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A NEW TRIMETHYLENECYCLOBUTANONE

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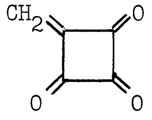
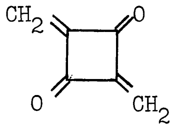
2,3-Bis(diphenylmethylene)-4-benzylidenecyclobutanone (VII) was prepared and its spectral data were compared with those of 2,4- (IX) and 3,4-bis(diphenylmethylene)cyclobutanedione (X).

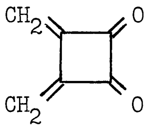
Of the five possible methylene analogs (I-V) of the hitherto unknown cyclobutanetetraone, tetraphenyl derivative[1] of II (IX), tetrachloro[2] and tetraphenyl derivative (X)[3] of III, and V itself[4] and its octachloro[5] and octaphenyl derivative[6] have been prepared. Nevertheless, no mono (I) and trimethylene analog (IV) have yet been reported. We wish to report the synthesis of pentaphenyl derivative of IV (VII), and the comparison of its spectral data with those of IX and X.



(I)



(II)



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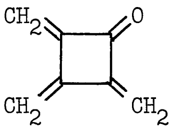
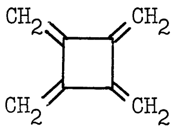


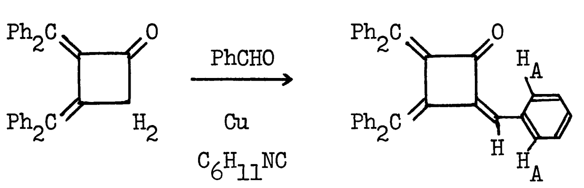
(IV)



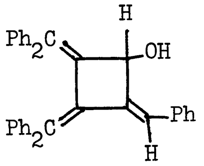
(V)

The compound VII was prepared by the condensation of 2,3-bis(diphenylmethylene)cyclobutanone (VI)[7] with benzaldehyde, according to an active methylene-ketone condensation procedure reported by T. Saegusa and his co-workers.[8] A mixture of VI (2 mmoles), benzaldehyde (4 mmoles), Cu-powder (3 mg atoms) and cyclohexyl isocyanide (3 mmoles) was stirred at room temperature for 12 hr. The reaction mixture was chromatographed on alumina with using CCl_4 as a solvent. From the first elution, VII was obtained, after recrystallization from benzene-ethanol, as red needles, in a 51.5% yield, mp 231-232 °C. The structure of VII was identified by the spectral data. IR (Nujol), 1745 (C=O) and 1550 cm^{-1} (C=C); UV ($CHCl_3$), 285 (24200), 305 (21400), 400 (24200) and 500 nm (ε, 7800); NMR ($CDCl_3$), 2.28 (m, Ph, 2H), 2.61(m, Ph, 13H), 3.22 (m, Ph, 10H) and 4.02 τ (s, =CH, 1H).

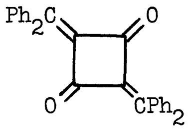
The geometry around the double bond of benzylidene group was established to be that of VII by the following reasons. The NMR signal at the lowest field (2.28 τ) can be assigned to the two ortho



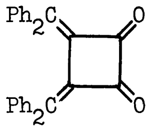
(VI) (VII)



(VIII)



(IX)



(X)

phenyl protons H_A, which are deshielded by a diamagnetic anisotropy of the carbonyl. The deshielding is likely since VIII prepared by the sodium borohydride reduction of VII, showed no signal at the field lower than 2.6 τ in $CDCl_3$; 2.62 (s, Ph, 15H), 3.19 (s, Ph, 10H), 4.05 (s, =CH, 1H), 4.23 (s, OH, 1H) and 7.79 τ (s, CH, 1H). The fact that the vinyl proton signals of VII (4.02 τ) and VIII (4.05 τ) appeared at almost the same field, also supports the structure of VII. However, all the phenyl protons of diphenylmethylene moieties of VII appeared at the field higher than 2.5 τ. Similar facts have been observed for IX[1] and X[3]. The results are probably due to a crowding among phenyl group which hinders to arrange phenyl and carbonyl on an effective coplane for deshielding.

The UV spectrum of VII differs from those of IX (in CH_3OH, 311 (10500), 347 (8100), 437 sh (35500) and 462 nm (ε, 53700))[1] and of X (in CH_3CN, 315 sh (6300), 465 sh (6200), 499 (12000) and 620 nm (ε, 3100)[3]. Although λ_{max} of those compounds increased in the sequence of $X > VII > IX$, ε_{max} increased in the sequence of $IX > VII > X$. On the other hand, the wavenumber of $\nu C=O$ increased in the sequence of X (1750)[3] > VII (1745) > IX (1692 cm^{-1})[1].

Chemical behaviors of VII, IX and X in methanolic potassium hydroxide are distinguishable each other. Although IX dissolves in the base in the form of enolate anion,[1] and X undergoes ring-opening with the base at room temperature to afford 2,3-bis(diphenylmethylene)-3-carbomethoxypropan-1-al,[9] VII did not react with the base even by the heating under reflux.

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