

a 2-ethyl substituent, the methyl band is similar in shape to that from a normal acid,⁶ but there is more overlap, and the error is surprisingly large (*cf.* Table I). This appears to be a persistent difficulty with branches larger than methyl. In the case of methyl 4-butyl-4-ethylnonanoate, the overlap of the methyl and methylene bands was so extensive that extrapolation was not attempted.

The location of a methyl group at the 2- or 3-position appears reliable. The 2-methyl doublet ($J = 6$ c.p.s.) appears downfield from the other methyl protons, never quite buried in the huge methylene band (Fig. 1, 2B, 2F). In addition, the multiplet for the single proton in the 2-position is centered at about τ 7.62 (*cf.* Fig. 1), whereas the triplet for a 2-methylene group is centered in the region τ 7.70–7.75. In the case of 2,2-dimethyloctadecanoate, the unsplit band for the two α -methyls is shifted downfield to τ 8.83.

In the case of the 3-methyl substituent, the 2-methylene band is an unsymmetrical doublet, with the major peak (the upfield one, as expected) at τ 7.87. The doublet for the 3-methyl substituent (Fig. 2C) is shifted significantly downfield and lies on the band from the terminal methyl so as to give the appearance of one split band. It is readily distinguished from the split band from the terminal isopropyl group (Fig. 2E), for the latter has sharper peaks, is somewhat upfield, and shows the expected greater intensity for the lower-field segment.

A methyl substituent more remote from carboxyl than the 3-position results in a combined methyl band of rather ill-defined appearance (Fig. 2D), and nothing can be learned of the location. The tracing from 6-methyloctadecanoate is nearly identical with that from 4-methyloctadecanoate.

Determination of spectra was accomplished on a Varian A-60 instrument, operating at 60 Mc./sec., with 6–8% solutions of the esters in carbon tetrachloride. Tetramethylsilane was used as external standard.

(6) The unsymmetrical triplet for the terminal methyl of the same form as in *n*-alkanes, has previously been noted; *e.g.*, *cf.* C. R. Smith, Jr., T. L. Wilson, R. B. Bates, and C. R. Scholfield, *J. Org. Chem.*, **27**, 3112 (1962).

Phenylation of Dinitroalkanes

KYONG PAE PARK AND LEALYN B. CLAPP

Chemistry Department, Brown University,
Providence, Rhode Island 02912

Received January 16, 1964

Publication by Kornblum and Taylor¹ of the method of phenylating nitroalkanes using Beringer's² diphenyliodonium salts prompts us to add a note on phenylation of dinitroalkanes. Using diphenyliodonium tosylate in *t*-butyl alcohol as solvent, phenyl derivatives of 1,1-dinitropropane and 1,1-dinitroethane were obtained from the potassium salts of the dinitroalkanes in 67 and 68% yields, respectively. Yields were less than 5% in *N,N*-dimethylformamide at room temperature

in contrast to Kornblum's findings with mononitroalkanes.

We were unable to phenylate the potassium salts of phenylnitromethane and phenyldinitromethane in either solvent.

Experimental

Potassium 1-Nitropropylnitronate.^{3,4}—In a 1-l. three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel, and cooled with an ice bath, potassium nitrite (85 g., 1 mole) was dissolved in 140 ml. of water. To this was added a solution of 124 g. (1 mole) of 1-chloro-1-nitropropane in 280 ml. of 95% methanol. The temperature was maintained between 0 and 10° while a cold solution of 1 mole of potassium hydroxide in 150 ml. of 95% methanol was added over a 15 min. period. Stirring was continued for 15 min. after completion of the addition and the reaction mixture was allowed to stand overnight in the refrigerator.

The yellow salt was stirred in 300 ml. of warm water to remove large amounts of potassium chloride, cooled in ice, and collected on a Buchner funnel, yielding 150–160 g. (87–93%). The dry potassium 1-nitropropylnitronate can be detonated but can be safely stored at room temperature for at least 10 years!

The less stable potassium salt of 1,1-dinitroethane⁴ was prepared in like manner.

1,1-Dinitro-1-phenylpropane.—Equimolar amounts of potassium 1-nitropropylnitronate (8.00 g., 0.0495 mole) and diphenyliodonium tosylate^{1,5} (22.30 g., 0.0495 mole) in 800 ml. of dry *t*-butyl alcohol were refluxed for 6 hr. The precipitated potassium tosylate was removed by filtration and the solvent was removed at ambient temperatures on a rotating evaporator.

The crude oily mixture was run onto a chromatographic column of acid-free alumina. Elution with petroleum ether (b.p. 30–60°) first removed iodobenzene and then 1,1-dinitro-1-phenylpropane as a pale yellow oil. Distillation at reduced pressure gave 7.0 g. (67%) of colorless product, b.p. 136° (4 mm.), n_D^{25} 1.5270; d_4^{25} 1.2340.

The infrared spectrum verified the presence of the *gem*-dinitro group with absorption at 7.45 and 7.55 μ .⁶ The n.m.r. spectrum verified the presence of one ethyl and one phenyl group in the compound.

Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.40; H, 4.80; N, 13.34. Found: C, 51.46; H, 4.88; N, 13.69.

1,1-Dinitro-1-phenylethane was prepared in a similar manner in 68% yield, b.p. 82–83° (2 mm.), n_D^{25} 1.5320, d_4^{25} 1.2875.

Anal. Calcd. for $C_8H_8N_2O_4$: C, 48.97; H, 4.11; N, 14.27. Found: C, 49.13; H, 4.29; N, 14.40.

In *N,N*-dimethylformamide, the reaction took a different course. Nine grams (0.020 mole) of diphenyliodonium tosylate and 3.24 g. (0.020 mole) of potassium 1-nitropropylnitronate was dissolved in 15 ml. of dry *N,N*-dimethylformamide⁷ by mechanical stirring at room temperature. Within 5 min. an exothermic reaction started but the temperature was kept at 25° by efficient cooling and stirring. After standing overnight the reaction mixture was poured into 100 ml. of ice-water and extracted with 250 ml. of ether in five portions. The ether extract was dried over anhydrous sodium sulfate, reduced to small volume by evaporation, and put on a chromatographic column of alumina. Elution with petroleum ether first gave iodobenzene and then 1.77 g. (72%) of nitrobenzene (b.p. 210°). The infrared spectrum of the nitrobenzene showed only a small absorption at the expected position for a *gem*-dinitro group (*vide supra*), estimated to indicate less than 5% phenylation of the dinitroalkane. The ultimate fate of the alkyl carbons, not immediately apparent, is under investigation.

(3) Preparation worked out by J. S. Belew, R. J. Labrie, and D. E. Bisgrove and supported in part by the Office of Ordnance Research Grant DA-19-020-ORD-592.

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