

AN "AROMATIC" BIS(TRIFLUOROMETHYL)TRIAFULVENE BY A  
CYCLOPROPENONE-BIS(TRIFLUOROMETHYL)KETENE CYCLOADDITION <sup>1</sup>

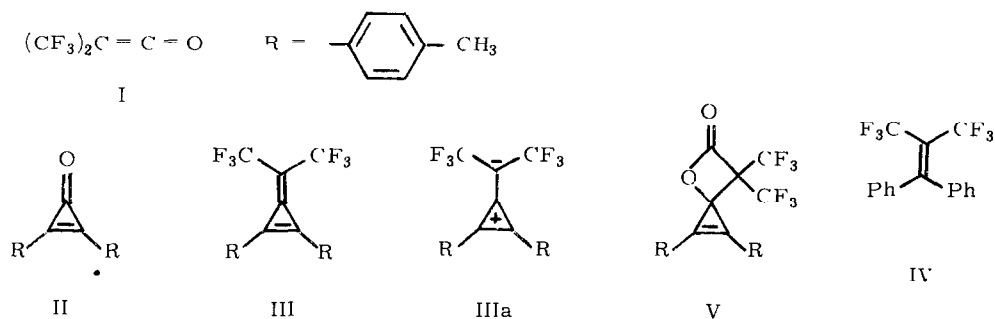
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(Received in UK 21 August 1973; accepted for publication 6 September 1973)

Bis(trifluoromethyl)ketene (I) has been shown to undergo cycloaddition reactions with a variety of unsaturated compounds, including simple olefines.<sup>2</sup> Simple ketones (e.g., acetone), however, are reluctant to cycloadd to I;<sup>3</sup> the reaction does not serve as a general route to 1,1-bis(trifluoromethyl)ethylenes. We wish to report the cycloaddition of *d*<sub>1</sub>-*p*-tolyl-cyclopropenone (II) to I, with the formation of 1,2-*d*<sub>1</sub>-*p*-tolyl-4,4-bis(trifluoromethyl)triafulvene (III). All the triafulvenes investigated so far have carried substituents at the exocyclic position capable of strong resonance interaction.<sup>4,5</sup> The CF<sub>3</sub> group is expected to have a strong inductive effect but little resonance interaction.<sup>6</sup> The synthesis of III permitted a study of the effect of such a substituent on the "aromaticity" of the triafulvene system. The properties of III (particularly its high dipolar character) may shed light upon the more general problem whether dipole moments may serve as a means for determining the "aromaticity" of nonalternant conjugated systems.<sup>7</sup>



Treatment of II<sup>8</sup> with I<sup>9</sup> in toluene solution at room temperature for 5 days afforded III as yellowish fluorescent needles: mp 139° (from methanol or cyclohexane) in 59% yield.<sup>10</sup> The compound could be sublimed at 130°/0.1 mm. The spectral properties of III are in complete accord with the assigned structure. The molecular ion in the mass spectrum<sup>11</sup> of III appeared at  $m/e$  368.0985 and was by far the most abundant signal (calcd. for C<sub>20</sub>H<sub>14</sub>F<sub>6</sub>,  $m/e$  368.09996). The infrared frequency at 1857 cm<sup>-1</sup> (nujol) is characteristic of 1,2-disubstituted triafulvenes.<sup>12-14</sup> The <sup>1</sup>H nmr spectrum of III closely resembled that of II:<sup>15</sup>  $\delta$ CDCl<sub>3</sub> 2.416 (s, 6H, CH<sub>3</sub>), 7.322 (d, J = 8.2 Hz, 4H, Ar ortho to triafulvene) and 7.802 ppm (d, J=8.2 Hz, 4H, Ar meta to triafulvene). The downfield shift of the protons ortho to the triafulvene ring (0.48 ppm relative to the respective meta-protons), which have previously been observed in 1,2-diarylcyclopropenium salts, 1,2-diphenyltriafulvenes and diarylcyclopropenones, is ascribed primarily to the (partial) positive charge in the three-membered ring.<sup>5, 12-13</sup> The <sup>19</sup>F nmr spectrum of III (in CDCl<sub>3</sub>)<sup>15</sup> contained only a singlet at 107.8 ppm. For comparison, the respective singlet of 1,1-bis(trifluoromethyl)-2,2-diphenylethylene (IV)<sup>16</sup> appeared at 106.7 ppm. UV  $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  (log  $\epsilon$ ) 237s nm (4.29), 244s (4.38), 253 (4.51), 300 (3.92), and 342 (4.30). In benzene, ethanol, and acetonitrile, the longest wavelength absorption maximum (representing the N  $\rightarrow$  V<sub>1</sub> transition) appeared at 342, 338, and 334 nm respectively. This blue shift of 8 nm on change of solvent from cyclohexane to acetonitrile is consistent with a decrease in the dipolar character of III in the transition from the ground to the first excited state.

Most striking is the electric dipole moment of III, 7.42 D in benzene solution ( $\alpha' = 74.97$ ,  $\beta' = 1.84$ ,  $MR_{\text{calcd}} = 86.40 \text{ cm}^3$ ,  $P_{2\infty} = 1195.4 \text{ cm}^3$ ).<sup>17</sup> A similar value has been obtained in cyclohexane solution, 7.43 D ( $\alpha' = 53.26$ ,  $\beta' = -1.85$ ,  $P_{2\infty} = 1170.6 \text{ cm}^3$ ). The significance of this high dipole moment is revealed by comparing it with the 2.79 D value of IV (benzene,  $\alpha' = 12.36$ ,  $\beta' = -1.00$ ,  $MR_{\text{calcd}} = 70.95 \text{ cm}^3$ ,  $P_{2\infty} = 227.1 \text{ cm}^3$ ). Thus,  $\mu(\text{III}) - \mu(\text{IV}) \sim 4.6 \text{ D}$ .<sup>18</sup> It should be recalled that the difference between the dipole moments of 4,4-dicyano-1,2-diphenyltriafulvene and 1,1-dicyano-2,2-diphenylethylene was only 2.1 D.<sup>5, 19</sup> It appears that the strong electron-withdrawing character of the two trifluoromethyl groups of III (enhanced by their proper location in the triafulvene system)<sup>6, 20</sup> favors an important contribution of an

"aromatic" dipolar structure (e. g., IIIa) in the ground state. This contribution is significantly greater than the respective contributions in other triafulvenes (reported so far) including 4,4-dicyano-1,2-diphenyltriafulvene. In our opinion, the dipole moment of III reflects the ability of the cyclopropenium nucleus to delocalize the (partial) positive charge over all three carbon atoms of the ring.<sup>21</sup> It is clearly a matter of gradation:<sup>7</sup> a certain deviation from a complete bond alternation picture towards "aromaticity" in the triafulvene system of III is called for.

Two modes of cycloaddition to I are available, across the C=O bond and across the C=C bond.<sup>2</sup> Similarly, ample evidence has accumulated for addition across the C=C bond and the C=O bond of cyclopropenones.<sup>22-23</sup> The formation of III in the reaction of I and II implies cycloaddition of the C=O bond of II across the C=C bond of I. A probable intermediate is the  $\alpha$ -spirolactone V, which could easily eliminate CO<sub>2</sub> to form the stable triafulvene system III. Attempts to isolate the intermediate V have been unsuccessful.

Acknowledgments. This work was financed in part by a grant from The Central Research Fund of the Hebrew University. We express our gratitude to Messrs. E. I. du Pont de Nemours and Company, Wilmington, Delaware, for a generous gift of bis(trifluoromethyl)ketene. We thank Professor Ernst David Bergmann and Professor Joseph Klein of the Hebrew University of Jerusalem, for their encouragement and interest.

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