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A CONVENIENT DEHYDROGENATION REAGENT: TRITYL TRIFLUOROACETATE GENERATED IN SITU

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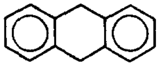
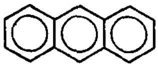
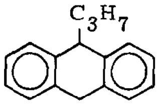
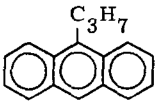
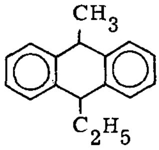
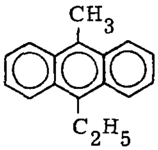
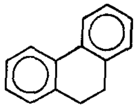
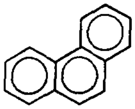
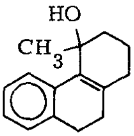
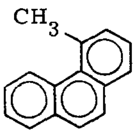
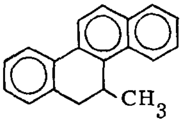
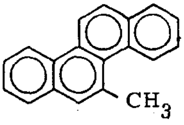
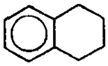
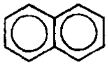
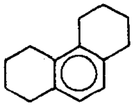
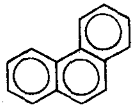
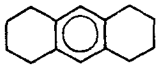
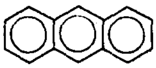
A search for improved methods of dehydrogenation led recently to the discovery of the efficacy of the alkyllithium-TMEDA reagent in combination with certain metal salts for this purpose.[1,2] We now wish to report a second novel dehydrogenation method which offers certain advantages, particularly in the synthesis of carcinogenic polycyclic hydrocarbons.

The new reagent, triphenylmethanol in trifluoroacetic acid, presumably involves trityl trifluoroacetate (I) as the active species. While apparently comparable in reactivity to trityl perchlorate and fluoroborate the utility of which in abstraction of hydride ions and dehydrogenation reactions is well-established[3], I is more convenient and economical than these latter reagents, and in certain cases provides higher yields. Interaction of I generated *in situ* with a series of hydroaromatic compounds occurred smoothly to afford the corresponding fully aromatic molecules in good yield (Table 1).

In a typical reaction, a solution of 9,10-dihydroanthracene (1.80 g, 10 mmol) (II) and triphenylmethanol (2.86 g, 11 mmol) in trifluoroacetic acid (12 ml) was maintained at reflux for 6 hours, then worked up by a conventional extraction procedure. Analysis of the crude product (4.43 g) by nmr[4], glpc[5], and tlc on silica gel impregnated with 2,4,7-trinitrofluorenone[6] in comparison with authentic samples indicated the presence of only anthracene and triphenylmethane. Removal of the latter by trituration with ether gave anthracene mp 215-216° (lit.[8] 216.2-216.4).

Under similar conditions 9,10-dihydrophenanthrene underwent essentially quantitative conversion to phenanthrene. More notably, the 9- and 10-alkyl-substituted derivatives of II which commonly provide relatively unsatisfactory results by other methods[9]

TABLE I. Dehydrogenation with Trityl Trifluoroacetate[10]

Compound	Product	Time, hr	Yield, %
		6	100
		6	65
		20	85
		6 1 1	100 80 84[11]
		3	77
		18	85
		15	100
		18	61
		20	32

also gave good yields of aromatic products. In particular, cis-9-ethyl-10-methyl-II which with other reagents[9] furnished relatively complex product mixtures from which only low yields of 9-ethyl-10-methyl-anthracene could be isolated, on treatment with I provided the latter compound in 85% yield. Also, 9-isopropyl-II which furnished dimeric products with the RLi-TMEDA reagent[2] was converted by I to 9-isopropylanthracene (65%). Tetrahydro ring systems, such as tetralin, which proved relatively resistant to the RLi-TMEDA reagent also underwent smooth conversion to aromatic products with I. Other synthetic applications of the new procedure include synthesis of 4-methylphenanthrene through simultaneous dehydration and dehydrogenation of the intermediate alcohol obtained from reaction of 4-keto-1, 2, 3, 4, 9, 10-hexahydrophenanthrene[12] with CH_3Li, and synthesis of 5-methylchrysene from 5-methyl-5, 6-dihydrochrysene obtained from reductive methylation of chrysene[13].

Analogous reaction of 9, 10-dihydrophenanthrene failed to take place in acetic acid neat after 21 hr at reflux, while in the presence of p-toluenesulfonic acid (1.3 mmol/5 mmol DHP) there was obtained phenanthrene in 27% and 56% yield after 1 hr and 6 hr, respectively. Substitution of t-butanol for trityl alcohol in the trifluoroacetic acid catalyzed reaction of III led to formation of substantial amounts of t-butylated phenanthrene derivatives[14]. Evidently, t-butylation is competitive with dehydrogenation. It should be noted that tritylation was not found to be a significant secondary reaction in any of the examples investigated.

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(1) R.G. Harvey and H. Cho, J. Amer. Chem. Soc., 96, 2434 (1974).

(2) R.G. Harvey, L. Nazareno, and H. Cho, Ibid., 95, 2376 (1973).

(3) W. Bonthrone and D.H. Reid, J. Chem. Soc., 2773 (1959).

(4) Proton nmr spectra were obtained on a Varian T-60 spectrometer; chemical shifts are reported relative to TMS in $CDCl_3$ or CCl_4.

(5) Gas chromatographic analyses were performed on a Varian 2700 chromatograph employing a 5.5 ft x 0.25 in. 10% SE-30, 60-80 mesh Chromosorb AW column.

(6) Tlc on 2,4,7-trinitrofluorenone (TNF) impregnated silica gel according to the published procedure[7] provided efficient separation of the hydrocarbon products which were generally also distinguishable as spots of different colors.

(7) R.G. Harvey and M. Halonen, J. Chromatog., 25, 294 (1966).

(8) "Handbook of Chemistry and Physics", The Chemical Rubber Co., 51st Edit., 1952, p. C-113.

(9) As reported recently[2], reaction of cis-9-ethyl-10-methyl-II with sulfur, palladium on charcoal, $AlCl_3$, I_2, $FeCl_3$, $SbCl_5$, chloranil, DDQ, trityl perchlorate, $Ce(NH_4)_2(NO_3)_6$, and $Pb(OAc)_4$ led generally to intractable mixtures from which only low yields of the aromatic product could be isolated. On the other hand, reaction of this hydrocarbon with n-butyllithium-TMEDA and $CdCl_2$ afforded 9-ethyl-10-methylanthracene quantitatively.

(10) All reactions were conducted according to the procedure described for II. Yields are based on nmr and glpc analysis of the products in comparison with the authentic compounds. The major products were in all cases isolated by chromatography on silica gel (or trituration with ether in the case of anthracene) and identified in comparison with authentic samples by nmr and other means.

(11) Reaction was conducted in trifluoroacetic acid (10 ml) containing trifluoroacetic anhydride (2.10 g, 11 mmol).

(12) R. Haworth, J. Chem. Soc., 1131 (1932).

(13) Conversion of 5-methyl-5,6-dihydrochrysene to 5-methylchrysene was previously achieved with trityl fluoroborate (R.G. Harvey, J. Org. Chem., 36, 3306 (1971); neither DDQ nor n-butyllithium-TMEDA were found effective in this transformation.

(14) The efficient t-butylation of aromatic phenols by t-butanol in trifluoroacetic acid was recently reported; U. Svanholm and V.D. Parker, J. Chem. Soc. Perkin I, 562 (1973).