Table I

Expt	Photolysis medium	Product	Yield, %
1	3.3% H_2SO_4	Triphenylmethane	21
	96.5% CH_3COOH	9-Phenylfluorene	22
	0.2% H_2O	Bis(9-phenylfluorenyl) peroxide	17
2	3.3% H_2SO_4	1,1,1,2-Tetraphenylethane	45
	80.1% CH_3COOH	Triphenylmethane	8
	16.4% $C_6H_5CH_3$	9-Phenylfluorene	12
	0.2% H_2O	9-Benzyl-9-phenylfluorene	10
3	1.5% H_2SO_4	Tetraphenylmethane	5–10
	96.2% CH_3COOH	(plus all products found in	
	2.3% C_6H_6	expt 1)	
4	72% H_2SO_4 (aqueous)	*p*-$A(C_6H_5)_2CC_6H_4C_6H_4C(C_6H_5)_2A'$-*p*	
		I, A = A′ = H	20
		II, A = A′ = OH	22
		III, A = H; A′ = OH	22
5	29.4% H_2SO_4	*p*-$(C_6H_5)_3CC_6H_4C(OH)(C_6H_5)_2$	
	69.4% CH_3COOH	IV	30
	1.2% H_2O	III	12
		Five hydrocarbons[a]	25
6	61% H_2SO_4	II	56
	36.5% CH_3COOH		
	2.5% H_2O		

[a] All appeared to be 9-phenylfluorene derivatives on the basis of their uv spectral properties, but were not characterized further.

carbonium ion. (It had been noted previously that the rate of dimerization in expt 4 was first order in ground-state carbonium ion.[2]) The evidence obtained also indicates that trityl radical, implicated in the more weakly acidic systems (expt 1, 2, 3, and 5), arises from V. When expt 1 was carried out in the presence of toluene, cumene, or cyclohexane (each at *ca.* 10^{-2} *M*), the disappearance of the starting carbinol was accelerated. (This is apparently due to the added hydrocarbons' providing an additional reaction pathway for the excited trityl cation, as shown by the products obtained in expt 2).[4] Per mole, cumene is 11.2 times as efficient as toluene, and cyclohexane is 0.37 times as efficient as toluene in this acceleration. These selectivity results indicate that mechanisms involving electron transfer from acetate or bisulfate anions[5] or from toluene or cumene[6] to excited trityl cation are not involved, but are instead consistent with hydrogen atom abstraction by triplet triphenylcarbonium ion. That it is the methine position that is the site of hydrogen atom capture in these weakly acidic systems is supported by the observations that, when C_6D_6 was used in expt 3, the isolated tetraphenylmethane was entirely tetraphenylmethane-d_5, and that when *ortho*- and *para*-deuterated triphenylcarbonium ion was used in expt 2, no deuterium loss was noted in the isolated triphenylmethane and 1,1,1,2-tetraphenylethane.[7] The mechanism of formation of triphenylmethane and the 9-phenylfluorenyl system will be discussed later.

Acknowledgment. The author wishes to thank Professor E. E. van Tamelen for suggesting this study and for providing advice throughout its course. Thanks are also due Professors Lawrence Altman and Cheves Walling for many helpful suggestions. This project was supported by the Army Research Office–Durham (Project No. CRD-AA-5227-C) and the Petroleum Research Fund (Grant 2892 (A1,4)), administered by the American Chemical Society.

(4) Presumably in the absence of added hydrogen donors, the excited trityl cation abstracts a hydrogen atom from the methyl group of acetic acid. Due to the removal of all acids in the work-up procedure, products from the acetic acid derived radical were not characterized.

(5) Added hydrocarbons would react with the anion-derived radicals, thereby reducing the amount of electron "retransfer" to regenerate trityl cation and the anion. However, acetoxy or bisulfate radicals would not be expected to exhibit such a large hydrogen abstraction selectivity. The sulfate radical anion is known to be an extremely potent hydrogen abstractor, generating in aqueous base hydroxyl radicals from water (L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 71, 2611 (1967)). The observed selectivity is three times greater than that reported for methyl radical (W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 170) and still greater than that which would be expected for acetoxy radical. In addition, if acetoxy radical had been formed, considerable decarboxylation would have been expected (M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.*, **65**, 15 (1943); T. W. Martin, J. M. Buck, and A. Henshall, *ibid.*, **88**, 1097 (1966)). In expt 2 a maximum of 2% of the theoretical amount of carbon dioxide was obtained.

(6) It has been proposed recently (E. I. Heiba, R. M. Dessau, and W. J. Koehl, *ibid.*, 91, 6830 (1969)) that the $Co(OAc)_3$ oxidation of alkylbenzenes in acetic acid proceeds *via* electron transfer from the arene to the cobalt(III), followed by proton loss from the resulting cation radical. These workers found that toluene is oxidized 3.3 times faster than cumene in that reaction. A mechanism of this type would also not account for the slight, but definite, effect of added cyclohexane in accelerating the disappearance of trityl cation.

(7) We thank Dr. Alan Duffield for taking the mass spectra (MS-9 direct inlet).

(8) National Institutes of Health Predoctoral Fellow, 1965–1968; address correspondence to Department of Chemistry, Columbia University, New York, N. Y. 10027.

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Tri-*t*-butylethylene[1]

Sir:

The members of the family of *t*-butylethylenes have remained elusive compounds; their facile synthesis, particularly of pure samples, has been balked by the bulky groups present and by the propensity of various precursors for rearrangement. Nevertheless *t*-butylethylene (**1**),[2a] 1,1-di-*t*-butylethylene (**2**),[2b] *cis*-1,2-di-*t*-butylethylene (**3**),[2c] and *trans*-1,2-di-*t*-butylethylene (**4**)[2d] have been previously prepared and have proven

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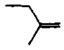
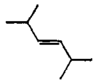
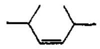
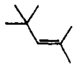
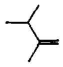
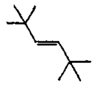
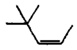
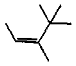
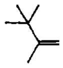
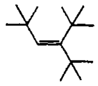
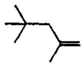
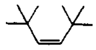
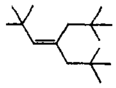
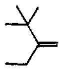
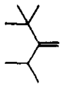
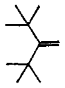
(1) Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN 100.

(2) (a) M. Delacre, *Bull. Soc. Chim. Fr.*, **35** (3), 343 (1906); (b) F. C. Whitmore and K. C. Laughlin, *J. Amer. Chem. Soc.*, **55**, 3732 (1933); (c) G. F. Hennion and T. F. Banigan, Jr., *ibid.*, **68**, 1202 (1946); (d) F. L. Howard, T. W. Mears, A. Fookson, and P. Pomerantz, *ibid.*, **68**, 2121 (1946).

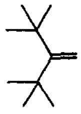
Table I. Raman Stretching Frequencies (cm^{-1}) of Alkyl-Substituted Olefins[a]

1,1-Disub	ν	*trans*-1,2-Disub	ν	*cis*-1,2-Disub	ν	Trisub	ν
	1658[b]		1676[b]		1660[b]		1678
	1649		1666.5		1655		1663.5
	1645		1656		1650		1658
	1638.5				1651.5		1583
	1640				(1631)[b] 1629		1636[c]
	1636						
	1635.8						
	1615.5						

[a] Cary 81 Raman instrument with a He-Ne laser source used for all values obtained in these laboratories. [b] Reference 12a. [c] 1,1-Dineopentyl-2-*t*-butylethylene, obtained from pyrolysis of the corresponding *p*-nitrobenzoate.[6]

fruitful subjects of investigation. The geminal di-*t*-butyl compound (2) has been a valuable intermediate


1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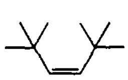
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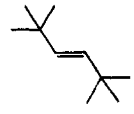
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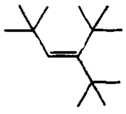
5

for the preparation of a variety of other crowded compounds[3] and the *cis*- and *trans*-di-*t*-butylethylenes have been used to determine the 10-kcal strain present in the *cis* isomer[4a,b] and in investigations of the unusual reactivity resulting from their highly branched structures.[4a,5] The preparation and characterization of the last but one of this family, tri-*t*-butylethylene (5), are the subjects of this communication.

Di-*t*-butylneopentylcarbinyl *p*-nitrobenzoate (6)[6] was heated to 160° at 1 mm with an initial melting at a bath temperature of 110° followed by resolidification leaving solid *p*-nitrobenzoic acid. The volatile material collected in a cold trap totaled a 54% yield of a mixture of unsaturated hydrocarbons. Analysis by glpc (10 ft × $^3/_8$ in. 30% SE-52 on Chromosorb W column, 160°, 75 ml/min of He) showed two fractions with retention times of about 20 min. The first, corresponding to 60% of the total, was collected and identified as tri-*t*-butylethylene (5) by its elemental analysis, mass spectral molecular ion (*m/e* 196), Raman spectrum (1583 cm^{-1}, C=C), and nmr spectrum [(CCl_4) δ 1.07, 1.09, and 1.22 (each s, 9, *t*-Bu), and 5.22 (s, 1, vinyl H)].

The second fraction above was collected and found to separate into two components by glpc (20 ft × $^3/_8$ in. 30% FFAP on Chromosorb W, 80°, 75 ml/min of He) with retention times of about 4 hr. These were collected and the first was identified as 1-*t*-butyl-1-neopentyl-2,2-dimethylcyclopropane (7) by its elemental analysis, mass spectral molecular ion (*m/e* 196), near ir (6115 cm^{-1}, cyclopropyl C-H overtone),[7] ir (3060 cm^{-1}, cyclopropyl C-H), the absence of any C=C stretching band in the Raman spectrum, and its nmr spectrum [(CCl_4) δ 0.65 (s, 2, CH_2 of cyclopropyl), 1.00 (s, 9, *t*-Bu), 1.02 (s, 9, *t*-Bu), 1.12 (s, 3, Me), 1.38 (s, 3, Me), and 1.60 and 1.74 (center peaks of AB quartet of diastereotopic CH_2 of neopentyl, J = 16 Hz)]. The second component from this separation was the known 2,3,5,5-tetramethyl-3-*t*-butylhexene-1 (8).[6,8]

The formation of these products can be rationalized by the scheme shown. The reaction is written as proceeding through an initial ion pair rather than by concerted loss of *p*-nitrobenzoic acid on the basis of the significant portion of rearrangement observed.[9] The extraordinary formation of a cyclopropane from a stable tertiary ion is presumably facilitated by the widened external angles and the consequent decrease in steric interaction in the product.[11]

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(3) (a) M. S. Newman, A. Arkell, and T. Funkunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960); (b) M. S. Newman and T. Funkunaga, *ibid.*, **85**, 1176 (1963); (c) E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodlett, and K. C. Brannock, *J. Org. Chem.*, **33**, 2738 (1968); (d) M. S. Newman and A. Leegwater, *ibid.*, **33**, 2144 (1968); (e) J.-É. Dubois and M. Boussu, *C. R. Acad. Sci., Ser. C.*, **268**, 1603 (1969).

(4) (a) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **81**, 1611 (1959); (b) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958).

(5) (a) R. C. Fahey, *ibid.*, **88**, 4681 (1966); (b) T. J. Logan and T. J. Flautt, *ibid.*, **82**, 3446 (1960).

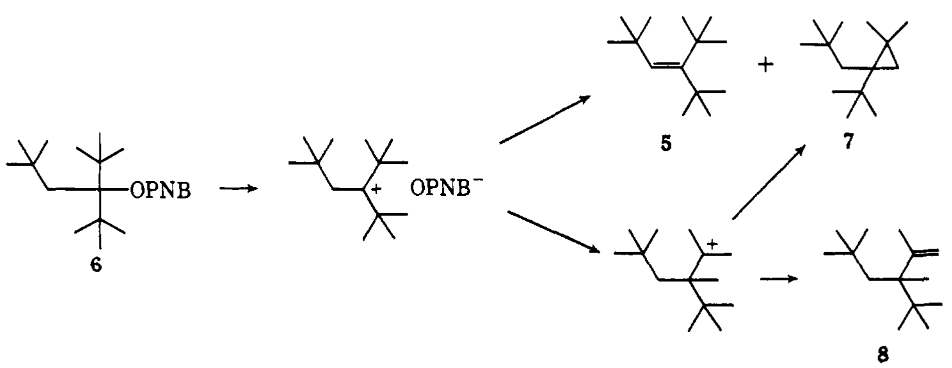
(6) P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968).

(7) W. H. Washburn and M. J. Mahoney, *ibid.*, **80**, 504 (1958); P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

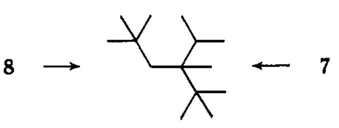
(8) Previously[6] the solvolysis of 6 in 60% aqueous dioxane containing an equivalent amount of NaOH was reported to give 5 and 8 in the ratio 11:89. However 5 was obtained in an impure state and the only evidence for its structure was the nmr of the impure material. Repetition of the solvolysis in the absence of base and with more careful examination of the reaction product revealed the cyclopropyl product 7 present to the extent of 5%.

(9) The question of whether gas phase pyrolysis of esters involves concerted elimination or ion pairs is being actively discussed.[10] Reactions in solid or molten state would presumably be much more likely to involve ion pairs.

(10) K. K. Lum and G. G. Smith, *Int. J. Chem. Kinet.*, **1**, 401 (1969); E. S. Lewis and E. R. Newman, *J. Amer. Chem. Soc.*, **91**, 7455 (1969).



Hydrogenation of **8** (60 psi, PtO_2 in acetic acid) leads to methylisopropyl-*t*-butylneopentylmethane (**9**): nmr [(CCl_4) δ 0.89 (s, 9, *t*-Bu), 0.98 (d, 6, J = 7 Hz, *i*-Pr Me's), 0.99 (s, 9, *t*-Bu), 1.10 (s, 3, Me), 1.35 and 1.49 (center peaks of AB quartet of diastereotopic CH_2 of neopentyl), and 2.05 (heptet, 1, J = 7 Hz, methine H of isopropyl)]. Hydrogenolysis of **7** (60 psi, PtO_2 in acetic acid containing $HClO_4$) also gave **9**.



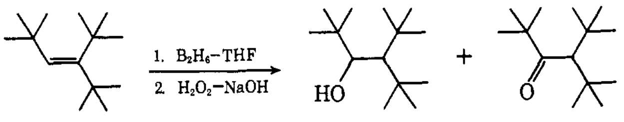
9

The consequences of crowding on the structures of olefins are exemplified by the stretching frequencies of the carbon–carbon double bonds of **2–5** and some other model compounds determined by Raman spectroscopy and listed in Table I. The continual drop in frequency with increasing crowding is readily apparent. Examples of such effects, albeit of smaller magnitude, have been observed previously[12,13] and for exocyclic olefins have been correlated with similar effects in the carbonyl derivatives.[14] Such shifts are generally deemed to arise from changes in bond angles.[12–14] It is often considered that the alteration in hybridization resulting from the bond-angle changes determines the observed variation in frequencies.[12c,14] On the other hand it has been argued[12b,13] that the frequency shift due to hybridization has been greatly exaggerated, and that the primary contributor to the shift is the coupling of the double bond stretching with the adjacent single bonds, such that compression and elongation of the single bonds occurs during the double bond vibration. These deformations are angle dependent and hence give rise to the frequency shift.

The observed decrease in frequency of *cis*-di-*t*-butylethylene and tri-*t*-butylethylene are difficult to rationalize as due to rehybridization, for the effect in the cycloalkanes is to *increase* the frequency with expanding C—C=C—C angles.[12c,13] A likely consequence of the strain in these branched compounds, as suggested by Rea,[12b] is that the groups would twist out-of-plane to minimize steric repulsions. The π overlap of the double bond would consequently be disturbed giving a weaker bond, with a resultant lowering of the stretching frequency.[12b] Support for this theory comes from comparison of the strain in *cis*-di-*t*-butylethylene (10 kcal/mol)[4a,b] and *o*-di-*t*-butylbenzene (22.3 kcal/mol);[15] the bond distance connecting the *t*-butyls is shorter in the olefin but the lower rigidity of the ethylenic link could permit twisting and consequent reduction of the strain.[15a]

Strained trisubstituted double bonds are also present in bicyclic compounds with bridgehead olefinic groups; reported examples and observed stretching frequencies include bicyclo[3.3.1]non-1-ene (1625 cm^{-1})[16a] (1620 cm^{-1}),[16b] bicyclo[4.2.1]non-1(2)-ene (1655 cm^{-1}),[16c] and bicyclo[4.2.1]non-1(8)-ene (1607 cm^{-1}).[16c]

Hydroboration–oxidation of **5** (*in situ* generation of diborane)[17] gave not only the expected alcohol (**10**) but also the known[3e] corresponding ketone (**11**) in approximately equal amounts. Further experiments are underway to determine the steps leading to the formation of **11**.



Acknowledgments. Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to the National Science Foundation for an equipment grant for purchasing the mass spectrometer. Thanks are due to Professor John R. Dyer for supplying 100-MHz nmr spectra, and to Professor James Durig of this department for the Raman spectra.

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(11) For the absence of cyclopropanes from the *t*-pentyl cation see P. S. Skell and I. Starter, *J. Amer. Chem. Soc.*, **82**, 2971 (1960) (deoxidation route), and M. S. Silver, *ibid.*, **83**, 3482 (1961) (solvolysis and deamination routes).

(12) (a) N. Sheppard and D. M. Simpson, *Quart. Rev. Chem. Soc.*, **6**, 1 (1952); (b) D. G. Rea, *Anal. Chem.*, **32**, 1638 (1960); (c) F. H. A. Rummens, *Recl. Trav. Chim. Pays-Bas*, **84**, 5 (1965).

(13) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen and Co., London, 1968, pp 22–26, 30–32, 132–135.

(14) S. Bank, W. D. Closson, and L. T. Hodgins, *Tetrahedron*, **24**, 381 (1968).

(15) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967).

(15a) Note Added in Proof. Bond stretching could also weaken the bond and give rise to the observed effects (except in the geminally disubstituted case). We thank Professor N. L. Allinger for trenchant comments on this point.

(16) (a) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970); (b) J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970); (c) J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969).

(17) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

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