taminated with ~28% *cis*-pulegenic acid. A pure sample of **7** proved difficult to obtain because of its conversion to lactone **6**.

Methyl *cis,cis*-2-isopropenyl-5-methyl-1-cyclopentanecarboxylate (**14**), prepared by treatment of acid **7** with diazomethane and purified by glpc, showed ir absorption at 5.75, 6.07, and 11.18 μ; nmr (CCl_4) 0.97 (d, 3, CH_3), 1.72 (s, 3, $CH_3C{=}C$), 2.85–3.05 (m, 1, $CHCO_2Me$), 3.48 (s, 3, OCH_3), and 4.71 (s, 2, $C{=}CH_2$).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.50; H, 10.22.

***cis,cis*-Dihydronepetalactone (10) and *cis cis*-Isodihydronepetalactone (11).**—A solution of crude **7** in *THF* was added to 28 ml of 0.57 *M* 9-BBN under a nitrogen atmosphere. A total of 0.90 equiv of hydrogen gas was evolved. An additional 24 ml of 9-BBN solution was added and the solution was stirred at ambient temperature for 13 hr. The reaction was worked up in the usual manner and the basic aqueous solution was acidified and allowed to stir overnight. Extraction with ether afforded 2.65 g of liquid whose ir spectrum showed the presence of a hydroxy acid and only a small amount of lactone. The liquid was heated at 175° for 1 hr, and some acidic material was removed by dissolving the oil in ether and washing with sodium bicarbonate solution. The ether was removed and glpc (20% Carbowax 20M column at 195°) indicated the presence of two major components and three minor components (2%) which were not investigated further. The major component were isolated by glpc.

cis,cis-Isodihydronepetalactone (**11**) (15–20% of the mixture) showed a retention time of 68 min; $[\alpha]^{28}D$ −92.4° (*c* 4.30, $CHCl_3$); ir (CCl_4) 5.70 μ; nmr 0.92 (d, 3, J = 6 Hz, CH_3), 1.12 (d, 3, J = 5.5 Hz, CH_3), 3.69 and 4.28 (m, 2, J_{AB} = 11.5 Hz, J_{AX} = 6.5 Hz, J_{BX} = 7.5 Hz, $CHCH_2O$); mass spectrum *m/e* (rel intensity) 168 (7), 113 (37), 110 (46), 95 (44), 82 (33), 81 (92), 69 (47), 67 (56), 55 (40), 41 (100), and 39 (74).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.62; H, 9.76.

cis,cis-Dihydronepetalactone (**10**) (75–80% of the mixture) showed a retention time of 82 min; $[\alpha]^{28}D$ −15.6° (*c* 11.0, $CHCl_3$); ir (CCl_4) 5.74 μ; nmr 0.90 (d, 3, J = 6.5 Hz, CH_3), 0.92 (d, 3, J = 7 Hz, CH_3), 3.0 (m, 1, J_{AX} = 10 Hz, J_{BX} = 8.5 Hz, CHCO), and 3.95 ppm (m, 2, J_{AB} = 7 Hz, J_{BX} = 8.5 Hz, CHCO), and 3.95 ppm (m, 2, J_{AB} = 7 Hz, J_{AX} = 1.5 Hz, J_{BX} = 0, $CHCH_2O$); mass spectrum *m/e* (rel intensity) 168 (5), 113 (55), 81 (38), 67 (45), 55 (30), 53 (28), 41 (100), and 39 (83).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.66; H, 9.69.

Registry No.—**1**, 35337-11-2; **3**, 35337-12-3; **7**, 35337-13-4; **10**, 35337-14-5; **11**, 35337-15-6; **13**, 35337-16-7; **14**, 35337-17-8.

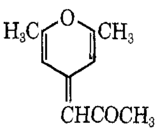
2,4,9-Trioxaadamantanes from Isobutylene and Pivaloyl Halides

MAYNARD S. RAASCH* AND CARL G. KRESPAN

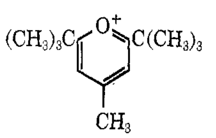
Contribution No. 1914 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received April 4, 1972

The Friedel–Crafts acylation of olefins has been one of the more thoroughly studied reactions.[1] Monoacylation is known to give chloro ketones and α,β- and β,γ-unsaturated ketones, whereas diacylation forms pyrilium salts. One type of triacylation is known in which formation of the pyrane **1** from 3 mol of acetyl chloride and 1 mol of isobutylene in the presence of aluminum chloride involves each of the terminal carbon atoms of isobutylene.[2] However, acylation of isobutylene with pivaloyl chloride in the presence of aluminum chloride has only been reported to give $(CH_3)_3CCOCH{=}C(CH_3)_2$[3] and a pyrilium salt (**2**) when stannic chloride is used.[4]

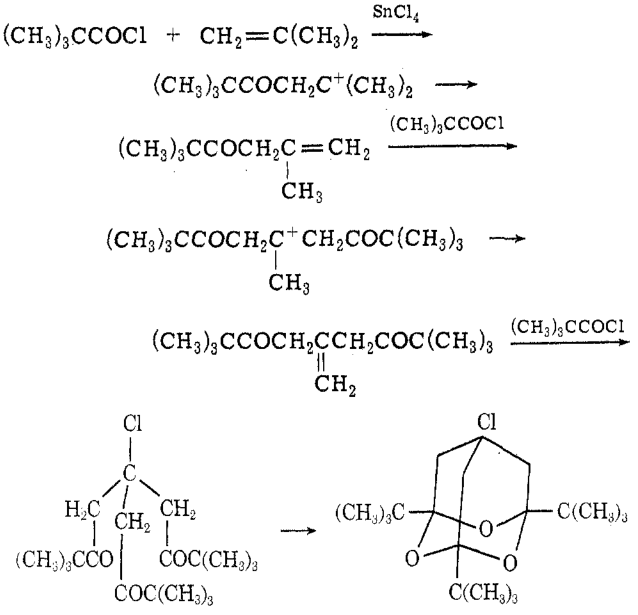


1



2

A new type of triacylation product has now been found in the reaction of pivaloyl halides with isobutylene. Simply by adding less than 0.1 molar equiv of stannic chloride to a liquid mixture of isobutylene and pivaloyl chloride at −15°, a 32–35% yield of 7-chloro-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane (**4**) can be filtered off. Another 6% can be obtained from the filtrate. The compound presumably arises through the intermediate formation of triketone **3** by a reaction sequence of the following type.



$$(CH_3)_3CCOCl + CH_2{=}C(CH_3)_2 \xrightarrow{SnCl_4} (CH_3)_3CCOCH_2C^+(CH_3)_2 \longrightarrow (CH_3)_3CCOCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{(CH_3)_3CCOCl} (CH_3)_3CCOCH_2\underset{\displaystyle CH_3}{\underset{|}{C^+}}CH_2COC(CH_3)_3 \longrightarrow (CH_3)_3CCOCH_2\underset{\displaystyle CH_2}{\underset{\|}{C}}CH_2COC(CH_3)_3 \xrightarrow{(CH_3)_3CCOCl}$$

3 **4**

That a tricarbonyl compound of the structure $R'C(CH_2COR)_3$ will cyclize to a 2,4,9-trioxaadamantane was established by Stetter and Dohr,[5] who ozonized trimethallylcarbinol. The triketone was not isolated but spontaneously formed the 7-hydroxytrioxaadamantane, which they converted to 7-chloro-1,3,5-trimethyl-2,4,9-trioxaadamantane. Only one other synthesis for 2,4,9-trioxaadamantanes, that of Stetter and Stark,[6] has been reported. This route involved the preparation of $HC(CH_2COCHN_2)_3$ and conversion with hydrogen chloride or bromide to $HC(CH_2COCH_2X)_3$, which cyclized.

The ir spectrum of 7-chloro-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane (**4**) was taken at 155, 165, and 183° but gave no indication of reversion to the carbonyl form. The chlorine atom, as in the Stetter and Dohr compound, was unaffected by refluxing al-

---

[1] C. D. Nenitzescu and A. T. Balaban in "Friedel–Crafts and Related Reactions," Vol. III, Part 2, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, pp 1033–1152.

[2] A. T. Balaban, P. T. Frangopol, A. R. Katritzky, and C. D. Nenitzescu, *J. Chem. Soc.*, 3889 (1962).

[3] M. E. Grundy, W. H. Hsü, and E. Rothstein, *ibid.*, 4136 (1952).

[4] A. T. Balaban and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **625**, 74 (1959).

[5] H. Stetter and M. Dohr, *Chem. Ber.*, **86**, 589 (1953).

[6] H. Stetter and H. Stark, *ibid.*, **92**, 732 (1959).

coholic potassium hydroxide, in accord with its bridgehead position. Nmr ($CDCl_3$) showed singlets at 0.99 and 2.16 ppm in a 9:2 ratio.

Use of pivaloyl bromide and stannic bromide gave the bromo analog in 28% yield. With chloropivaloyl chloride and stannic chloride a 0.5% yield of 7-chloro-1,3,5-tris(2-chloro-1,1-dimethylethyl)-2,4,9-trioxaadamantane was obtained.

Experimental Section

7-Chloro-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane.—Pivaloyl chloride (80 g, 0.66 mol) was placed in a 500-ml, three-necked flask equipped with magnetic stirrer, Dry Ice condenser, thermometer, and inlet tube. The flask was cooled to −30° and 50 g (0.9 mol) of liquid isobutylene was introduced. The inlet tube was replaced with a small dropping funnel and anhydrous stannic chloride (7 ml, 16 g, 0.06 mol) was added dropwise during 45 min while the temperature was maintained at *ca.* −15° by cooling with Dry Ice-acetone. The cooling bath was removed and the mixture was allowed to stand for 1 hr. The crystals of the trioxaadamantane were filtered off and rinsed with methanol. The original filtrate was kept separate from the methanol rinse. The yield at this point was 24 g (32%): mp 161–162° after recrystallization from acetone; ir 2976, 2882 (CH), 1389, 1359 (gem CH_3 groups), 1175–1050 cm^{-1} (multiple strong bands for C–O–C–O–C), no evidence of C=O, C=C, OH.

Anal. Calcd for $C_{19}H_{33}ClO_3$: C, 66.16; H, 9.64; Cl, 10.28; mol wt, 345. Found: C, 66.21; H, 9.78; Cl, 10.14; mol wt, 339 (cryoscopic in benzene).

After standing for a day, the original filtrate from the crystals was distilled to give 21.3 g (23%) of 2,2,5-trimethyl-4-hexen-3-one:[3] bp 67–68° (24 mm); $n^{25}\text{D}$ 1.4437; nmr (neat) 0.75 [s, $(CH_3)_3C$], 1.52 and 1.72 [unsharp doublets, $=C(CH_3)_2$], 5.98 ppm (broad peak, =CH). The pot residue yielded 4.7 g (6%) more of the trioxaadamantane. In a run in which the liquid product was distilled immediately, HCl had not split out and 5-chloro-2,2,5-trimethyl-3-hexanone, $(CH_3)_3CCOCH_2CCl(CH_3)_2$, distilled out: bp 71–72° (12 mm); $n^{25}\text{D}$ 1.4367; nmr (neat) 0.97 [s, $C(CH_3)_3$], 1.53 [s, $ClC(CH_3)_2$], 2.92 ppm (s, CH_2), no =CH peak. On standing overnight, the chloro ketone turned dark and evolved HCl. External tetramethylsilane was used as nmr reference for all compounds.

The reaction between pivaloyl chloride and isobutylene was tried in the stoichiometric ratio of 3:1, without solvent and with hexane as a solvent, but the yields of the trioxaadamantane filtered off were only 11 and 9%, respectively. When a mole ratio of 1:1 was used, without solvent, the yield filtered off was 35%.

7-Bromo-1,3,5-tri-*tert*-butyl-2,4,9-trioxaadamantane.—The reaction was carried out as for the chloro compound using 25 g (0.15 mol) of pivaloyl bromide,[7] 8 g (0.14 mol) of isobutylene, and 4 g (0.009 mol) of stannic bromide.[8] The mixture did not become noticeably exothermic at −15°, but when the cooling bath was removed the temperature eventually rose to 33° and crystals separated. The cooled mixture was filtered and the crystals were rinsed with methanol to give 5.4 g (28%) of the trioxaadamantane. Recrystallization from acetone left 4.6 g: mp 166°; ir 2967, 2882 (CH), 1393, 1376 (*gem*-CH_3 groups), 1175–1050 cm^{-1} (multiple bands for C–O–C–O–C); nmr ($CDCl_3$) 0.99 [s, $(CH_3)_3C$], 2.38 ppm (CH_2).

Anal. Calcd for $C_{19}H_{33}BrO_3$: C, 58.60; H, 8.54; Br, 20.52. Found: C, 58.84; H, 8.41; Br, 20.21.

7-Chloro-1,3,5-tris(2-chloro-1,1-dimethylethyl)-2,4,9-trioxaadamantane.—Dropwise addition of stannic chloride (5 ml, 11.3 g, 0.043 mol) to 100 g (0.65 mol) of chloropivaloyl chloride[9] and 50 g (0.9 mol) of isobutylene at −15° produced an exothermic reaction and a viscous polymer layer separated. The mixture was allowed to stand for 16 hr. A few crystals in the liquid phase were filtered off. The polymer layer was extracted with hot acetone to yield a few more crystals. The yield of the trioxaadamantane was 0.5 g (0.5%): mp 156–157° from acetone; ir 2994, 2890 (CH), 1374, 1359 (*gem*-CH_3 groups), 1182, 1121, 1038 cm^{-1} (C–O–C–O–C); nmr ($CDCl_3$) 1.14 [s, $C(CH_3)_2$], 2.32 (s, ring CH_2), 3.67 ppm (s, CH_2Cl).

Anal. Calcd for $C_{19}H_{30}Cl_4O_3$: C, 51.01; H, 6.76; Cl, 31.71. Found: C, 51.07; H, 6.80; Cl, 31.57.

Passing isobutylene into a mixture of chloropivaloyl chloride and stannic chloride gave a similar result.

Registry No.—**4,** 35336-97-1; 2,2,5-trimethyl-4-hexen-3-one, 14705-30-7; 5-chloro-2,2,5-trimethyl-3-hexanone, 35336-99-3; 7-bromo-1,3,5-tri-*tert*-butyl-2,-4,9-trioxaadamantane, 35337-00-9; 7-chloro-1,3,5-tris-(2-chloro-1,1-dimethylethyl)-2,4,9-trioxaadamantane, 35337-01-0; isobutylene, 115-11-7.

---

[7] Y. Yamase, *Bull. Chem. Soc. Jap.*, **34**, 480 (1961).

[8] Research Organic/Inorganic Chemical Corp., Sun Valley, Calif.

[9] F. Nerdel and U. Kretzschmar, *Justus Liebigs Ann. Chem.*, **688**, 61 (1965).

Mononitration of Perylene. Preparation and Structure Proof of the 1 and 3 Isomers

J. J. LOOKER

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received March 8, 1972

The limitations of the published method[1] for the preparation of 3-nitroperylene have recently been pointed out, and an improved procedure was disclosed employing attack by nitrite ion on the perylene radical cation.[2] These limitations have also led us to search for a better method of preparing this nitro compound. We wish to report a simple procedure that not only affords 3-nitroperylene in good yield, but also gives the previously unknown 1 isomer. Formation of the latter is of interest, since the only other example of substitution at position 1 occurred during the reaction of perylene with alkyllithium reagents.[3–5]

When perylene is nitrated in dioxane with dilute nitric acid, a mixture containing two mononitroperylenes is obtained. This mixture is readily separated by column chromatography into a rather insoluble, higher melting (210–212°) isomer (56%) and a lower melting (170–171°) isomer (24%). The higher melting isomer is identical with the compound obtained by the procedure of Dewar and Mole.[1] They proposed, but did not prove, that this compound was 3-nitroperylene (**1a**).

In order to make an unequivocal assignment of structure, the behavior of each isomer toward triethyl phosphite was examined. Only 1-nitroperylene should readily cyclize[6] to an amine. The 3 isomer should give tar,[6] or possibly a phosphoramidate, as observed with 4-dimethylaminonitrosobenzene.[7]

The lower melting isomer (170–171°) gave a good yield (82%) of amine **3** when heated with triethyl phosphite. The higher melting isomer gave a phosphorus-containing compound which is assigned structure **4**, based on its analysis ane spectral properties (Experimental Section). Thus the lower melting isomer is 1-

---

[1] M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956).

[2] C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, **93**, 1811 (1971).

[3] H. E. Zieger and J. E. Rosenkranz, *J. Org. Chem.*, **29**, 2469 (1964).

[4] H. E. Zieger and E. M. Laski, *Tetrahedron Lett.*, 3801 (1966).

[5] H. E. Zieger, *J. Org. Chem.*, **31**, 2977 (1966).

[6] J. I. G. Cadogan, *et al.*, *J. Chem. Soc.*, 4831 (1965).

[7] P. J. Bunyan and J. I. G. Cadogan, *ibid.*, 42 (1963).