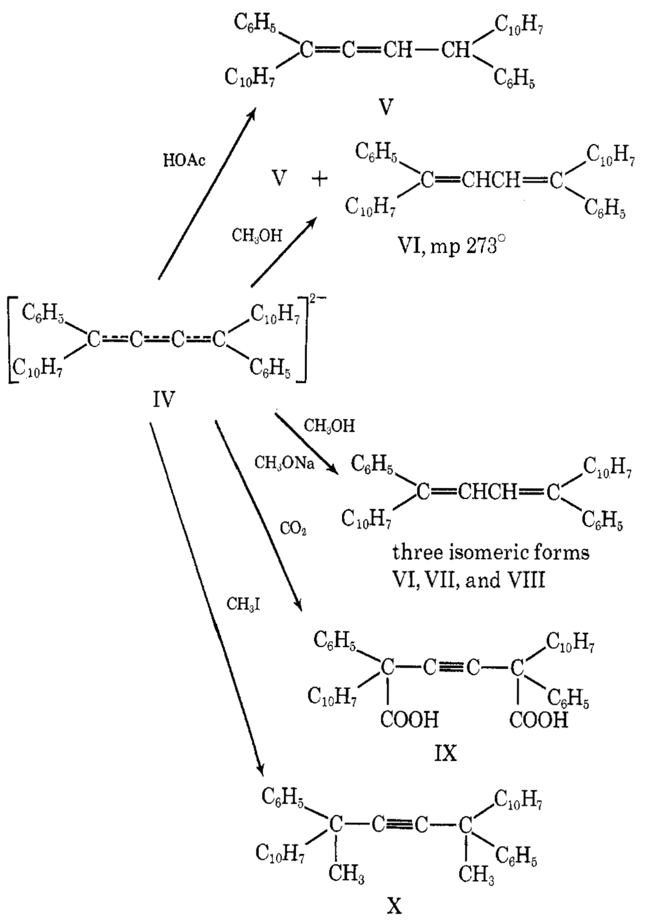
We have recently reported some of the reactions of dianions derived from 1,1,4,4-tetraphenylbutatriene[1] (I) and 1,4-bisbiphenylenebutatriene[2] (II). Both of these trienes are symmetrically substituted and their dianions are stabilized by considerable resonance energy. It was thought that a comparison of some reactions of dianions from less symmetrical butatrienes with reactions of the dianions derived from I and II would be of interest.

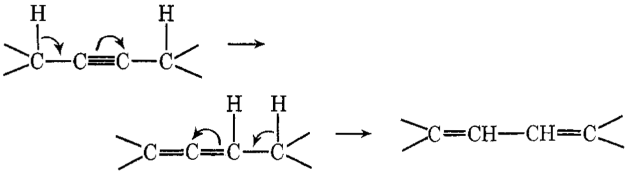
Scheme I



Scheme II



The first dianion which was studied was prepared according to the outline in Scheme I. 1,4-Diphenyl-1,4-di(1-naphthyl)butatriene (III) theoretically may exist in cis and trans forms. Attempts to chromatographically separate the isomers failed.[3] Our attempts to separate isomers also failed. From an examination of models, it would appear that steric interference would make the cis form less probable. The reactions of the dianion from III are shown in Scheme II. We believe that all of these additions involve the same initial step, namely, 1,4 addition. In the case of protonation, the 1,4-dihydro compound, which is kinetically favored, rearranges to the thermodynamically more stable 1,2-diene and finally to the even more stable conjugated diene. In the other cases, *i.e.*, carbonation and methylation, the required hydrogen for the prototropic changes is not present.



1,4-Diphenyl-1,4-di(1-naphthyl)-1,2-butadiene (V) possessed a characteristic[4] infrared absorption at 1950 cm^{-1}. The nmr spectrum consisted of an aromatic multiplet at δ 7.24, an olefinic doublet at δ 6.2 (1, J_{AB} = 6 Hz), and a tertiary proton doublet at δ 5.6 (1, J_{AB} = 6 Hz). The tertiary proton has been shifted downfield owing to deshielding by the aromatic rings.

The 1,2-diene was also prepared by the reduction of the triene III with aluminum amalgam.[5] The diene prepared by this method was identical in every way with the sample obtained from the protonation of the dianion IV. A small amount of the conjugated diene, 1,4-diphenyl-1,4-di(1-naphthyl)-1,3-butadiene (VI), mp 273°, was also isolated. VI showed no allenic absorption at 1950 cm^{-1} and showed the usual conjugated absorption in the uv at 293 and 344 mμ. It was subse-

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[1] S. F. Sisenwine and A. R. Day, *J. Org. Chem.*, **32**, 1770 (1967).

[2] J. M. Edinger and A. R. Day, *ibid.*, **36**, 240 (1971).

[3] R. Kuhn and J. Jahn, *Chem. Ber.*, **86**, 759 (1953).

[4] J. H. Wotiz and D. E. Mancuso [*J. Org. Chem.*, **22**, 207, (1957)] examined 58 allenic compounds and concluded that the infrared band at 1950 cm^{-1} was characteristic of allene bonds.

[5] R. Kuhn and H. Fischer, *Chem. Ber.*, **94**, 3060 (1961).